Simple exchange hole models for long-range-corrected density functionals

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Density functionals with a range-separated treatment of the exchange energy are known to improve upon their semilocal forerunners and fixed-fraction hybrids. The conversion of a given semilocal functional into its short-range analog is not straightforward, however, and not even unique, because the latter has a higher information content that has to be recovered in some way. Simple models of the spherically-averaged exchange hole as an interpolation between the uniform electron gas limit and a few-term Hermite function are developed here for use with generalized-gradient approximations, so that the energy density of the error-function-weighted Coulomb interaction is given by explicit closed-form expressions in terms of elementary and error functions. For comparison, some new non-oscillatory models in the spirit of earlier works are also built and studied, their energy densities match rather closely (within less than 5\%) but do lack the exact uniform electron gas limit.

It is the generalized-gradient approximation\(^1\) that paved the way for the density functional theory\(^2,3\) into the mysterious kingdom of theoretical chemistry. Even more fruitful may seem to be the hybrids\(^4\) with a fixed fraction of exact exchange, they are widely used, but their “strange” asymptotic behavior of the effective potential is more than an æsthetic problem. Luckily, a wonderful “strange” asymptotic behavior of the effective potential was soon shown\(^5\) to be even more helpful to the time dependence\(^6\) of the exchange hole model. We have found new and simpler solutions\(^7,8\) that satisfy the underlying sum rules, while a consistent construction of the exchange hole from the exact exchange energy has a simple functional form

\[
E_x = \frac{1}{2} \int \rho(r) \int \frac{\rho_x(r, r + R)}{|R|} \, d^3R \, d^3r
\]

with all its wisdom condensed in the enhancement factor

\[
s(r) = \frac{\left| \nabla \rho(r) \right|}{2p(r)\rho(r)}
\]

and its analytic form

\[
p(r) = \sqrt{3 \pi^2 \rho(r)}
\]

On the other hand, the exact exchange energy

\[
E_x = \frac{1}{2} \int \rho(r) \int \rho_x(r, r + R) \, d^3R \, d^3r
\]

can be given in terms of the exchange hole \(\rho_x(r_1, r_2)\) whose spherically-averaged part is only needed and is then approximated

\[
\rho_x(r, r + R) = \rho(r) \, q(p(r)|R|, s(r))
\]

using the shape function \(q(r, s)\) that holds more information than is otherwise hidden, by the integration, behind \(f(s)\). If the shape function is known, the error-function-weighted short-range part of the exchange energy

\[
E_x^\text{erf} = \frac{1}{2} \int \rho(r) \int \frac{\rho_x(r, r + R)}{|R|} \text{erfc}(\omega|R|) \, d^3R \, d^3r
\]
can be cast in the form

\[ E^\omega_x = c_x \int \rho^{1/3}(r) f \left( \frac{p(r)}{\omega}, s(r) \right) \, dq \]  

(8)

with the new enhancement factor \( f(\lambda, s) \) now being a function of two dimensionless variables (\( \lambda \) is length-like),

\[ f(\lambda, s) = -\frac{8}{3} \int_0^\infty r \, q(r, s) \, dr. \]  

(9)

Finding a good shape function \( q(r, s) \) given an enhancement factor \( f(s) \) is the problem we want to solve here. In doing so, we should respect the sign of \( q(r, s) \leq 0 \), the normalization

\[ \frac{4}{3} \int_0^\infty r^2 q(r, s) \, dr = -1, \]  

(10)

and the energy connection

\[ \frac{8}{5} \int_0^\infty r \, q(r, s) \, dr = -f(s), \]  

(11)

while the known on-top value and curvature\(^{22}\)

\[ \lim_{r, s \to 0} q(r, s) = -\frac{1}{2} + (\frac{1}{10} - \frac{1}{27} \pi^2) \, r^2 + \ldots \]  

(12)

are very helpful to build a good overall shape. The uniform electron gas has an oscillatory function

\[ q(r) = -\frac{4}{3} \left( \frac{\sin r - r \cos r}{r^3} \right)^2 \]  

(13)

with a rather long tail of \(-\frac{2}{3} \pi^{-4}\), whereas finite band gap systems have it more localized and mostly smooth. What we have written up to here is the common knowledge\(^{18,19,33}\) in the field, with all this in mind, we will now build and compare the new models of our own.

