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Analytical representation of the Becke-Roussel exchange functional

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Abstract

The unique meta-GGA (generalized gradient approximation) exchange functional of Becke and Roussel (BR89) and the correlation functional of Becke related to it (B94) are represented for the first time in an analytical form. All functional derivatives are then obtained analytically, which allows an efficient self-consistent implementation. A brief assessment of this “BR89B94” meta-GGA scheme is made considering molecular atomization energies and equilibrium geometries, with the latter being reported for the first time. The hybrid version of it yields one of the most accurate atomization energies to date, but its bond distances are less satisfactory. Some interesting features of the BR exchange hole are discussed.

1. Introduction

The Becke-Roussel (BR89) exchange functional [1] has attracted attention recently in Kohn-Sham density functional theory (KS-DFT) in relation to the real-space post-Hartree-Fock-DFT approach to the non-dynamical correlation [2,3], and the DFT model of Van-der-Waals interactions [4]. Its accurate performance has been established to some extent earlier [1,5]. The model is based on the following ansatz for the spherically averaged exchange hole (negatively defined here):

$$\bar{h}_x(a, b; s) = -\frac{a}{16\pi b s} \left[(a|b-s|+1)e^{-a|b-s|} - (a|b+s|+1)e^{-a|b+s|} \right], \quad (1)$$

where a , b are positive, position-dependent parameters and s is the inter-electronic distance. This ansatz originates from the form of the exchange hole of hydrogen atom. It provides the required normalization of the hole for any positive values of a and b :

$$4\pi \int_0^\infty \bar{h}_{x\sigma}(a, b; s) s^2 ds = -1 \quad (2)$$

It is plausible to assume that in atomic and molecular systems the exchange hole would resemble that of the hydrogen atom, which implies some degree of universality of this hole. A similar idea was explored also in the work of Gill and Pople [6]. This is in contrast to the alternative universality hypothesis that is behind the local spin density approximation (LSD) starting from a very different limit, the uniform electron gas. The two parameters a and b are used so as to obey the known value and curvature of the spherically averaged exact exchange hole at small s [1]:

$$\bar{h}_{x\sigma}(\mathbf{r}, 0) = -\rho_\sigma(\mathbf{r}), \bar{h}_{x\sigma}(\mathbf{r}, s)|_{s \rightarrow 0} = -\rho_\sigma(\mathbf{r}) - Q_\sigma(\mathbf{r})s^2, \quad (3)$$

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$$Q_{\sigma}(\mathbf{r}) = \frac{1}{6} \left[\nabla^2 \rho_{\sigma}(\mathbf{r}) - 2D_{\sigma}(\mathbf{r}) \right], D_{\sigma} = 2\tau_{\sigma} - \frac{1}{4} \frac{|\nabla \rho_{\sigma}|^2}{\rho_{\sigma}}, \quad (4)$$

where ρ_{σ} is the electron density of spin σ , $\mathbf{r}$ is the co-ordinate vector of the reference electron. These properties are provided when the parameters a and b obey the following system of equations:

$$a^3 e^{-ab} = 8\pi\rho_{\sigma}, \quad (5)$$

$$a^2 b - 2a = \frac{6bQ_{\sigma}}{\rho_{\sigma}}. \quad (6)$$

The above conditions lead to a specific nonlinear equation for x in a spin-resolved form with $x=ab$ ($x \geq 0$) [1]:

$$\frac{x_{\sigma} e^{-2x_{\sigma}/3}}{(x_{\sigma} - 2)} = y_{\sigma}(x) \equiv \frac{2}{3} \pi^{2/3} \frac{\rho_{\sigma}^{5/3}}{Q_{\sigma}} \quad (7)$$

Solving this equation at each reference point gives the function x_{σ} which in turn determines uniquely the exchange hole, the exchange energy (E_X) and the corresponding exchange energy density ("Slater potential", U_X):

$$E_X = \frac{1}{2} \sum_{\sigma} \int_{\infty^3} \rho_{\sigma}(\mathbf{r}) U_{x_{\sigma}}(\mathbf{r}) d\mathbf{r}, \quad (8)$$

$$U_{x_{\sigma}}(\mathbf{r}) = 4\pi \int_{\infty^3} s ds \bar{h}_{x_{\sigma}}(\mathbf{r}, s) = -2\pi^{1/3} \rho^{1/3} \left(\frac{e^{x_{\sigma}/3}}{x_{\sigma}} \right) \left[1 - e^{-x_{\sigma}} - \frac{1}{2} x_{\sigma} e^{-x_{\sigma}} \right]. \quad (9)$$

