Chapter 16

Semilocal Approximations for the Kinetic Energy

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Approximations to the non-interacting kinetic energy $T_\mathrm{s}[\rho]$, which take the form of semilocal analytic expressions are collected. They are grouped according to the quantities on which they explicitly depend. Additionally, the approximations for quantities related to $T_\mathrm{s}[\rho]$ (kinetic potential and non-additive kinetic energy), for which the analytic expressions for the "parent" approximation for the functional $T_\mathrm{s}[\rho]$ are unknown, are also given.

Contents

16.1. Notation and conventions

Atomic units $[m_e = e = \hbar = 1/(4\pi\varepsilon_0) = 1]$ are used in all formulas. The notation for functions and constants that will be used throughout the text is the following:

- $\rho = \rho(\mathbf{r})$ – the electron density.
- $s = |\nabla\rho| \,/\, \left(2\left(3\pi^2\right)^{1/3}\rho^{4/3}\right)$ – the dimensionless reduced density gradient.
- $x = (5/27)\,s^2$ – a quantity proportional to the square of s.
- $C_\mathrm{F} = (3/10)\left(3\pi^2\right)^{2/3} \simeq 2.8712$ – the Thomas-Fermi constant.

- $b = 2\left(6\pi^2\right)^{1/3}$ – a conversion factor.
- Capital T – integrated kinetic energy.
- Small t – kinetic-energy density per volume unit.

The analytic expressions of the non-interacting kinetic-energy functionals $T_s[\rho]$ will be given for the spin-compensated case ($\rho_\uparrow = \rho_\downarrow$). For spin-polarized electron densities, the corresponding expression for $T_s[\rho_\uparrow, \rho_\downarrow]$ can be easily obtained by applying the extension formula of Oliver and Perdew:[1]

$$T_s[\rho_\uparrow, \rho_\downarrow] = \frac{1}{2}\left(T_s[2\rho_\uparrow] + T_s[2\rho_\downarrow]\right) \tag{16.1.1}$$

The labels used for the approximations reflect the name given by the authors, the most common convention used in the literature, or the names of the authors.

16.2. Known exact functionals

For two types of systems, the exact analytic form of $T_s[\rho]$ is known:

- **Thomas and Fermi**:[2,3]

$$T_s^{\mathrm{TF}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d^3r \tag{16.2.2}$$

  The Thomas-Fermi functional[2,3] is exact for the homogeneous electron gas. Applying it for inhomogeneous systems leads to an approximation known as the Thomas-Fermi functional or the local density approximation (LDA) functional.

- **von Weizsäcker**:[4]

$$T_s^{\mathrm{W}}[\rho] = \frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d^3r \tag{16.2.3}$$

  This functional is exact for one-electron and spin-compensated two-electron systems.
  Applying it for other systems leads to an approximation known as the von Weizsäcker functional.

16.3. Local density approximation — LDA

The label LDA is sometimes used in a more general way for any approximation which depends solely on the electron density like the TF functional [Eq. (16.2.2)]. In addition to TF, a few such functionals were proposed in the literature.

GaussianLDA Lee and Parr:[5]

$$T_s^{\mathrm{GaussianLDA}}[\rho] = \frac{3\pi}{2^{5/3}} \int \rho^{5/3}(\mathbf{r}) d^3r \tag{16.3.4}$$

Note that the coefficient $3\pi/2^{5/3} \simeq 2.9686$ is about 3% larger than the coefficient $C_{\rm F}$ of the TF functional [Eq. (16.2.2)].

ZLP Fuentealba and Reyes:[6]

$$T_{\rm s}^{\rm ZLP}[\rho] = c_1 \int \rho^{5/3}(\mathbf{r}) \left[1 - c_2 \left(\frac{\rho(\mathbf{r})}{2}\right)^{1/3} \ln \left(1 + \frac{1}{c_2 \left(\frac{\rho(\mathbf{r})}{2}\right)^{1/3}} \right) \right] d^3r \quad (16.3.5)$$

where $c_1 = 3.2372$ and $c_2 = 0.00196$. It was constructed following the "conjointness conjecture"[7] applied to the ZLP[8] approximation for the exchange-correlation energy. Note that in Eq. (9) in Ref. 6 the symbol ρ should be replaced by ρ_σ for the given coefficients. For the numerical verification see Ref. 9.