We want Eq. (11) to have the exact uniform electron gas limit at \( s = 0 \), and the only way to meet this is when

\[ q(r, 0) = \tilde{q}(r), \]  

(14)

so our first model will be an interpolation

\[ q(r, s) = (1 - w(s)) \tilde{q}(r) + w(s) q_2(r, a(s), c(s)) \]  

(15)

between \( \tilde{q}(r) \) and a three-term Hermite function

\[ q_2(r, a, c) = -\left[ \frac{1}{2} + \left( 2 \sqrt{\alpha} a^5 - \frac{1}{5} a^2 - \frac{2}{5} c \right) r^2 + c a^2 r^4 \right] \times \exp \left( -a^2 r^2 \right). \]  

(16)

It already follows Eq. (10), while from Eq. (11) we get

\[ c(s) = 4 \sqrt{\pi} a^3(s) - \frac{9}{2} a^4(s) \left( 1 + \frac{f(s) - 1}{w(s)} \right) + \frac{3}{2} a^2(s), \]  

(17)

and nothing seems to be more natural than

\[ w(s) = 1 - \exp \left( -\gamma s^2 \right) \]  

(18)

with \( \gamma \) set as

\[ \gamma = \frac{6075\alpha^4 \mu - 20}{4320\sqrt{\pi} \alpha^5 - 6075\alpha^4 + 900\alpha^2 - 54} \]  

(19)

to fulfill Eq. (12), here \( \alpha \equiv a(0) \) and \( \mu \) is from

\[ \lim_{s \to 0} f(s) = 1 + \mu s^2 + \ldots \]  

(20)

(understanding that \( f(s) \) should always be an even function of \( s \)). After all this, we are left with the freedom to choose a good function \( a(s) \) limited mainly by the sign of \( q(r, s) \leq 0 \).

The integral of Eq. (9) over the function of Eq. (15) has a simple closed-form expression

\[ f(\lambda, s) = (1 - w(s)) \tilde{u}(\lambda) + w(s) u_2(\lambda, a(s), c(s)) \]  

(21)

with the known\(^{11}\) uniform electron gas function

\[ \tilde{u}(\lambda) = 1 + \frac{2}{3 \lambda^2} + \left( 4 - \frac{2}{\lambda^2} \right) \frac{1 + \exp \left( -\lambda^2 \right)}{\lambda^2} - \frac{4 \sqrt{\pi} \exp(\lambda)}{3 \lambda} \]  

(22)

which for small \( \lambda \) should be evaluated using (a few terms of) the series

\[ \tilde{u}(\lambda) = \sum_{n=1}^{\infty} \frac{(-1)^n}{(n + 2)! (n + \frac{1}{2}) \lambda^{2n}}, \]  

(23)

and the well-behaved functions

\[ u_2(\lambda, a, c) = \frac{4}{3} \lambda^2 v_0(a \lambda) + \frac{8}{5} \left( 2\sqrt{\pi} a^5 - \frac{1}{5} a^2 - \frac{2}{5} c \right) \lambda^4 v_1(a \lambda) + \frac{8}{5} c a^2 \lambda^6 v_2(a \lambda), \]  

(24)

\[ v_n(t) = v_0(t) \left( 1 + t^2 \right), \]  

(25)

\[ v_0(x) = 1/(2x(1 + x)), \]  

\[ v_1(x) = (1 + 2x)/(4x^3(1 + x)^2), \]  

\[ v_2(x) = (3 + 9x + 8x^2)/(8x^5(1 + x)^3). \]