Eq.(7) is a complicated nonlinear equation and can only be solved numerically at each reference point, as suggested by Becke and Roussel [1]. Similar problem arises in the post-Hartree-Fock real-space correlation (RSC) model of Becke [2,3] where the shape of the BR exchange hole is used as an auxiliary function in a different context. For the latter, Arbuznikov and Kaupp [7] have proposed recently an analytical interpolation that avoids solving a nonlinear equation. However, the original BR exchange functional was not considered in their work. With this in mind, we present here a detailed analysis of the function $x(y)$ used in the original functional [1]. We will derive an analytical interpolation of $x(y)$ of high accuracy that will be used to achieve a self-consistent implementation of the BR exchange functional. Some interesting features of the BR exchange hole will be noted in passing.

2. Analytical Interpolation of the BR Functional

The original BR exchange model is based on solving the nonlinear equation (7) numerically for the unknown function $x(y)$. The inverse function $y(x)$, depicted on Fig. 1, is known, defined by Eq.(7) via the electron density and the exchange-hole curvature. It consists of two pieces delineated by a discontinuity point at $x=2$. The lower piece of $y(x)$ is located in the negative range of y for $0 \leq x < 2$ and has the following asymptotic form:

$$\lim_{x \rightarrow 0} y(x) \rightarrow -\frac{1}{2}x + \frac{1}{12}x^2, \quad (10)$$

$$\lim_{x \rightarrow 2} y(x) \rightarrow e^{-4/3} \left[\frac{2}{x-2} - \frac{1}{3} - \frac{2}{9}(x-2) \right] \rightarrow -\infty. \quad (11)$$

The upper piece of $y(x)$ is positive for $2 < x \leq \infty$, and tends to $+\infty$ by the same Eq.(11) when x approaches the singular point $x=2$ from above. When x goes to plus infinity, the upper piece of $y(x)$ tends to zero as:

$$\lim_{x \rightarrow +\infty} y(x) \rightarrow e^{-2x/3} \left[1 + \frac{2}{x} + \frac{4}{x^2} \right]. \quad (12)$$

Equation (7) can be solved numerically with respect to x on a grid of points along the y axis, and the shape of $x(y)$ can be envisaged numerically as in Fig. 2. Meaningful are only positive values of $x(y)$. Similar to $y(x)$, the function $x(y)$ consists of two pieces in the positive domain, delineated by a point of discontinuity at $y=0$. Both pieces tend to the same limit of $x=2$ when y tends to either minus infinity (the lower piece) or to plus infinity (the upper piece). This situation is rather different from the interpolation problem considered in ref.[7]. Their function is continuous with no singularities. In our case, the function $x(y)$ resembles the inverse hyperbolic function $\operatorname{arccsch}(y)$ to some extent. A more detailed analysis revealed that only the upper piece of $x(y)$ located in $0 \leq y \leq +\infty$ can be accurately interpolated by a properly shifted $\operatorname{arccsch}(x)$ function, as described further on.

In previous studies of the BR model [1,5,7], it was presumed that the variable y can be both positive or negative, for there is always a positive solution for $x(y)$ in the whole range of $-\infty \leq y \leq +\infty$ [1]. The curvature of the BR exchange hole is given by $-Q$ (from Eq.(3)). It is positive when the (negatively defined) hole is well localized around the reference point. In such cases the hole has a single minimum at the reference point where y is negative (Q is negative) and $x(y)$ is confined in the range $0 \leq x \leq 2$ (i.e. in the lower piece). When the curvature is negative (positive Q), the exchange hole has a local maximum at the reference point and a sphere (shell) of local minima around it at a certain distance (in 3D view). These features of the BR exchange hole are clearly discerned from Fig.2 of ref.[1] on the example of the neon atom: the transition from a positive curvature to a negative curvature of the exchange hole at the reference point occurs when the reference electron is brought far enough from the nucleus [1]. Having the function $x(y)$ in its lower piece where the hole curvature is positive is a rather different situation from having $x(y)$ in its upper piece where the hole curvature is negative. This difference is especially pronounced at small and vanishing values of $|y|$, close to the point of discontinuity $y=0$. We have verified that $x(y)$ remains finite in its upper piece for any arbitrary small but non zero value of y . Such a behavior resembles the function $\operatorname{arccsch}(x)$. In the vicinity of $y \approx -0$ the lower piece of $x(y)$ decreases much faster when y vanishes than $x(y)$ grows for $y \approx +0$ in its upper piece.