LP97 Liu and Parr:[10]

$$T_{\rm s}^{\rm LP97}[\rho] = 3.26422 \int \rho^{5/3}(\mathbf{r}) d^3r - 0.02631 \left(\int \rho^{4/3}(\mathbf{r}) d^3r \right)^2 + 0.000498 \left(\int \rho^{11/9}(\mathbf{r}) d^3r \right)^3 \quad (16.3.6)$$

Note that the coefficient in front of the third term was given incorrectly in Ref. 10.

16.4. Gradient expansion approximation — GEA*n*

The gradient expansion approximation (GEA) until the nth order:

$$T_{\rm s}^{{\rm GEA}n}[\rho] = \sum_{i=0}^{n} T_{{\rm s},i}[\rho] = \sum_{i=0}^{n} \int t_i\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \ldots\right) d^3r \quad (16.4.7)$$

where only the terms for i even are non-zero. The analytical form of the terms up to $i = 6$ have been derived:

$$t_0 = t^{\rm TF} = C_{\rm F}\rho^{5/3} \quad (16.4.8)$$

$$t_2 = \frac{1}{9} t^{\rm W} = \frac{1}{72}\frac{|\nabla\rho|^2}{\rho} \quad (16.4.9)$$

$$t_4 = \frac{(3\pi^2)^{-2/3}}{540}\rho^{1/3}\left(\left(\frac{\nabla^2\rho}{\rho}\right)^2 - \frac{9}{8}\frac{\nabla^2\rho}{\rho}\frac{|\nabla\rho|^2}{\rho^2} + \frac{1}{3}\frac{|\nabla\rho|^4}{\rho^4} \right) \quad (16.4.10)$$

$$t_6 = \frac{\left(3\pi^2\right)^{-4/3}}{45360}\rho^{-1/3}\left(13\frac{\left|\nabla\left(\nabla^2\rho\right)\right|^2}{\rho^2} + \frac{2575}{144}\left(\frac{\nabla^2\rho}{\rho}\right)^3 + \frac{249}{16}\frac{|\nabla\rho|^2}{\rho^2}\frac{\nabla^4\rho}{\rho} + \frac{1499}{18}\frac{|\nabla\rho|^2}{\rho^2}\left(\frac{\nabla^2\rho}{\rho}\right)^2 - \frac{1307}{36}\frac{|\nabla\rho|^2}{\rho^2}\frac{\nabla\rho\cdot\nabla\left(\nabla^2\rho\right)}{\rho^2} + \frac{343}{18}\left(\frac{\nabla\rho\cdot\nabla\nabla\rho}{\rho^2}\right)^2 + \frac{8341}{72}\frac{\nabla^2\rho}{\rho}\frac{|\nabla\rho|^4}{\rho^4} - \frac{1600495}{2592}\frac{|\nabla\rho|^6}{\rho^6} \right) \quad (16.4.11)$$

These terms were obtained by various authors: t_0 by Thomas and Fermi,[2,3] t_2 by Kompaneets and Pavlovskii[11] and by Kirzhnits,[12] t_4 by Hodges,[13] and t_6 by Murphy.[14] t_2 and t_4 were obtained after integration by part of[15,16]

$$t_2^{\rm J} = \frac{1}{72}\frac{|\nabla\rho|^2}{\rho} + \frac{1}{6}\nabla^2\rho \tag{16.4.12}$$

$$t_4^{\rm J} = \frac{(3\pi^2)^{-2/3}}{4320}\rho^{1/3}\left(12\frac{\nabla^4\rho}{\rho} - 30\frac{\nabla\rho\cdot\nabla\left(\nabla^2\rho\right)}{\rho^2} - 14\left(\frac{\nabla^2\rho}{\rho}\right)^2 - 7\frac{\nabla^2\left(|\nabla\rho|^2\right)}{\rho^2}\right.$$
$$\left. + \frac{140}{3}\frac{|\nabla\rho|^2\nabla^2\rho}{\rho^3} + \frac{92}{3}\frac{\nabla\rho\cdot\nabla\left(|\nabla\rho|^2\right)}{\rho^3} - 48\frac{|\nabla\rho|^4}{\rho^4}\right) \tag{16.4.13}$$

respectively. Choosing $n = 0$, 2, and 4 in Eq. (16.4.7) leads to approximations with the following labels: GEA0 which is just the TF functional [Eq. (16.2.2)], GEA2 which is also denoted with TF$\frac{1}{9}$W, and GEA4.