There are two kinds of enhancement factors: either bounded by a constant, \( 1 \leq f(s) \leq 1 + \kappa \), or unbounded \( f(s) \to \infty \) as \( s \to \infty \). We will deal first with those of the former kind, the simplest\(^{22}\) and widely used\(^{22}\)

\[ f(s) = 1 + \kappa - \kappa / \left( 1 + \mu s^2 / k \right), \]  

(26)

and another useful\(^{35}\)

\[ f(s) = 1 + \kappa - \kappa \exp \left( -\mu s^2 / k \right), \]  

(27)

both having only two parameters derivable from first principles, the gradient coefficient\(^{36}\)

\[ \mu \approx 0.21951497275770229511302159518575214898986 \]  

(28)
(we have carefully computed the integral numerically to all digits given), and an estimated, $\kappa = 0.804$ from the global lower bound on the exchange energy.

Our simplest $a(s)$ in Eqs. (15) and (17) is then a constant $a(s) = A$ whose value can be nailed down by setting

$$\lim_{s \to \infty} c(s) = 0,$$

so that $A$ is a root of the cubic equation

$$24\sqrt{\pi} A^3 - 27(1 + \kappa) A^2 + 2 = 0,$$

for $\kappa = 0.804$ we get

$$A \approx 1.10663098728012266096724171466275,$$

and for $\mu$ of Eq. (28), from Eq. (19) with $\alpha = A$,

$$\gamma \approx 0.42623661647528045432173010376694.$$ (32)

This is our simplest model that can also work with other more flexible forms of $f(s)$ as long as they are bounded by a constant, it is straightforward to implement and it has, through Eq. (17), the input $f(s)$ as a multiplicative factor in the expression for $\lambda(s)$. Plots show that $c(s) > 0$, monotonic for Eq. (27) but with a slight wave up and down for Eq. (28).

As a prototype of an unbounded $f(s)$, we take the most well-known and widely used

$$f(s) = 1 + \frac{\mu s^2}{1 + \mu s \ln(\eta s + \sqrt{1 + \eta^2 s^2})},$$

(33)

$$\nu = \sqrt{9/(2\pi^2)},$$

(34)

$$\eta = 2^4 6^2 \nu^2,$$

(35)

where $\mu$ can be either adjusted to fit some data or the theoretical constant of Eq. (28). $\nu$ is fixed by the asymptotic behavior of the energy density, (and we must note that $\eta$ could as well have been an adjustable parameter — its value of Eq. (35) is nothing but arbitrary). Here, we should have an $a(s)$ that always grows with $s$, otherwise there would have been $c(s) < 0$ and $q(r, s) > 0$. To meet Eq. (28), it can be shown that the first two terms of

$$\lim_{s \to \infty} a(s) = \frac{9 f(s)}{8 \sqrt{\pi}} - \frac{16 \sqrt{\pi}}{243 f^2(s)} - \frac{4906 \pi \sqrt{\pi}}{531441 f^4(s)} + \ldots$$

(36)

would have been needed, and the third and higher terms would help $c(s)$ reach zero faster. We cannot take these first two terms exactly as written for $a(s)$, however, because there would be $c(s) < 0$ for some small $s$, but the simplest

$$a(s) = \frac{9 f(s)}{8 \sqrt{\pi}}$$

(37)

already yields a working overall solution.

By the way, putting the bounded $f(s)$ of Eqs. (26) or (27) into Eq. (37) would also work and give us another $f(\lambda, s)$ of Eq. (21) that is clearly not the same as our first model with the constant $a(s) = A$, and when we plot the ratio of these $f(\lambda, s)$, we see that the one based on Eq. (37) is down to 15% smaller for some $\lambda$ and $s$. This gives us a hint at their diversity and makes us think of how to narrow down the choice of $a(s)$. Besides Eq. (29), we can nail it down at the other end, $s = 0$, by

$$c(0) = 0,$$

which makes $\alpha = a(0)$ the root of the seventh-degree polynomial parametrized by $\mu$, that can be written as

$$\frac{240 \sqrt{\pi} a^3 - 270 a^2 + 20}{14580 \sqrt{\pi} a^7 - 6075 a^4 + 729 a^2} = \mu,$$

(39)

for $\alpha$ has to be solved for together with $\gamma$ of Eq. (19).