There is a second branch of $x(y)$ located in the positive range of y , but in the physically forbidden negative domain of $x(y)$ as shown on Fig.2. The point $y=0$ is therefore also a branching point for the solutions of the nonlinear Eq.(7). At this branching point the topology of the exchange hole changes drastically. The two positive pieces of $x(y)$ require therefore separate interpolation procedures. Recall that the lower piece is in the range $0 \leq x \leq 2$, for $-\infty \leq y \leq 0$. By inverting the asymptotic expansion of $y(x)$ at small x , Eq.(10), we obtain the following exact asymptotic limit of $x(y)$ that is accurate for $-0.1 \leq y \leq 0$:

$$\lim_{y \rightarrow -0} x(y) \rightarrow 3 - \sqrt{9 + 12y} \rightarrow 0. \quad (13)$$

In the opposite limit when y tends to $-\infty$, we obtain the following exact asymptotic form that yields accurate estimations in the range $-\infty \leq y \leq -2$:

$$\lim_{y \rightarrow -\infty} x(y) \approx \frac{5}{4} - \frac{9}{4}ye^{4/3} - \frac{3}{4}\sqrt{17 + 6ye^{4/3} + 9y^2e^{8/3}} \rightarrow 2. \quad (14)$$

To facilitate the analytical differentiation of the BR functional, it is desirable to approximate each piece of $x(y)$ with one single function. Following some reverse analogy with the problem

considered in ref.[7], we have found that the following trigonometric ansatz is quite suitable for the lower piece of $x(y)$:

$$x(y) = -\arctan(a_1 y + a_2) + a_3, -\infty \leq y \leq 0, \quad (15)$$

where the coefficients a_i are fitting constants. Those were optimized by solving numerically several systems of equations with respect to a_i generated by Eq.(15) at various wisely selected points of y . We achieved a further improvement in accuracy by employing in addition a modulating factor $f(y)$:

$$x(y) = [-\arctan(a_1 y + a_2) + a_3]f(y), -\infty \leq y \leq 0 \quad (16)$$

The factor $f(y)$ is optimized in a secondary optimization loop using the Thiele interpolation formula of continued fractions [8]. The corrections from this factor are important mainly in the region of small $|y|$. The final form of our analytical representation of $x(y)$ in its lower piece reads:

$$\begin{aligned} x(y) &= g(y) \frac{P_1(y)}{P_2(y)}, -\infty \leq y \leq 0, \\ g(y) &= -\arctan(a_1 y + a_2) + a_3 \end{aligned} \quad (17)$$

where $P_i(y)$ are fifth order polynomials:

$$P_1(y) = \sum_{i=0}^5 c_i y^i; P_2(y) = \sum_{i=0}^5 b_i y^i. \quad (18)$$

The optimal values of the coefficients a_i , b_i and c_i in Eq.(17, Eq.18) obtained in this work are given in Appendix. This form of $x(y)$ has asymptotic expansions that match closely the values of the exact asymptotic relations in Eq.(13, Eq. 14):

$$\lim_{y \rightarrow -0} x(y) = -1.999977y + 0.663026y^2 + 0.482251y^3 \quad (19)$$

$$\lim_{y \rightarrow -\infty} x(y) = 2 + \frac{1}{y} 0.527194 - \frac{1}{y^2} 0.046324 \quad (20)$$

Results with this form of $x(y)$ and the exact solution are presented in Table 1, with y values sampled in a wide range. One can see that the analytical fit provides a high accuracy with mean-absolute-deviation (MAD) = 7.73×10^{-7} , and mean-absolute-percentage-deviation (MAPD) = 0.0005%.

The upper piece of $x(y)$ is located in the positive domain $0 < y \leq +\infty$, where $x(y)$ is bound from below by a limit of $x \geq 2$ (Fig.2). By inverting the asymptotic expansion of $y(x)$ when x tends to 2 from above, Eq.(11), we obtain the following exact asymptotic form of $x(y)$ in its upper piece, accurate within the range $2 \leq y \leq +\infty$:

$$\lim_{y \rightarrow +\infty} x(y) \approx \frac{5}{4} - \frac{9}{4} y e^{4/3} + \frac{3}{4} \sqrt{17 + 6y e^{4/3} + 9y^2 e^{8/3}} \rightarrow 2 \quad (21)$$

