

Improved meta-GGA Correlation Functional of the Lap Family[†]

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Abstract: A new correlation functional of the Lap series is derived based on a more elaborated form of correlation wave vectors. Its validation is carried out within two different codes: deMon-KS3 and Q-Chem 3.0. In deMon the implementation in a post-SCF manner is similar to the preceding BLap3 and Bm τ 1 schemes. In Q-Chem the new functional is programmed self-consistently using the integration by parts procedure for the matrix elements. The post-SCF version of the functional deals with three fitting parameters; the previous Lap3 and τ 1 functionals have four and five parameters, respectively. The SCF implementation requires only two fitting parameters. Preliminary comparative tests are discussed.

1. Introduction

Since the mid 1980s and the early 1990s, the development of new exchange-correlation (XC) functionals is on the frontier of density functional theory (DFT). One of the present authors (E.P.) had the luck to get in the right place at the right time for functional development, by joining the Montreal group of Professor Dennis Salahub in 1991. The early 1990s was a time when generalized-gradient approximation (GGA) was triumphing for several years as a top-notch exchange-correlation theory. In the fall of 1992 Axel Becke in his talk on the Canadian Theoretical Chemistry Symposium in Montreal launched the idea of fusing exact exchange into the GGA machinery. This and his seminal papers on the subject¹ started the era of hybrid functionals. The dramatic increase of accuracy brought about by the hybrid approach shifted for awhile attention away from other possibilities for improvement. The Montreal group was particularly interested in developing such alternatives that would not require the more expensive exact exchange. A paper submitted in the beginning of 1994² showed that some improvement over GGA can be achieved by employing a correlation functional that involves the electron kinetic-energy density (τ) and the Laplacian of the electron density as functional variables. By the time the manuscript referred

to in ref 2 was submitted, functionals of a similar type were known only for exchange.^{3–5} At the Sanibel symposium in 1994 Becke⁶ reported another correlation functional that employs τ and the Laplacian of the density based on different arguments. The interest of the Montreal group on such functionals has persisted, and some further development (BLap3,⁷ Bm τ 1⁸) continued. Extensive validation tests were also reported by this and other groups showing that for some problems (weak hydrogen bonds,^{9–11} reaction barriers,^{12–14} proton affinities,¹⁵ transition-metal compounds^{8,12}) these new functionals may rival the hybrid methods. Other exchange and correlation functionals involving τ were proposed later on by different groups.^{16–19} All these were named ‘meta-GGA’ functionals by Perdew and co-workers^{17,18} In ref 18 it was mentioned that “The current revival of interest in meta-GGAs may be due to Salahub and collaborators”. It became gradually clear that the meta-GGA avenue hides some uncharted potentials. An accurate nonempirical meta-GGA scheme was also developed (the TPSS functional).^{19,22} More recently, accurate multiparameter hybrid-meta-GGA schemes were constructed improving reaction barriers and metal–ligand bonding.^{20,21}

In this work we explore one possibility of improving correlation functionals from the Lap family.^{2,7} These functionals employ the so-called correlation wave vectors. A more elaborated form of these wave vectors is employed here, as described in section 2. The meta-GGA correlation functional

[†] Dedicated to Professor Dennis R. Salahub on the occasion of his 60th birthday.

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Lap3⁷ is used as a starting point, and the new correlation functional is generated from it in section 3. Some preliminary validation tests are then discussed.

2. Theory

Various methods of deriving correlation functionals within the Kohn–Sham (KS) DFT have been developed to date. A summary of all these is beyond the scope of the present work. We focus here on the approach described in refs 2, 7, and 23. It is based on solving explicitly the adiabatic connection formula separately for each spin–spin component of the correlation energy using spin polarized, λ -dependent pair correlation functions (PCF). These functions depend on the interelectronic distance, the electron density n_σ and possibly its derivatives, and the correlation wave vectors (known also as inverse correlation lengths or scaling factors): $g_{\sigma\sigma}^{(\lambda)}(r_{12}; n_\sigma, n_\sigma', k_\sigma, k_\sigma')$. Once such PCFs are found, the exchange–correlation energy as defined in the KS-DFT scheme can be determined via the adiabatic connection formula^{24,25}

$$E_c^\dagger = \int_0^1 d\lambda \int d1 d2 \frac{1}{r_{12}} n_\dagger(1)n_\dagger(2) [g_{\dagger\dagger}^{(\lambda)}(r_{12}) - 1] \quad (1)$$