For $\mu$ of Eq. (28) we get

$$\alpha \approx 0.53566481894751540210390580247207,$$

and this $\gamma$ is roughly 5 times greater than that of Eq. (32), we think the greater $\gamma$ to be better because then the oscillatory $\tilde{q}(r)$ fades away more quickly in Eq. (16). It is easy to build monotonic interpolations $\alpha \leq a(s) \leq A$ for a bounded $f(s)$ to get a small $c(s) > 0$: for Eq. (26)

$$a(s) = \alpha + a_2 s^2/(1 + a_2 s^2/(A - \alpha)),$$

(41)

$$a_2 = (A - \alpha)^2 (9(1 + \kappa) A - 2) / (9\kappa^2 A^3),$$

(42)

yields $c(s) < 0.023$ for all $s$; whereas for Eq. (27)

$$a(s) = A - a_c \exp(-\mu s^2/\kappa)$$

$$+ (a_c + \alpha) \exp(-2\mu s^2/\kappa),$$

(43)

$$a_c = 9\kappa A^3 / (9(1 + \kappa) A^2 - 2),$$

(44)

yields $c(s) < 0.016$ for all $s$. Likewise, for Eq. (28)

$$a(s) = \frac{9}{8 \sqrt{\pi}} \cdot \frac{1 + \mu s \text{ asinh}(\eta s) + \mu^2}{1 + \mu s \text{ asinh}(\eta s)}$$

$$+ \frac{\alpha - \frac{9}{8 \sqrt{\pi}} + \frac{16 \sqrt{\pi}}{243} - \frac{16 \sqrt{\pi}}{243} (1 + \mu s \text{ asinh}(\eta s))^2}{(1 + \mu s \text{ asinh}(\eta s) + \mu^2)^2},$$

(45)

makes $c(s) < 0.036$ for all $s$. This experience helps us get rid of $c(s)$ altogether, ending up with an even simpler model

$$q(r, s) = (1 - w(s)) \tilde{q}(r) + w(s) q_1(r, a(s)),$$

(46)

$$q_1(r, a) = -\left[\frac{1}{2} + (2\sqrt{\pi} a^3 - \frac{1}{2}) a^2 r^2\right] \exp(-a^2 r^2),$$

(47)

$$f(\lambda, s) = (1 - w(s)) \tilde{u}(\lambda) + w(s) u_1(\lambda, a(s)),$$

$$u_1(\lambda, a) = \frac{4}{5} \lambda^3 v_0(a, \lambda) + \frac{1}{5} (2\sqrt{\pi} a^3 - \frac{1}{5} a^3) \lambda^2 v_1(a, \lambda),$$

(48)

that can be used in two ways: either by redefining

$$w(s) = \frac{27 a^2 s (f(s) - 1)}{24 \sqrt{\pi} a^3 s - 27 a^2 s + 2}.$$
for use with some $a(s)$ like in Eqs. [11], [13], and [15]; or by holding true to Eq. [18] while fearlessly solving the cubic equation for $a(s)$ to get

$$a(s) = \left[ 3\sqrt{2}\varphi(s) \sin \left( \frac{1}{3} \arcsin \frac{4\sqrt{2}r}{9\varphi^3(s)} \right) \right]^{-1}, \tag{49}$$

$$\varphi(s) = \sqrt{1 + (f(s) - 1)/w(s)}. \tag{50}$$

This last idea is so strikingly simple that nothing is left to be shaved away with Ockham’s razor, and we like it the most.