Note that $x(y)$ has a discontinuity at $y=0$ here and we were not able to obtain analytically its asymptotic expansion in this limit. We have found that this piece of $x(y)$ can be very well approximated by a shifted arccsch(x) function, as it has a similar form and a similar behavior at small y . To achieve an even higher accuracy we have employed again a modulating factor $f(y)$ that is optimized in a secondary optimization loop similarly to the lower piece of $x(y)$, Eq. (16). The final form of our analytical representation of the upper piece of $x(y)$ is:

$$\begin{aligned} x(y) &= \tilde{g}(y) \frac{\tilde{P}_1(y)}{\tilde{P}_2(y)}, 0 < y \leq +\infty, \\ \tilde{g}(y) &= \operatorname{arccsch}(By) + 2, B = 2.085749716493756, \end{aligned} \quad (22)$$

where the modulation factor is again a ratio of two polynomials:

$$\tilde{P}_1(y) = \sum_{i=0}^5 d_i y^i; \tilde{P}_2(y) = \sum_{i=0}^5 e_i y^i, \quad (23)$$

The optimal coefficients in Eq.(23) obtained in this work are given in the Appendix.

The results from this interpolation have a MAD= 4.11×10^{-7} and MAPD= 2.03×10^{-5} . In our final implementation of the BR model we use Eq.(22, Eq. 23) for the upper piece of $x(y)$, and Eq.(17, Eq.18) for the lower piece.

Finding an accurate analytical representation of the function $x(y)$ is beneficial not only for the BR89 exchange functional. Becke has developed also an efficient meta-GGA correlation functional (B94) [9] which utilizes the BR89 exchange functional. The correlation energy density of B94 is a sum of opposite-spin and parallel-spin components, each derived separately:

$$\varepsilon_c^{\text{opp}} = -0.8\rho_\alpha\rho_\beta z_{\alpha\beta}^2 \left[1 - \frac{\ln(1 + z_{\alpha\beta})}{z_{\alpha\beta}} \right], \quad (24)$$

$$\varepsilon_c^{\text{par}} = \varepsilon_c^{\alpha\alpha} + \varepsilon_c^{\beta\beta}, \varepsilon_c^{\sigma\sigma} = -0.01\rho_\sigma D_\sigma z_{\sigma\sigma}^4 \left[1 - \frac{2}{z_{\sigma\sigma}} \ln \left(1 + \frac{z_{\sigma\sigma}}{2} \right) \right], \quad (25)$$

where D_σ is the τ -dependent term entering the expression of the exact exchange hole curvature, Eq.(4), and $z_{\sigma\sigma}$, are spin-dependent correlation lengths defined from physical arguments [9]:

$$z_{\alpha\beta} = 0.63 (R_F^\alpha + R_F^\beta); z_{\sigma\sigma} = 1.76 R_F^\sigma, \quad (26)$$

$$R_F^\sigma = -\frac{1}{U_{X\sigma}}. \quad (27)$$

$U_{X\sigma}$ is the exchange energy density of the BR89 exchange functional given as a function of x_σ by Eq.(9). Thus, the function $x(y)$ governs both the BR89 exchange and the B94 correlation functionals in a complicated manner. Results from this particular meta-GGA exchange-correlation scheme, BR89B94, were reported so far only in ref.[9] but within a post-LDA implementation using a numerical solution for $x(y)$. Later on Neumann et.al [5] studied the BR89 exchange in combination with the P86 GGA correlation functional [10] in a SCF manner, again with a numerical solution for $x(y)$. The analytical representation of the BR89B94 functional allows exploring its full capabilities, including the efficient calculation of the SCF energy and its gradients with respect to nuclear motions. It also avoids potential instabilities associated with numerical solutions particularly for small argument values.

3. Preliminary Results and Discussion

We have first examined the accuracy of our analytical interpolation on a set of nine atoms and nine molecules at their experimental geometries. All calculations were done with the Q-Chem program, 3.1 release [11]. The G3 theory basis set G3LARGE [12,13] and an unpruned grid consisting of 128 radial and 194 angular points were employed. All functionals considered, including the meta-GGA ones, are implemented in a fully SCF manner in the way described in ref.[14]. Table 2 compares total electron energies, their separate exchange and correlation components and atomization energies obtained with the BR89B94 functional with either analytical or numerical resolution for the function $x(y)$. A very good agreement between the two algorithms is systematically observed, with MAD for total electron energies of 6.7×10^{-5} a.u. Energy differences like atomization energies differ by only a fraction of a kcal/mol. We compare our results also with the original BR89B94 values reported in ref. [9]. The agreement on average is good (with CN having the largest error) considering that Becke and

Roussel have used a numerical basis [1] whereas we have used Gaussian basis set. Other differences between the two sets of results include the numerical quadratures, and possibly slightly different bond lengths used. We use here experimental geometries corrected for ro-vibrational effects as recommended in ref.[18]. Also to keep in mind that ref.[9] presents only D_o from which we have obtained the corresponding BR values of D_e by subtracting the experimentally derived zero-point vibrational contribution.