$$E_{xc}^{\sigma\sigma} = \frac{1}{2} \int_0^1 d\lambda \int d1 d2 \frac{1}{r_{12}} n_\sigma(1)n_\sigma(2) [g_{\sigma\sigma}^{(\lambda)}(r_{12}) - 1] \quad (2)$$

where λ is the coupling strength parameter as defined in the adiabatic connection method. The above formulas presume the following partitioning of the Kohn–Sham exchange–correlation energy density ϵ_{xc} into separate spin–spin components:

$$E_{xc}[n_\dagger, n_\downarrow] = \int dr n(\mathbf{r}) \epsilon_{xc}(\mathbf{r}), \quad n = n_\dagger + n_\downarrow \quad (3)$$

$$\epsilon_{xc}(n_\dagger, n_\downarrow) = \sum_\sigma \epsilon_{xc\sigma}(n_\sigma) + \epsilon_c^\dagger(n_\dagger, n_\downarrow) \quad (4)$$

$$\epsilon_{xc\sigma}(n_\sigma) = \epsilon_{xc\sigma}(n_\sigma) + \epsilon_c^{\sigma\sigma}(n_\sigma) \quad (5)$$

The latter expression, together with eq 2, define the exchange-only energy in the KS scheme as the $\lambda \rightarrow 0$ limit of the exchange–correlation energy.

Using pair-correlation functions and/or the associated exchange and correlation holes in real space has been one of the most popular approaches in deriving exchange and correlation functionals.^{3,25–30} Even though an exact first principles derivation of PCFs is prohibitive, some important properties of these are known, such as normalization conditions, cusp conditions and hole curvature, asymptotic behavior, and coordinate scaling properties. This gives a powerful tool in constructing ad hoc real space models based on physical arguments. Related to this is the existence of some degree of universality in the way electrons correlate in different systems, especially at small interelectronic distance.³¹ The behavior of the electrons at small and vanishing interelectronic distance is governed by specific cusp conditions for the PCF.^{32,33} These conditions are λ dependent and spin specific.³³ A family of spin-polarized, λ dependent PCFs that obeys automatically the opposite-spin cusp conditions was proposed in ref 23 (a typo in the way the parameter m enters the PCF is corrected in eq 8 below)

$$g_{\dagger\dagger}^{(\lambda)}(\mathbf{R}, r) = 1 - \exp(-k_{\dagger\dagger}^2 r^2) [F_1(\lambda) - F_2(\lambda)] \quad (6)$$

$$F_1(\lambda) = m - \Phi_{\dagger\dagger}^{(\lambda)}(m + \lambda r) \quad (7)$$

$$F_2(\lambda) = \exp(-k_{\dagger\dagger}^2 r^2) \left[m - 1 - \Phi_{\dagger\dagger}^{(\lambda)}(m + \lambda r) + (\Phi_{\dagger\dagger}^{(\lambda)})^2 \left(1 + \lambda r + \frac{\lambda^2 r^2}{4} \right) \right] \quad (8)$$

where $r = r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. For any m and $k_{\dagger\dagger}$, this PCF obeys the opposite-spin cusp conditions and has the following nonzero cusp:

$$\lim_{r \rightarrow 0} g_{\dagger\dagger}^{(\lambda)}(\mathbf{R}, r) = [\Phi_{\dagger\dagger}^{(\lambda)}(k_{\dagger\dagger})]^2 > 0 \text{ for any } 0 \geq \lambda \leq 1 \quad (9)$$

Finding a suitable parallel-spin PCF that would obey the respective (more complicated) cusp conditions is difficult because these involve the exchange and the same-spin correlation altogether.³³

The focus of this section is on the correlation wave vectors. The inverse of the wave vector of a given spin–spin component is related to the corresponding correlation length that governs the range of the correlated motion about a given reference electron. Solving the adiabatic connection formula 1 with the above PCF for $m = 2$ yields a correlation energy that is a function solely of the electron density and the wave vector $k_{\dagger\dagger}$ (see refs 7 and 23)

$$\epsilon_c^\dagger = \frac{n_\dagger n_\downarrow}{n} Q^\dagger(k_{\dagger\dagger}), \quad n = n_\dagger + n_\downarrow \quad (10)$$

$$Q^\dagger(k) = -\frac{b_1}{1 + b_2 k} + \frac{b_3}{k} \ln\left(\frac{b_4 + k}{k}\right) + \frac{b_5}{k} - \frac{b_6}{k^2} \quad (11)$$