Thus, given a $f(s)$ of any meaningful kind, we find its $\mu$ of Eq. [20], get $\alpha$ from Eq. [39], and $\gamma$ from Eq. [19], so we have $w(s)$ of Eq. [18], hence $a(s)$ of Eqs. [49] and [50], that yields us $f(\lambda, s)$ of Eq. [17] with Eqs. [22] and [25].

Here our tale would have had a happy end, but we feel that someone may call it a heresy to work with an oscillatory shape function having a thin but too long tail. In the spirit of the early works,\textsuperscript{18,19,21} we will now build some new and simple non-oscillatory models (of interest on their own) and compare the outcomes $f(\lambda, s)$ one-to-one to see only a small difference.

We begin with our two new amazingly beautiful non-oscillatory exchange hole models for the uniform electron gas that follow Eqs. [10], [11], [12] and have the $-\frac{1}{4}r^{-4}$ tail from Eq. [13]: the split-exponent version

$$\bar{q}(r) = -\frac{\alpha}{4} \left[ 1 - (1 + \beta^2 r^2) \exp \left( -\beta^2 r^2 \right) \right] r^{-4} - \left[ \frac{1}{2} - \frac{9\beta^4}{8} + \left( \frac{1}{2} \alpha^2 - \frac{9}{8} \alpha^2 \beta^4 + \frac{1}{4} \beta^6 - \frac{1}{10} \right) r^2 \right] \times \exp \left( -\alpha^2 r^2 \right), \tag{51}$$

$\alpha$ and $\beta$ being roots of the polynomial system

$$\begin{cases} 90\beta^6 + (100 - 225\beta^4)\alpha^2 + (360\beta - 240\sqrt{\pi})\alpha^5 = 12, \\ (45\beta^2 - 45)\alpha^4 - (45\beta^4 - 20)\alpha^2 + 15\beta^6 = 2, \tag{52} \end{cases}$$

$$\begin{aligned} \beta &\approx 1.018374108606862926108404234418115726, \\ \alpha &\approx 0.731832253115642144951075675174173985, \tag{53} \end{aligned}$$

and the shared-exponent version

$$\begin{aligned} \bar{q}(r) &\approx -\frac{\alpha}{4} \left[ 1 - (1 + \alpha^2 r^2) \exp \left( -\alpha^2 r^2 \right) \right] r^{-4} - \left[ \frac{1}{2} - \frac{9}{8}\alpha^4 + \left( \frac{1}{2}\alpha^2 - \frac{3}{8}\alpha^2 \beta^4 - \frac{1}{10} \right) r^2 \right] \times \exp \left( -\alpha^2 r^2 \right), \\ &+ \left( \frac{1}{36}\alpha^6 - \frac{1}{2}\alpha^4 + \frac{4\sqrt{\pi}}{3}\alpha^7 - \frac{3}{4}\alpha^8 \right) r^4 \exp \left( -\alpha^2 r^2 \right), \\ &+ 225\alpha^6 - 480\sqrt{\pi}\alpha^5 + 675\alpha^4 - 100\alpha^2 + 6 = 0, \tag{54} \end{aligned}$$

$$\begin{aligned} \alpha &\approx 0.78078754277121518041379059432608235. \tag{55} \end{aligned}$$

In both cases, all three functions $q(r), r\bar{q}(r)$, and $r^2q(r)$ have slim shapes without any shoulders for $r \geq 0$, whereas their forerunners,\textsuperscript{18,21}, to become shoulderless, needed one more degree of freedom to be fixed by a sophisticated information-entropy-maximization\textsuperscript{14} principle. We hope that our finding may help others in their future work.