16.5. Generalized gradient approximation — GGA

The general form of GGA functionals reads

$$T_{\rm s}^{\rm GGA}[\rho] = \int f\left(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|\right) d^3r = C_{\rm F}\int \rho^{5/3}(\mathbf{r})F(s(\mathbf{r}))d^3r \tag{16.5.14}$$

where $F(s)$ is the so-called enhancement factor. The enhancement factor of the von Weizsäcker functional [Eq. (16.2.3)] is given by

$$F^{\rm W}(s) = \frac{5}{3}s^2 \tag{16.5.15}$$

while for the GEA truncated at the 0th and 2nd orders [Eqs. (16.4.7)-(16.4.9)], the enhancement factors are

$$F^{\rm GEA0}(s) = 1 \tag{16.5.16}$$

$$F^{\rm GEA2}(s) = 1 + \frac{5}{27}s^2 \tag{16.5.17}$$

respectively.

A large group of approximations in the GGA family were constructed following the "conjointness conjecture" of Lee, Lee, and Parr[7] according to which the enhancement factor of an exchange GGA functional can be used (with possible reoptimization of the free coefficients) for the kinetic energy. The following convention is used for labeling the conjoint functionals: if not only the analytic form but also the free coefficients are the same as in the exchange functional, then the functional is called *conjoint X*, where *X* stands for the name of the "parent" exchange functional. In the case of reoptimization of the coefficients, the standard convention applies (see Sec. 16.1).

TFλW The functionals in this family differ only in the value of the constant λ:

$$T_{\rm s}^{\rm TF\lambda W}[\rho] = T_{\rm s}^{\rm TF}[\rho] + \lambda T_{\rm s}^{\rm W}[\rho] \tag{16.5.18}$$

GEA0 and GEA2 correspond to $\lambda = 0$ and 1/9, respectively. Other values of λ were proposed in the literature, e.g., $\lambda = 1.290/9$ (modified 2nd order gradient expansion proposed by Lee *et al.*[17]). See Ref. 18 for a compilation of the different values of λ proposed in the literature. The enhancement factor of the TFλW functional is

$$F^{\rm TF\lambda W}(s) = 1 + \lambda \frac{5}{3} s^2 \tag{16.5.19}$$

P82 Pearson:[19]

$$F^{\rm P82}(s) = 1 + \frac{5}{27} \frac{s^2}{1 + s^6} \tag{16.5.20}$$

DKPadé DePristo and Kress:[20]

$$F^{\rm DKPad\acute{e}}(x) = \frac{1 + 0.95x + 14.28111x^2 - 19.57962x^3 + 26.64765x^4}{1 - 0.05x + 9.99802x^2 + 2.96085x^3} \tag{16.5.21}$$

LLP Lee, Lee, and Parr:[7]

$$F^{\rm LLP}(s) = 1 + \frac{0.0044188 b^2 s^2}{1 + 0.0253 bs \,\mathrm{arcsinh}(bs)} \tag{16.5.22}$$

This is the enhancement factor of the exchange functional B88 of Becke[21] refitted for the kinetic energy.

OL1 and OL2 Ou-Yang and Levy:[22]

$$F^{\rm OL1}(s) = 1 + \frac{5}{27} s^2 + 0.00677 \frac{20}{3} \left(3\pi^2\right)^{-1/3} s \tag{16.5.23}$$

$$F^{\rm OL2}(s) = 1 + \frac{5}{27} s^2 + \frac{0.0887}{C_{\rm F}} \frac{2\left(3\pi^2\right)^{1/3} s}{1 + 8\left(3\pi^2\right)^{1/3} s} \tag{16.5.24}$$

The coefficients in front of the third terms in OL1 and OL2 were inverted in the original paper of Ou-Yang and Levy (caption of Table I in Ref. 22). The correctness of the coefficients given here was confirmed by numerical values of $T_s[\rho]$.[23–25] The correct scaling properties of $T_s[\rho]$ require that the coefficient in front of the last terms in OL1 and OL2 are not free but must be non-negative.

P92 Perdew:[26]

$$F^{\rm P92}(s) = \frac{1 + 88.396 s^2 + 16.3683 s^4}{1 + 88.2108 s^2} \tag{16.5.25}$$

T92 Thakkar:[23]

$$F^{\mathrm{T92}}(s) = 1 + \frac{0.0055b^2s^2}{1 + 0.0253bs\,\mathrm{arcsinh}(bs)} - \frac{0.072bs}{1 + 2^{5/3}bs} \tag{16.5.26}$$

LC94 Lembarki and Chermette:[27]

$$F^{\mathrm{LC94}}(s) = \frac{1 + 0.093907s\,\mathrm{arcsinh}(76.32s) + \left(0.26608 - 0.0809615e^{-100s^2}\right)s^2}{1 + 0.093907s\,\mathrm{arcsinh}(76.32s) + 0.57767 \cdot 10^{-4}s^4} \tag{16.5.27}$$

This is the enhancement factor of the exchange functional PW91 of Perdew and Wang[28] refitted for the kinetic energy.