where b_i are theoretical coefficients yielded by the algebra. The form of the wave vector $k_{\dagger\dagger}$ is not uniquely determined to this end and remains to be specified. Different functionals can in fact be generated from eqs 10 and 11 depending on what form of the correlation wave vector $k_{\dagger\dagger}$ is used. The same is true for the parallel-spin component of the correlation energy density $\epsilon_c^\sigma(n_\sigma)$ as defined by eq 5. In the Lap3 functional this energy is approximated by an ad hoc modification of eqs 10 and 11 (see ref 7 for details)

$$\epsilon_c^{\sigma\sigma} = \left(1 - \frac{1}{N_\sigma}\right) \frac{1}{2} \frac{n_\sigma^2}{n} Q^{\sigma\sigma}(k_\sigma) \quad (12)$$

$$Q^{\sigma\sigma}(k_\sigma) \approx C_p Q^\dagger(k_\sigma) \quad (13)$$

where N_σ is the total number of electrons with spin σ entering the Fermi-Amaldi type self-interaction correction (SIC) factor, and C_p is a ‘reduction’ parameter ranging between 0 and 1, that governs the relative share of parallel-spin correlation beyond the Fermi exchange. Again, various energy expressions can be generated using different forms of k_σ . The simplest choice for k_σ that follows from scaling and dimensional arguments and by analogy with the uniform electron gas is (“a rho to one-third” proportionality)

$$k_\sigma(\mathbf{r}) = \alpha_p k_{fg} \quad (14)$$

where α_p is a scaling parameter, and $k_{f\sigma}$ is the spin-polarized local Fermi wave vector:

$$k_{f\sigma}(\mathbf{r}) = a'_x n_\sigma^{1/3}(\mathbf{r}) = a_x [n(\mathbf{r})(1 \pm \xi(\mathbf{r}))]^{1/3},$$

$$\sigma = \uparrow(+), \sigma = \downarrow(-) \quad (15)$$

$a'_x = (6\pi^2)^{1/3}$, $a_x = (3\pi^2/2)^{1/3}$. The spin-polarization parameter ξ is defined as

$$n_\uparrow = \frac{1}{2}n(1 + \xi); \quad n_\downarrow = \frac{1}{2}n(1 - \xi) \quad (16)$$

The local Fermi wave vector is an important characteristic of the uniform electron gas reflecting the range of the Fermi interaction about a reference electron. Within approximation 14, the smaller the electron density, the larger the correlation length increasing as $1/n_\sigma^{1/3}$. More subtle is the problem of how to model the opposite-spin wave vector. To our knowledge, the only known approximation to date is the one proposed by Becke in the context of his 1988 correlation functional²⁷ (we call it here ‘Becke ansatz’). It is based on the plausible assumption that the correlation length for opposite-spin interaction is proportional to the arithmetic mean of the correlation lengths for the two same-spin interactions. With the local form of the wave vectors this leads to

$$k_{\uparrow\downarrow}(\mathbf{r}) = \beta_p \frac{2k_{\uparrow\uparrow}k_{\downarrow\downarrow}}{(k_{\uparrow\uparrow} + k_{\downarrow\downarrow})} \quad (17)$$

where β_p is another scaling parameter. In refs 2 and 7 it was set to $\beta_p = \alpha_p$ for simplicity. The only proof of this ansatz is ‘in the pudding’: it was thoroughly tested in the context of different functionals,^{2,6–8,27} and it normally leads to reasonable results. Using these formulas for the wave vectors in eqs 10–13 yields a correlation functional that depends solely on the electron spin densities (‘gradientless functional’). It is however not a uniform electron gas approximation per se. An important difference is²³ that eqs 10–13 obey the finite scaling bound, which is an exact property of finite systems but not of the uniform electron gas³⁴

$$\lim_{\gamma \rightarrow \infty} E_c[n_\gamma] > -\infty \quad (18)$$

where n_γ is homogeneously scaled electron density $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$.