From Eq. [55], we build

$$\begin{aligned} q(r, s) &= -\frac{\alpha}{4} \left[ 1 - (1 + \alpha^2 r^2) \exp \left( -\alpha^2 r^2 \right) \right] r^{-4} \times \exp \left( -h(\chi) a^2(s) r^2 - \gamma s^2 \right) \\ &- \left[ \frac{1}{2} - \frac{9}{8}\alpha^4 \exp \left( -\gamma s^2 \right) + b(s) r^2 + c(s) r^4 \right] \times \exp \left( -a^2(s) r^2 \right), \tag{57} \end{aligned}$$

with $a(0) = \alpha$ of Eq. [55], while $b(s)$ and $c(s)$ have to fulfill Eqs. [10] and [11],

$$\begin{aligned} b(s) &= (12s - 8\sqrt{\pi})a^3(s) + \frac{27}{4}(f(s) - y(s))a^4(s) \\ &+ \left( \frac{15}{2}\alpha^2 \exp(-\gamma s^2) - \frac{1}{6} \right) a^2(s), \tag{58} \end{aligned}$$

$$\begin{aligned} c(s) &= (4\sqrt{\pi} - 6z(s)) a^7(s) + \frac{3}{2}(y(s) - f(s)) a^6(s) \\ &+ \left( \frac{1}{3} - \frac{4}{3}\alpha^4 \exp(-\gamma s^2) \right) a^4(s), \tag{59} \end{aligned}$$

using the integrals over the first $r^{-4}$ term of Eq [57],

$$\begin{aligned} z(s) &= \alpha Z \left( a^2 h(\chi) a(s) \right) \exp \left( -\gamma s^2 \right), \tag{60} \\ y(s) &= \alpha^2 Y \left( a^2 h(\chi) a(s) \exp \left( -\gamma s^2 \right), \right. \\ Z(x) &= \frac{1 + 2x^2}{\sqrt{1 + x^2}} - 2x, \tag{62} \\ Y(x) &= 1 + x^2 \ln \frac{x^2}{1 + x^2}, \tag{63} \end{aligned}$$

for $x \gg 1$, these should be computed as

$$\begin{aligned} Z(x) &= \frac{1}{\left( 1 + 2x^2 + 2\sqrt{1 + x^2} \right) \sqrt{1 + x^2}}, \tag{64} \\ Y(x) &= 1 - x^2 \ln \left( 1 + x^2 \right) = \sum_{k=0}^{\infty} \frac{(-1)^k}{(k + 2)x^{2k+2}} \tag{65} \end{aligned}$$

To follow the curvature of Eq. [12] at $s = 0$, we need

$$\gamma = 27\alpha^4 - 48\sqrt{\pi}\alpha^3 + 54\alpha^2 - 4, \tag{66}$$

The first term in Eq. [57] should smoothly switch from having the $-\frac{1}{4}r^{-4}$ tail to a short-range exponential behavior, to overcome the logarithmic singularity as $s \to 0$ in its integrals over $r$, such as in Eqs. [61] and [63]. We multiply $a(s)$ by the healing function $h(\chi)s$,

$$h(x) = \exp \left( -\frac{\exp \left( \frac{1}{2} - x^2 \right)}{\sqrt{2} |x|} \right), \tag{67}$$

that has its value and all derivatives zero at $s = 0$. For $\chi$, we can take either the greatest $\chi_0$ that still yields $b(s) \geq 0$, or the greatest $\chi_1$ that still yields a monotonic $b(s)$, by solving

$$\begin{cases} b^{(n)}(s_n; \chi_0) = 0, \\ b^{(n+1)}(s_n; \chi_0) = 0, \tag{68} \end{cases}$$
for $s_n$ and $\chi_n$, where $u^{(n)}(s; \chi) \equiv \partial^n b(s; \chi) / \partial s^n$; we can also set $\chi = 0$ to see what happens. Given some $a(s)$, there is an explicit closed-form expression for Eq. (49),

$$f(\lambda, s) = \bar{u}(\lambda, \alpha, h(\chi) s(a(s)) \exp (-\gamma s^2)$$

$$+ \left( \frac{4}{3} - a^2 \exp (-\gamma s^2) \right) \lambda^2 v_0(a(s) \lambda)$$

$$+ \frac{8}{3} b(s) \lambda^4 v_1(a(s) \lambda) + \frac{8}{3} c(s) \lambda^6 v_2(a(s) \lambda),$$