FR95A Fuentealba and Reyes:[6]

$$F^{\mathrm{FR95A}}(s) = 1 + \frac{0.004596b^2s^2}{1 + 0.02774bs\,\mathrm{arcsinh}(bs)} \tag{16.5.28}$$

This is the enhancement factor of the exchange functional B88 of Becke[21] refitted for the kinetic energy.

FR95B Fuentealba and Reyes:[6]

$$F^{\mathrm{FR95B}}(s) = \left(1 + 2.208s^2 + 9.27s^4 + 0.2s^6\right)^{1/15} \tag{16.5.29}$$

This is the enhancement factor of the exchange functional PW86 of Perdew and Wang[29] refitted for the kinetic energy.

VSK98 Vitos, Skriver, and Kollár:[30]

$$F^{\mathrm{VSK98}}(x) = \frac{1 + 0.95x + 3.564x^3}{1 - 0.05x + 0.396x^2} \tag{16.5.30}$$

VJKS00 Vitos *et al.*:[31]

$$F^{\mathrm{VJKS00}}(s) = \frac{1 + 0.8944s^2 - 0.0431s^6}{1 + 0.6511s^2 + 0.0431s^4} \tag{16.5.31}$$

E00 Ernzerhof:[32]

$$F^{\mathrm{E00}}(s) = \frac{135 + 28s^2 + 5s^4}{135 + 3s^2} \tag{16.5.32}$$

TW02 Tran and Wesolowski:[25]

$$F^{\mathrm{TW02}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa}s^2} \tag{16.5.33}$$

where $\kappa = 0.8438$ and $\mu = 0.2319$. This is the enhancement factor of the exchange functional PBE of Perdew, Burke, and Ernzerhof[33,34] refitted for the kinetic energy.

PBE*n* Karasiev, Trickey, and Harris:[35]

$$F^{\mathrm{PBE}n}(s) = 1 + \sum_{i=1}^{n-1} C_i^{(n)} \left(\frac{s^2}{1 + a^{(n)} s^2} \right)^i \tag{16.5.34}$$

This is the enhancement factor of the exchange functional mPBE of Adamo and Barone[36] refitted for the kinetic energy. Three approximations ($n = 2$, 3, and 4) of the above general form were considered in Ref. 35. The coefficients $C_i^{(n)}$ and $a^{(n)}$ are given in Table 16.1.

Table 16.1. Coefficients of the enhancement factor of PBE*n* [Eq. (16.5.34)].

Functional	$C_1^{(n)}$	$C_2^{(n)}$	$C_3^{(n)}$	$a^{(n)}$
PBE2	2.0309			0.2942
PBE3	−3.7425	50.258		4.1355
PBE4	−7.2333	61.645	−93.683	1.7107

exp4 Karasiev, Trickey, and Harris:[35]

$$F^{\mathrm{exp4}}(s) = C_1 \left(1 - e^{-a_1 s^2}\right) + C_2 \left(1 - e^{-a_2 s^4}\right) \tag{16.5.35}$$

where $C_1 = 0.8524$, $C_2 = 1.2264$, $a_1 = 199.81$, and $a_2 = 4.3476$.

CR Constantin and Ruzsinszky:[37]

$$F^{\mathrm{CR}}(s) = \frac{1 + \left(a_1 + \frac{5}{27}\right) s^2 + a_2 s^4 + a_3 s^6 - a_4 s^8}{1 + a_1 s^2 + a_5 s^4 + \frac{3}{40\beta - 5} a_4 s^6} \tag{16.5.36}$$

Three approximations (corresponding to $\beta = 1/5$, $1/6$, and 0.185) of the above general form were considered in Ref. 37. The corresponding sets of coefficients a_i are given in Table 16.2.

Table 16.2. Coefficients of the enhancement factor of CR [Eq. (16.5.36)].