The discussed gradientless functional was implemented (without the parallel-spin term) as a one-parameter local XC scheme in combination with the standard local-spin-density (LSD) exchange²³ as well as with a homemade modified local exchange.³⁵ The results for atomization energies and especially for bond lengths were on average better than the standard LSD. One possible reason for this is the fulfillment of the finite scaling bound, eq 18. Also, this functional and the gradientless potential that stems from it are self-interaction free.³⁷ Still, it remains a local functional in the sense that the correlation energy density depends solely on the local value of the electron density at a given reference point and does not ‘feel’ its neighborhood. A question then arises: how about other forms of the correlation wave vectors. Is it possible to generate a nonlocal functional

starting from eqs 10–13? One possibility for this was considered in ref 2 based on the notion of local electron temperature $k_B T_{s\sigma}$ as defined in the local thermodynamic approach of DFT (LTD).^{4,36} In spin polarized form this ‘temperature’ reads

$$k_B T_{s\sigma}(\mathbf{r}) = \frac{2}{3} \frac{t_{s\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} \quad (19)$$

where $t_{s\sigma}$ is the electron kinetic energy density by the LTD definition

$$t_{s\sigma} = \tau_\sigma - \frac{1}{8} \nabla^2 n_\sigma \quad (20)$$

and τ_σ is the (‘Laplacian-free’) electron kinetic energy density

$$\tau_\sigma = \frac{1}{2} \sum_i |\nabla \varphi_{i\sigma}|^2 \quad (21)$$

$\varphi_{i\sigma}$ are the KS SCF spin orbitals. Both definitions lead to the same total kinetic energy. With the particular choice of 1/8 for the coefficient multiplying the Laplacian, $t_{s\sigma}$, remains positively defined in most cases (section 4). The local electron temperature was used to model the spherically averaged exchange hole $\bar{h}_{\sigma\sigma}$ employed in the LTD approach:⁵

$$\bar{h}_{\sigma\sigma}(\mathbf{R}, r) \approx n_\sigma(\mathbf{R}) e^{-r^2 k_B T_{s\sigma}(\mathbf{R})} \quad (22)$$

This, together with eqs 19–21 suggests the following LTD ansatz for the parallel-spin correlation wave vectors:²

$$k_\sigma^2 \approx \alpha_e^2 \frac{2}{3} \frac{t_{s\sigma}}{n_\sigma} \quad (23)$$

In the present work we use a slightly different equivalent form of it:

$$k_\sigma^2 \approx \alpha_e^2 \frac{10}{3} \frac{t_{s\sigma}}{n_\sigma}, \quad \alpha_e^2 = \frac{\alpha_e'^2}{5} \quad (24)$$

When α_e and α_p from eq 14 are set equal, formula 24 provides a smooth transformation of the nonlocal wave vector to its local counterpart, eq 14, in the ‘gradientless limit’. This is the limit when all derivatives of the electron density vanish and the kinetic energy density is given by its uniform gas (spin-polarized) expression:

$$t_{s\sigma} = \tau_\sigma = C_{\text{TF}\sigma} n_\sigma^{5/3}, \quad C_{\text{TF}\sigma} = \frac{3}{10} (3\pi^2)^{2/3} 2^{2/3} \quad (25)$$

In the context of the LTD model, the electron correlation length increases (the wave vector k_σ decreases) when the electrons are ‘freezing down’ and their kinetic energy is decreasing.

For the opposite-spin wave vector we use the Becke ansatz in the context of definition 24:

$$k_{\uparrow\downarrow}(\mathbf{r}) = \beta_e \frac{2b_{s\uparrow}b_{s\downarrow}}{(\sqrt{n_\uparrow}b_{s\uparrow} + \sqrt{n_\downarrow}b_{s\downarrow})} \quad (26)$$

$$b_{s\sigma} = \sqrt{\frac{10}{3}t_{s\sigma}} \equiv \frac{1}{6}\sqrt{120\tau_{\sigma} - 15\nabla^2 n_{\sigma}} \quad (27)$$

Using this model for the wave vectors in eqs 10–13 generates a fully nonlocal correlation functional. By fully nonlocal we mean that it is not representable by any finite gradient expansion about either the uniform-gas limit or some other local form of the correlation energy. Using the nonlocal wave vectors, eqs 24 and 26, in the corresponding PCF, eq 6, transforms the latter into a fully nonlocal PCF similar to the PCFs used in the weighted density approximation.³⁸

Having τ as a functional variable has some advantages. It is a fine-tuned real space descriptor of inhomogeneity in atoms and molecules.³⁹ The curvature of the exact exchange hole also depends on τ and the Laplacian of the density, which has been a motivation of using these as functional variables.^{3,6,30} The LTD analogy discussed above is yet another complementary motivation for the same.²