(69)

$$\bar{u}(\lambda, \alpha, \beta) = \alpha^2 \bar{v}((\alpha^2 + \beta^2) \lambda^2, \beta^2 \lambda^2)$$

$$+ \beta^2 \bar{v}((\alpha^2 + \beta^2) \lambda^2, \beta^2 \lambda^2),$$

(70)

$$\bar{v}(\sigma, \tau) = \frac{\sigma}{1 + \sqrt{1 + \sigma} + \sqrt{1 + \tau}},$$

(71)

$$\bar{v}(\sigma, \tau) = 2 \ln \frac{1 + \sqrt{1 + \tau}}{1 + \sqrt{1 + \sigma}}.$$  

(72)

For $f(s)$ of Eq. (26), we take $a(s)$ from Eq. (41) with $\alpha$ from Eq. (50), $a''(0) = 2a_2$ for $\gamma$ of Eq. (66), solve Eq. (68) to get

$$\chi_0 \approx 0.489520810866673031024609627137989575,$$

$$\chi_1 \approx 0.34629974067288586033506591442974003,$$

(73)

and now we can compare $\bar{f}(\lambda, s)$ of Eq. (69) to our best $f(\lambda, s)$ of Eqs. (47) and (49). In Fig. 1 the two functions are plotted and we see how regular they are and how little they differ, even more impressive is the colorful family of curves in Fig. 2 for their ratio $\bar{f}(\lambda, s)/f(\lambda, s)$. This way, we get a measure of their similarity,

$$1 \leq \bar{f}(\lambda, 0)/\bar{u}(\lambda) < 1.0142,$$

$$\chi = 0 : \ 0.986 < \bar{f}(\lambda, s)/f(\lambda, s) < 1.024,$$

$$\chi = \chi_1 : \ 0.950 < \bar{f}(\lambda, s)/f(\lambda, s) < 1.032,$$

$$\chi = \chi_0 : \ 0.903 < \bar{f}(\lambda, s)/f(\lambda, s) < 1.023.$$  

(74)

In the uniform electron gas limit, the nodeless shape function of Eq. (54) yields the integral $\bar{f}(\lambda, 0)$ that matches the exact $\bar{u}(\lambda)$ of Eq. (22) to within 1.5%, while for $s > 0$ the models are only a few times farther away from each other, being closest for $\chi = 0$. Thus, $\chi$ plays no dramatic role, and it seems better to cut the tail in depth by $\exp (-\gamma s^2)$ than at length by $\exp (-h(\chi) s^2(s^2))$, to enjoy a rewarding simplification of the equations. In this way, the function of Eq. (51) can also be used, and a cubic equation for $a(s)$ can then be set up, but we leave it out here to save space.

It is now clear that both kinds of shape functions — both the oscillatory of Eq. (46) and the non-oscillatory of Eq. (57) — would yield nearly the same integral output of Eq. (22) under the same constraints of Eqs. (19), (21), and (22). To our mind, the oscillatory function gives the best solution: we get an explicit closed-form expression for $f(\lambda, s)$ in terms of the given $f(s)$ using Eqs. (15), (49), (59), and (77). Furthermore, it has the exact uniform electron gas limit. Nevertheless, our experience with the non-oscillatory functions was not in vain and these can be used in the further work on new functionals.

It might be time for a thorough benchmark of the new model on a wide set of molecules, but we put it off for now until we learn how to combine it with a dispersion-correction functional42-43.

We find our long-range corrected version of the PBE4 functional with $\frac{1}{\omega} = 3$ au (an easy-to-remember whole number) to be already a good next step after its $\frac{1}{\omega}$-fixed-fraction hybrid44, and it can be used routinely in mechanistic studies of molecular structure and reactivity toward a full understanding of chemical kinetics.

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