β	1/5	1/6	0.185
a_1	1.122609	1.301786	1.293576
a_2	0.900085	3.715282	2.161116
a_3	−0.227373	0.343244	−0.144896
a_4	0.014177	0.032663	0.025505
a_5	0.731298	2.393929	1.444659

MGE2 Constantin *et al.*:[38]

$$F^{\mathrm{MGE2}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa}s^2} \tag{16.5.37}$$

where $\kappa = 0.804$ and $\mu = 0.23889$. This is the enhancement factor of the exchange functional PBE of Perdew, Burke, and Ernzerhof.[33,34]

Conjoint B86A Lacks and Gordon:[39]

$$F^{\mathrm{B86A}}(s) = 1 + 0.00387\frac{b^2s^2}{1 + 0.004b^2s^2} \tag{16.5.38}$$

This is the enhancement factor of the exchange functional B86A of Becke.[40]

Conjoint PW86 Lacks and Gordon:[39]

$$F^{\mathrm{PW86}}(s) = \left(1 + 1.296s^2 + 14s^4 + 0.2s^6\right)^{1/15} \tag{16.5.39}$$

This is the enhancement factor of the PW86 exchange functional of Perdew and Wang.[29]

Conjoint B86B Lacks and Gordon:[39]

$$F^{\mathrm{B86B}}(s) = 1 + 0.00403\frac{b^2s^2}{(1 + 0.007b^2s^2)^{4/5}} \tag{16.5.40}$$

This is the enhancement factor of the exchange functional B86B of Becke.[41]

Conjoint DK87 Lacks and Gordon:[39]

$$F^{\mathrm{DK87}}(s) = 1 + \frac{7b^2s^2}{324(36\pi^4)^{1/3}}\frac{1 + 0.861504bs}{1 + 0.044286b^2s^2}. \tag{16.5.41}$$

This is the enhancement factor of the exchange functional DK87 of DePristo and Kress.[42]

Conjoint B88 Tran and Wesolowski:[25]

$$F^{\mathrm{B88}}(s) = 1 + \frac{0.0042}{2^{1/3}C_{\mathrm{x}}}\frac{b^2s^2}{1 + 0.0252bs\,\mathrm{arcsinh}(bs)} \tag{16.5.42}$$

where $C_{\mathrm{x}} = (3/4)\,(3/\pi)^{1/3}$. This is the enhancement factor of the exchange functional B88 of Becke.[21]

Conjoint PW91 Lacks and Gordon:[39]

$$F^{\mathrm{PW91}}(s) = \frac{1 + 0.19645s\,\mathrm{arcsinh}(7.7956s) + \left(0.2743 - 0.1508e^{-100s^2}\right)s^2}{1 + 0.19645s\,\mathrm{arcsinh}(7.7956s) + 0.004s^4} \tag{16.5.43}$$

This is the enhancement factor of the exchange functional PW91 of Perdew and Wang.[28]

Conjoint xFit Lacks and Gordon:[39]

$$F^{x\mathrm{Fit}}(s) = \frac{1}{1+10^{-8}s^2}\left(1+\frac{10^{-8}+0.1234}{0.024974}s^2+29.790s^4+22.417s^6\right.$$
$$\left.+12.119s^8+1570.1s^{10}+55.944s^{12}\right)^{0.024974} \tag{16.5.44}$$

This is the enhancement factor of the exchange functional xFit of Lacks and Gordon.[43]

Conjoint PBE Perdew *et al.*:[44]

$$F^{\mathrm{PBE}}(s) = 1+\kappa-\frac{\kappa}{1+\frac{\mu}{\kappa}s^2} \tag{16.5.45}$$

where $\kappa = 0.804$ and $\mu = 0.21951$. This is the enhancement factor of the exchange functional PBE of Perdew, Burke, and Ernzerhof.[33,34]

16.6. Other semilocal approximations

TB78 Tal and Bader:[45]

$$T_{\mathrm{s}}^{\mathrm{TB78}}[\rho] = T_{\mathrm{s}}^{\mathrm{TF}}[\rho_{\mathrm{s}}] + T_{\mathrm{s}}^{\mathrm{W}}[\rho_{\mathrm{s}}] + \sum_{A=1}^{M} T_{\mathrm{s}}^{\mathrm{W}}[\rho_{\mathrm{r},A}] \tag{16.6.46}$$

where

$$\rho_{\mathrm{r},A}(\mathbf{r}) = \rho(\mathbf{R}_A)e^{-2Z_A|\mathbf{r}-\mathbf{R}_A|} \tag{16.6.47}$$

and

$$\rho_{\mathrm{s}}(\mathbf{r}) = \rho(\mathbf{r}) - \sum_{A=1}^{M} \rho_{\mathrm{r},A}(\mathbf{r}) \tag{16.6.48}$$

M, $\mathbf{R}_A$, and Z_A are the number, positions, and charges of the nuclei, respectively.