Next, we calculated a set of atomization energies and equilibrium geometries (Table 3) obtained using the analytical representation of the BR89B94 functional. The compact test set described in ref.[19,ref.14] was used in part here: carefully selected 20 diatomic molecules and 19 small to medium size polyatomic molecules:

H₂, N₂, F₂, O₂, S₂, P₂, Cl₂, HF, CO, NO, PN, CN, NH, CS, CH, OH, HCl, SiO, NaCl, NaF, HCN, H₂O, H₂S, CO₂, NH₃, PH₃, N₂O, H₂O₂, SiH₄, CH₄, C₂H₂, C₂H₄, C₂H₆, H₂CO, CH₃OH, C₆H₆, C₄H₆(trans-butadiene), C₄H₅N (pyrrole), C₅H₅N (pyridine).

About one third of these molecules are difficult cases at least at GGA level of DFT. Such a test composition allows more distinct comparison between different functionals. Using a very large set of molecules with a small fraction of “difficult” cases would be less informative [19]. Results from some popular functionals, BLYP [20,21], BtLap [20,14], B3LYP [22,23], BMK [24], M06 [25,26], are also given in Table 3 for comparison. All atomization energies D_e are computed at the respective optimized geometries without the zero-point vibrational correction. Since there are some slight differences in the exact values referred to in the literature, we summarize in Table 4 the exact atomization energies and bond lengths used here after a careful analysis and compilation of various experimental and theoretical literature data [16–18], [27, 28].

Comparing the absolute mean errors (MAE) for atomization energies D_e , the performance of the BR89B94 scheme is of about the same accuracy as BLYP, both having a slightly larger MAE than the meta-GGA functional BtLap reported recently [14]. These three functionals do not involve exact exchange. We used here the original parameterization of BR89B94 [9] that was based on post-LDA calculations at experimental geometries. We expect that a slight re-scaling of the two fitting parameters of this scheme would improve the accuracy further (work in progress). A one parameter hybrid scheme based on the BR89B94 functional (BR89B94_{hyb}) was also suggested in ref.[9], used in a post-LDA manner:

$$E_{xc} = 0.154E_{xc,exact} + 0.846E_{xc,BR89} + 1.0E_{c,B94} \quad (28)$$

To optimize this hybrid scheme, Becke re-scaled slightly the expression of the opposite-spin correlation length, Eq.(26) [9]:

$$z_{\alpha\beta} = 0.66 \left(R_F^\alpha + R_F^\beta \right) \quad (29)$$

Results with BR89B94_{hyb} implemented in a SCF manner are given in Table 3. Regarding atomization energies, this somewhat forgotten hybrid scheme yields the most accurate estimates on this test set. Much more extended tests on a large variety of systems are ongoing and will be reported later. Note that BR89B94_{hyb} has only three fitting parameters, one mixing parameter and two in the B94 correlation. B3LYP has eight parameters, while BMK and M06 are interpolation hybrid schemes with 17 parameters.

Regarding the bond distances in Table 3, the performance of the BR89B94 scheme is not so satisfactory, causing a noticeable elongation of some of the diatomic bond lengths (S₂, NaF, NaCl, NO, Cl₂). Since the parameters of this functional were optimized only on relative energies [9], some re-parameterization is required to improve the geometry estimates. The hybrid extension of this functional however, gives much better accuracy in this respect.

Although its MAE is somewhat larger than the other hybrid functionals presented in Table 3, the BR89B94_{hyb} functional is still better than the pure DFT schemes tested here. The above mentioned diatomic bond lengths present a difficulty for BR89B94_{hyb} as well, the reasons for which are currently under scrutiny (work in progress).