CN84 Cummins and Nordholm:[46]

$$T_{\mathrm{s}}^{\mathrm{CN84}}[\rho] = \int t^{\mathrm{CN84}}(\mathbf{r})d^3r \tag{16.6.49}$$

where

$$t^{\mathrm{CN84}}(\mathbf{r}) = \max\left(t^{\mathrm{TF}}(\mathbf{r}), t^{\mathrm{W}}(\mathbf{r})\right) \tag{16.6.50}$$

PG85 Pearson and Gordon:[47]

$$T_{\mathrm{s}}^{\mathrm{PG85}}[\rho] = \int t^{\mathrm{PG85}}(\mathbf{r}) d^3 r \tag{16.6.51}$$

where

$$t^{\mathrm{PG85}}(\mathbf{r}) = \begin{cases} \sum_{i=0}^{n-1} t_{2i}(\mathbf{r}) + \frac{1}{2} t_{2n}(\mathbf{r}) & \text{if } t_2(\mathbf{r}) \leqslant t_0(\mathbf{r}) \\ t_0(\mathbf{r}) & \text{if } t_2(\mathbf{r}) > t_0(\mathbf{r}) \end{cases} \tag{16.6.52}$$

mGEA4 Allan *et al.*:[48]

$$T_{\mathrm{s}}^{\mathrm{mGEA4}}[\rho] = T_{\mathrm{s}}^{\mathrm{TF}}[\rho] + \frac{1}{9} T_{\mathrm{s}}^{\mathrm{W}}[\rho] + \frac{1}{2} T_{\mathrm{s},4}[\rho] \tag{16.6.53}$$

PP88 Plindov and Pogrebnya:[49]

$$T_{\mathrm{s}}^{\mathrm{PP88}}[\rho] = T_{\mathrm{s}}^{\mathrm{TF}}[\rho] + \frac{1}{9} T_{\mathrm{s}}^{\mathrm{W}}[\rho] + \int \frac{t_4(\mathbf{r})}{1 + \frac{1}{8} \frac{t_4(\mathbf{r})}{t_2(\mathbf{r})}} d^3 r \tag{16.6.54}$$

MGGA Perdew and Constantin:[50]

$$F^{\mathrm{MGGA}} = F^{\mathrm{W}} + \left(F^{\mathrm{GE4-M}} - F^{\mathrm{W}}\right) f_{ab} \left(F^{\mathrm{GE4-M}} - F^{\mathrm{W}}\right) \tag{16.6.55}$$

where

$$F^{\mathrm{GE4-M}} = \frac{F^{\mathrm{GEA4}'}}{\sqrt{1 + \left(\frac{F_4}{1+\frac{5}{3}s^2}\right)^2}} \tag{16.6.56}$$

and

$$f_{ab}(z) = \begin{cases} 0 & z \leqslant 0 \\ \left(\frac{1+e^{a/(a-z)}}{e^{a/z}+e^{a/(a-z)}}\right)^b & 0 < z < a \\ 1 & z \geqslant a \end{cases} \tag{16.6.57}$$

Equation (16.6.56) is the enhancement factor of a modified 4th order GEA, where $F^{\mathrm{GEA4}'}$ and F_4 are the enhancement factors of the functionals $T_{\mathrm{s}}^{\mathrm{GEA4}'} = \int \left(t_0 + t_2^{\mathrm{J}} + t_4\right) d^3 r$ and $T_{s,4} = \int t_4 d^3 r$, respectively [see Eqs. (16.4.7)–(16.4.13)]. In Eq. (16.6.57), $a = 0.5389$ and $b = 3$ are two parameters which were optimized.

GDS08 Ghiringhelli and Delle Site:[51]

$$T_{\mathrm{s}}^{\mathrm{GDS08}}[\rho] = T_{\mathrm{s}}^{\mathrm{W}}[\rho] + \int \rho(\mathbf{r}) \left(A + B \ln(\rho(\mathbf{r}))\right) d^3 r \tag{16.6.58}$$

where $A = 0.860$ and $B = 0.224$.