In conclusion, we derived and implemented for the first time a highly accurate analytical representation of the BR89B94 meta-GGA exchange-correlation scheme. It allows us to explore more fully its capabilities and leads to somewhat more robust implementation. Using the original parameterization of ref. [9] we find that the accuracy of this functional is reasonable as far as atomization energies concern, but not so good for geometry estimates. However, the one-parameter hybrid extension of it yields the best atomization energies compared to some popular current functionals. The geometry estimates with BR89B94_{hyb} are an improvement over the nonhybrid version of it, with the exception of a few diatomic molecules.

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Appendix

The proposed analytical form of the exchange functional BR89 can be summarized as (following Eq.(8)):

$$U_{x\sigma}(\mathbf{r}) = -2\pi^{1/3}\rho^{1/3}\left(\frac{e^{x_{\sigma}/3}}{x_{\sigma}}\right)\left[1 - e^{-x_{\sigma}} - \frac{1}{2}x_{\sigma}e^{-x_{\sigma}}\right], \quad (\text{A1})$$

$$x_{\sigma} = g(y_{\sigma})\frac{P_1(y_{\sigma})}{P_2(y_{\sigma})}, y_{\sigma}(x) \equiv \frac{2}{3}\pi^{2/3}\frac{\rho_{\sigma}^{5/3}}{Q_{\sigma}}, \quad (\text{A2})$$

where:

$$g(y) = -\arctan(a_1y + a_2) + a_3, -\infty \leq y \leq 0, \quad (\text{A3})$$

$$P_1(y) = \sum_{i=0}^5 c_i y^i; P_2(y) = \sum_{i=0}^5 b_i y^i, -\infty \leq y \leq 0; \quad (\text{A4})$$

$$g(y) = \operatorname{arccsch}(By) + 2, 0 < y \leq +\infty, \\ B = 2.085749716493756 \quad (\text{A5})$$

$$P_1(y) = \sum_{i=0}^5 d_i y^i; P_2(y) = \sum_{i=0}^5 e_i y^i, 0 < y \leq +\infty \quad (\text{A6})$$

The values of the coefficients a_i entering Eq.(17, Eq. A3) read:

$$a1 = 1.5255251812009530$$

$$a2 = 0.4576575543602858$$

$$a3 = 0.4292036732051034$$

The values of the coefficients c_i and b_i entering Eq.(18, Eq.A4) read:

$$c0 = 0.7566445420735584 \quad b0 = 0.4771976183772063$$

$$c1 = -2.6363977871370960 \quad b1 = -1.7799813494556270$$

$$c2 = 5.4745159964232880 \quad b2 = 3.8433841862302150$$

$$c3 = -12.657308127108290 \quad b3 = -9.5912050880518490$$

$$c4 = 4.1250584725121360 \quad b4 = 2.1730180285916720$$

$$c5 = -30.425133957163840 \quad b5 = -30.4251338516036600$$

The values of the coefficients d_i and e_i entering Eq.(23, Eq.A6) read:

$$d0 = 0.00004435009886795587 \quad e0 = 0.00003347285060926091$$

$$d1 = 0.58128653604457910000 \quad e1 = 0.47917931023971350000$$

$$d2 = 66.7427645159406100000 \quad e2 = 62.39226833857424000000$$

$$d3 = 434.267808972297700000 \quad e3 = 463.14816427938120000000$$

$$d4 = 824.776576605223900000 \quad e4 = 785.23603501040290000000$$

$$d5 = 1657.96527315821200000 \quad e5 = 1657.96296822327300000000$$

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Figure 1.
The starting function $y(x)$ defined via Eq.(7). This function is discontinuous at $x=2$.

Figure 2.
The required function $x(y)$ constructed from numerical estimates. The point of discontinuity at $y=0$ is also a branching point.

Table 1

Comparison of exact vs interpolated values of the function $x(y)$

$y < 0$	Exact $x(y)$	fitted $x(y)^a$	$y > 0$	Exact $x(y)$	Fitted $x(y)^b$
-0.001	0.000200007	0.000200004	0.0001	14.045919490	14.045919490
-0.01	0.020065982	0.020065542	0.001	10.672890134	10.672890134
-0.1	0.205805180	0.205805180	0.1	4.3713083907	4.3713083907
-0.5	0.980143530	0.980143530	0.5	2.8520020822	2.8520020822
-1.0	1.448513440	1.448513440	1.0	2.4752876179	2.4752876179
-2.0	1.726947198	1.726947198	3.0	2.1702309340	2.1702315305
-4.0	1.865532967	1.865532967	5.0	2.1035015269	2.1035015269
-8.0	1.933402964	1.933402964	8.0	2.0651537106	2.0651535646
-10.0	1.946830450	1.946830450	10.0	2.0522448435	2.0522448435
-100.0	1.994723437	1.994723443	100.0	2.0052672984	2.0052695780
MAD ^c		$7.73 \cdot 10^{-7}$			$4.11 \cdot 10^{-7}$
MAPD		0.0005 %			$2.03 \cdot 10^{-5}$ %

^aInterpolation of the lower piece of $x(y)$, Eq.(17, Eq. 18).