MGEA4 Lee *et al.*:[17]

$$T_{\mathrm{s}}^{\mathrm{MGEA4}}[\rho] = \int \left(t_0(\mathbf{r}) + 1.789 t_2(\mathbf{r}) - 3.841 t_4(\mathbf{r})\right) d^3 r \tag{16.6.59}$$

RDA Karasiev *et al.*:[52]

$$T_{\rm s}^{\rm RDA}[\rho] = T_{\rm s}^{\rm W}[\rho] + \int t_0(\mathbf{r}) F_\theta^{m0}(\mathbf{r}) d^3r \tag{16.6.60}$$

where

$$F_\theta^{m0} = A_0 + A_1 \left(\frac{\tilde{\kappa}_{4a}}{1+\beta_1 \tilde{\kappa}_{4a}}\right)^2 + A_2 \left(\frac{\tilde{\kappa}_{4b}}{1+\beta_2 \tilde{\kappa}_{4b}}\right)^4 + A_3 \frac{\kappa_{2c}}{1+\beta_3 \kappa_{2c}} \tag{16.6.61}$$

with

$$\tilde{\kappa}_{4a} = \sqrt{s^4 + ap^2} \tag{16.6.62}$$

$$\tilde{\kappa}_{4b} = \sqrt{s^4 + bp^2} \tag{16.6.63}$$

$$\kappa_{2c} = s^2 + cp \tag{16.6.64}$$

and $p = \nabla^2 \rho / \left(4 \left(3\pi^2\right)^{2/3} \rho^{5/3}\right)$. The constants in Eqs. (16.6.61)-(16.6.64) are $A_0 = 0.50616$, $A_1 = 3.04121$, $A_2 = -0.34567$, $A_3 = -1.89738$, $\beta_1 = 1.29691$, $\beta_2 = 0.56184$, $\beta_3 = 0.21944$, $a = 46.47662$, $b = 18.80658$, and $c = -0.90346$.

16.7. *N*- and *r*-dependent approximations

In the approximations collected below, the analytic expressions for the kinetic energy depend explicitly not only on ρ (and its derivatives) but also on the number of electrons N and/or on the position (i.e., distance r from the nucleus). The r-dependent expressions are applicable only for mono-atomic systems.

HCD84 Haq, Chattaraj, and Deb:[53]

$$T_{\rm s}^{\rm HCD84}[\rho] = T_{\rm s}^{\rm TF}[\rho] - \frac{1}{40} \int \frac{\mathbf{r} \cdot \nabla \rho(\mathbf{r})}{r^2} d^3r \tag{16.7.65}$$

GD94 Ghosh and Deb:[54]

$$T_{\rm s}^{\rm GD94}[\rho] = T_{\rm s}^{\rm TF}[\rho] + \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int \frac{\rho^{4/3}(\mathbf{r})}{r\left(1 + \frac{r\rho^{1/3}(\mathbf{r})}{0.043}\right)} d^3r \tag{16.7.66}$$

F97 Fuentealba:[55]

$$T_{\rm s}^{\rm F97}[\rho] = C_{\rm F} \int \rho^{5/3}(\mathbf{r}) \frac{1}{1 - 0.213 e^{-8.8(\rho(\mathbf{r})/2)^{2/3} r^2}} d^3r \tag{16.7.67}$$

NLP99 Nagy, Liu, and Parr:[56]

$$T_{\mathrm{s}}^{\mathrm{NLP99}}[\rho] = 0.179883 \int r^{-2}\rho(\mathbf{r})d^3r + 0.0622411 \left(\int r^{-1}\rho(\mathbf{r})d^3r\right)^2 - 8.88819 \cdot 10^{-4} \left(\int r^{-2/3}\rho(\mathbf{r})d^3r\right)^3 + 7.29627 \cdot 10^{-6} \left(\int r^{-1/2}\rho(\mathbf{r})d^3r\right)^4 \quad (16.7.68)$$

ABSP80 Acharaya *et al.*:[57]

$$T_{\mathrm{s}}^{\mathrm{ABSP80}}[\rho] = T_{\mathrm{s}}^{\mathrm{W}}[\rho] + \left(1 - \frac{1.412}{N^{1/3}}\right) T_{\mathrm{s}}^{\mathrm{TF}}[\rho] \quad (16.7.69)$$

GR82 Gázquez and Robles:[58]

$$T_{\mathrm{s}}^{\mathrm{GR82}}[\rho] = T_{\mathrm{s}}^{\mathrm{W}}[\rho] + \left(1 - \frac{2}{N}\right)\left(1 - \frac{1.303}{N^{1/3}} + \frac{0.029}{N^{2/3}}\right) T_{\mathrm{s}}^{\mathrm{TF}}[\rho] \quad (16.7.70)$$