^bInterpolation of the upper piece of $x(y)$, Eq.(22, Eq. 23).

^cThe mean absolute errors are from a larger number of values than presented in the table.

Table 2

Total energy components ($-1 \times \text{a.u.}$) and atomization energies D_e (kcal/mol, no ZPE) obtained with, and without the analytical representation of BR89B94.

He	PW^{1a}			PW^{1b}			BR^c			PW^{1a}			PW^{1b}			BR^c			$exact^d$			$exact^d$		
	E_x	E_c	E_{tot}	1.03415	0.041372	2.91780	1.039	0.042	0.042	1.039	0.042	0.042	1.039	0.042	0.042	1.039	0.042	0.042	1.026	0.042	0.042	E_x	E_c	E_{tot}
																						E_c	E_{tot}	E_{at}
Ne	E_x			12.14603			12.19	12.11	12.11	12.19	12.11	12.11	12.19	12.11	12.11	12.19	12.11	12.11	12.11	12.11	12.11	E_x	E_c	E_{tot}
	E_c			0.36242			0.365	0.390	0.390	0.365	0.390	0.390	0.365	0.390	0.390	0.365	0.390	0.390	0.390	0.390	0.390	E_c	E_{tot}	E_{at}
	E_{tot}			128.98224			128.98227			128.98227			128.98227			128.98227			128.98227			E_{tot}	E_{at}	
Ar	E_x			30.06283			30.09	30.19	30.19	30.09	30.19	30.19	30.09	30.19	30.19	30.09	30.19	30.19	30.19	30.19	30.19	E_x	E_c	E_{tot}
	E_c			0.72806			0.730	0.722	0.722	0.730	0.722	0.722	0.730	0.722	0.722	0.730	0.722	0.722	0.722	0.722	0.722	E_c	E_{tot}	E_{at}
	E_{tot}			527.45448			527.45457			527.45457			527.45457			527.45457			527.45457			E_{tot}	E_{at}	
C	E_x			5.08154			5.08187			5.08187			5.08187			5.08187			5.08187			E_x	E_c	E_{tot}
	E_c			0.15332			0.15343			0.15343			0.15343			0.15343			0.15343			E_c	E_{tot}	E_{at}
	E_{tot}			37.86761			37.86791			37.86791			37.86791			37.86791			37.86791			E_{tot}	E_{at}	
N	E_x			6.61396			6.61406			6.61406			6.61406			6.61406			6.61406			E_x	E_c	E_{tot}
	E_c			0.18879			0.18878			0.18878			0.18878			0.18878			0.18878			E_c	E_{tot}	E_{at}
	E_{tot}			54.62044			54.62054			54.62054			54.62054			54.62054			54.62054			E_{tot}	E_{at}	
O	E_x			8.22177			8.22182			8.22182			8.22182			8.22182			8.22182			E_x	E_c	E_{tot}
	E_c			0.24393			0.24392			0.24392			0.24392			0.24392			0.24392			E_c	E_{tot}	E_{at}
	E_{tot}			75.10364			75.10370			75.10370			75.10370			75.10370			75.10370			E_{tot}	E_{at}	
F	E_x			10.05262			10.05266			10.05266			10.05266			10.05266			10.05266			E_x	E_c	E_{tot}
	E_c			0.302997			0.302994			0.302994			0.302994			0.302994			0.302994			E_c	E_{tot}	E_{at}
	E_{tot}			99.77505			99.77509			99.77509			99.77509			99.77509			99.77509			E_{tot}	E_{at}	
S	E_x			24.94265			24.94268			24.94268			24.94268			24.94268			24.94268			E_x	E_c	E_{tot}
	E_c			0.600913			0.600909			0.600909			0.600909			0.600909			0.600909			E_c	E_{tot}	E_{at}
	E_{tot}			398.07699			398.07704			398.07704			398.07704			398.07704			398.07704			E_{tot}	E_{at}	
Cl	E_x			27.42032			27.42036			27.42036			27.42036			27.42036			27.42036			E_x	E_c	E_{tot}
	E_c			0.664233			0.664227			0.664227			0.664227			0.664227			0.664227			E_c	E_{tot}	E_{at}
	E_{tot}			460.09049			460.09055			460.09055			460.09055			460.09055			460.09055			E_{tot}	E_{at}	

^a Present work with the analytical interpolation of $x(y)$, $MAD(E_{tot}) = 6.7 \times 10^{-5}$ a.u.