GB85 Ghosh and Balbás:[59]

$$T_{\mathrm{s}}^{\mathrm{GB85}}[\rho] = T_{\mathrm{s}}^{\mathrm{W}}[\rho] + T_{\mathrm{s}}^{\mathrm{TF}}[\rho] + \left(0.1369 + \frac{0.153}{N^{1/3}} - \frac{0.071}{N^{2/3}}\right) \times \int \left(\frac{\mathbf{r}\cdot\nabla\rho(\mathbf{r})}{r^2} - \frac{\nabla^2\rho(\mathbf{r})}{2}\right) d^3r \quad (16.7.71)$$

16.8. Miscellaneous

Approximation for the kinetic potential The modified Thomas-Fermi (MTF) model of Chai and Weeks:[60]

$$v_t^{\mathrm{MTF}}([\rho],\mathbf{r}) = \frac{5}{3}C_{\mathrm{F}}\rho^{2/3}(\mathbf{r}) - \frac{\alpha}{4}\frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})} \quad (16.8.72)$$

where $\alpha = 1/2$. Note that there exists no functional $T_{\mathrm{s}}^{\mathrm{MTF}}$ such that $v_t^{\mathrm{MTF}} = \delta T_{\mathrm{s}}^{\mathrm{MTF}}/\delta\rho$, because the second term in Eq. (16.8.72) can not be obtained as a functional derivative.

Approximation for the non-additive kinetic energy Approximation to the bi-functional $T_{\mathrm{s}}^{\mathrm{nad}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}]$ by Lastra, Kaminski, and Wesolowski:[61]

$$T_s^{\mathrm{nad(NDSD)}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}] = C_{\mathrm{F}} \int \left((\rho_{\mathrm{A}}(\mathbf{r}) + \rho_{\mathrm{B}}(\mathbf{r}))^{5/3} - \rho_{\mathrm{A}}^{5/3}(\mathbf{r}) - \rho_{\mathrm{B}}^{5/3}(\mathbf{r})\right) d^3r + \int f\left(\rho_{\mathrm{B}}(\mathbf{r}), \nabla\rho_{\mathrm{B}}(\mathbf{r})\right)\rho_{\mathrm{A}}(\mathbf{r})\, v_t^{\mathrm{limit}}([\rho_{\mathrm{B}}],\mathbf{r})d^3r + C[\rho_{\mathrm{B}}] \quad (16.8.73)$$

where

$$v_t^{\text{limit}}([\rho_\text{B}], \mathbf{r}) = \frac{1}{8}\frac{|\nabla\rho_\text{B}(\mathbf{r})|^2}{\rho_\text{B}^2(\mathbf{r})} - \frac{1}{4}\frac{\nabla^2\rho_\text{B}(\mathbf{r})}{\rho_\text{B}(\mathbf{r})} \tag{16.8.74}$$

$$\begin{aligned} f(\rho_\text{B}, \nabla\rho_\text{B}) = {} & \left(e^{\lambda\left(-s_\text{B}+s_\text{B}^{\text{min}}\right)}+1\right)^{-1}\left(1-\left(e^{\lambda\left(-s_\text{B}+s_\text{B}^{\text{max}}\right)}+1\right)^{-1}\right) \\ & \times\left(e^{\lambda\left(-\rho_\text{B}+\rho_\text{B}^{\text{min}}\right)}+1\right)^{-1} \end{aligned} \tag{16.8.75}$$

(with the constants $\lambda = 500$, $s_\text{B}^{\text{min}} = 0.3$, $s_\text{B}^{\text{max}} = 0.9$ and $\rho_\text{B}^{\text{min}} = 0.7$), and $C[\rho_\text{B}]$ is a ρ_A-independent functional. The acronym NDSD (Non-Decomposable approximation to the potential involving only Second Derivatives) reflects the fact that there exists no such functional approximation $\tilde{T}_\text{s}[\rho]$ from which $T_s^{\text{nad(NDSD)}}[\rho_\text{A}, \rho_\text{B}]$ can be obtained as $T_s^{\text{nad(NDSD)}}[\rho_\text{A}, \rho_\text{B}] = \tilde{T}_\text{s}[\rho_\text{A} + \rho_\text{B}] - \tilde{T}_\text{s}[\rho_\text{A}] - \tilde{T}_\text{s}[\rho_\text{B}]$.

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