^b Present work with numerical solution for $x(y)$.

^c Results from ref.[1.ref.9] with the original BR89B94 scheme.

^dThe exact E_c 's of atoms are from ref.[15] based on exact Kohn-Sham exchange reference, rather than Hartree-Fock reference. The experimentally derived ("exact") values of D_e used in this work are obtained by a careful compilation of the data from ref.[16,ref.17].

Table 3

Mean absolute errors (MAE) for atomization energies D_e (kcal/mol, no ZPE) of 39 molecules, and MAE for bond lengths R_e (Å) in 36 molecules (45 bonds).

XC	20 diatomics	MAE for D_e		All 39 mol.
		XC with no HF exch.	19 polyatomics	
BLYP	5.58		5.23	5.41
BtLap	3.08		3.81	3.44
BR89B94	3.60		7.32	5.41
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		XC with HF exch.		
BMK	2.72		2.49	2.61
M06	2.69		2.57	2.63
B3LYP	2.51		1.82	2.17
BR89B94 _{hyb}	1.67		2.09	1.87
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XC	diatomics	MAE for R_e		All 45 bonds
		XC with no HF exch.	polyatomics	
BLYP	0.0174		0.0112	0.0140
BtLap	0.0155		0.0105	0.0127
BR89B94	0.0335		0.0117	0.0214
<hr/>				
		XC with HF exch.		
BMK	0.0112		0.0081	0.0095
M06	0.0083		0.0081	0.0082
B3LYP	0.0073		0.0046	0.0058
BR89B94 _{hyb}	0.0205		0.0036	0.0111

Table 4

Experimentally derived D_e (eV) [16,17] and R_e (Å) [27,28] used in this work. R_e includes vibrational, and ro-vibrational corrections whenever available [18].

Mol	D_e	R_e	Mol	D_e	R_e	Bond	R_e
H ₂	4.75	0.7414	HCN	13.52	1.1534	C–N	1.1534
N ₂	9.91	1.0977	H ₂ O	10.07	1.0653	C–H	1.0653
F ₂	1.67	1.4124	H ₂ S	7.91	0.9572	O–H	0.9572
O ₂	5.23	1.2075	CO ₂	16.87	1.3282	S–H	1.3282
S ₂	4.41	1.8892	NH ₃	12.90	1.1601	C–O	1.1601
P ₂	5.08	1.8934	PH ₃	10.48	1.0116	N–H	1.0116
Cl ₂	2.51	1.9870	N ₂ O	11.73	1.4200	P–H	1.4200
HF	6.11	0.9169	H ₂ O ₂	11.65	1.1284	N–N	1.1284
CO	11.24	1.1283	SiH ₄	13.94	1.1841	N–O	1.1841
NO	6.63	1.1508	CH ₄	18.18	1.4556	O–O	1.4556
PN	6.22	1.4909	C ₂ H ₂	17.58	0.9619	O–H	0.9619
CN	7.85	1.1718	C ₃ H ₄	24.40	1.4811	Si–H	1.4811
NH	3.62	1.0362	C ₂ H ₆	30.82	1.0859	C–H	1.0859
CS	7.43	1.5349	H ₂ CO	16.20	1.0807	C–H	1.0807
CH	3.63	1.1199	CH ₃ OH	22.20	1.3307	C–C	1.3307
OH	4.61	0.9697	C ₆ H ₆	59.24	1.0608	C–H	1.0608
HCl	4.61	1.2746	C ₄ H ₆	43.85	1.2037	C–C	1.2037
SiO	8.34	1.5097	C ₃ H ₅ N	46.42	1.5326	C–C	1.5326
NaCl	4.25	2.3608	C ₃ H ₅ N	53.62	1.1007	C–H	1.1007
NaF	4.98	1.9259	CH ₃ OH		1.2047	C–O	1.2047
					1.0936	C–H	1.0936
					0.9451	O–H	0.9451
					1.4246	C–O	1.4246
					1.0831	C–H	1.0831
					1.3964	C–C	1.3964