Recently a new functional originating from the same family of PCF, eq 6, was considered⁴⁰ and used to obtain a compact analytical representation of the uniform electron gas correlation energy.⁴⁰ In due course of these derivations it became evident that the correlation wave vectors, as given by eqs 14 and 17, are still missing something. Based on an analytical fit to literature benchmark values of the correlation energy it was shown⁴⁰ that the scaling parameters α_p and β_p should be multiplied by certain functions of the electron density (or equivalently the density parameter $r_s = (3/4\pi n)^{1/3}$):

$$k_{\sigma}(\mathbf{r}) = \alpha_p \alpha_{\text{eff}}(r_s) k_{i\sigma} \quad (28)$$

$$k_{\uparrow}(\mathbf{r}) = \beta_p \beta_{\text{eff}}(r_s) \frac{2k_{\uparrow}k_{\downarrow}}{(k_{\uparrow} + k_{\downarrow})} \quad (29)$$

$$\beta_{\text{eff}}(r_s) = \eta_1 + \eta_2 \exp(-\eta_3 r_s^{1/3}) r_s^{1/4} + \eta_4 \exp(-\eta_5 r_s^{1/3}) r_s^{1/3} \quad (30)$$

$$\alpha_{\text{eff}}(r_s) = \eta_6 + \eta_7 \exp(-\eta_8 r_s^{1/3}) r_s^{2/3} + \eta_9 \exp(-\eta_{10} r_s^{1/3}) r_s^{1/3} \quad (31)$$

The optimal values of the coefficients η_i were obtained in ref 40 based on an interpolation of the uniform electron gas benchmarks data of refs 41–43.

Employing such density dependent screening functions in the local form of the correlation wave vectors was necessary to achieve a good interpolation of the transition between the high-density and the low-density limits of the uniform electron gas.⁴⁰ The present work aims at verifying whether incorporating these screening functions (with some additional scaling) in the nonlocal wave vectors would affect the accuracy of a nonlocal functional that employs them, such as Lap3 for example. One may suspect that for atoms and molecules the corresponding screening functions would be quite different from those suitable for the uniform electron gas. Nevertheless, we believe that even though finite systems like atoms and molecules are different from the uniform electron gas, some similarity may exist in the way electron correlation changes upon a transition from regions of high electron density to regions of low electron density. This is

of course only a hypothesis ('a similarity hypothesis') that can in part be verified by the quality of the results discussed next.

3. Derivation of the tLap Correlation Functional

The new correlation functional is obtained from eqs 10–13 using the following novel form of the correlation wave vectors (compare with eqs 24 and 26)

$$k_{\sigma}^2 = \alpha_e^2 \alpha_{\text{eff}}^2(n) \frac{10}{3} \frac{t_{s\sigma}}{n_{\sigma}} \quad (32)$$

$$k_{\uparrow}(\mathbf{r}) = \beta_e \beta_{\text{eff}}(n) \frac{2b_{s\downarrow} b_{s\uparrow}}{(\sqrt{n_{\downarrow}} b_{s\downarrow} + \sqrt{n_{\uparrow}} b_{s\uparrow})} \quad (33)$$

where the factors $b_{s\sigma}$ are given by eq 27, $\alpha_{\text{eff}}(n)$ and $\beta_{\text{eff}}(n)$ are the density-dependent screening functions, eqs 30 and 31, after changing the variable r_s to n . We have implemented this correlation functional ('tLap' from "tau+Laplacian") in two different codes: in a developing version of Q-Chem 3.0⁴⁷ and in a modified version of the deMon-KS3 code.⁴⁶ The latter is an old noncommercial release of the deMon program.

The new form of the wave vectors induces some modifications of the functional structure. In the original Lap3 functional, one of the theoretical b_i coefficients, namely b_3 in eqs 11 and 13, had to be rescaled in order to optimize reasonably the results. This was thought to be due to the approximate PCF used. Preliminary tests of the tLap functional revealed that this empirical adjustment was actually necessary to compensate for an imprecision of the wave vectors used. In the tLap functional a relaxation of the b_3 coefficient is no longer required. In fact, the optimal results are obtained when this coefficient keeps its theoretical value together with the rest of b_i : $b_1 = 2.763169$; $b_2 = 1.757515$; $b_3 = 1.741397$; $b_4 = 0.568985$; $b_5 = 1.572202$; $b_6 = 1.885389$

Yet another empirical parameter is no longer necessary, the reduction factor C_p in the parallel-spin correlation energy component, eq 13. In the tLap functional it is set to $C_p \equiv 1$, while the balance between opposite-spin and parallel-spin correlation is tuned by the two scaling parameters α_e and β_e in eqs 32 and 33. These are the only two fitting parameters in the tLap functional.

The implementation of the new functional in deMon-KS3 in a post-SCF fashion is similar to the Lap3 and τ_1 functionals. The exchange functional of Becke(88)⁴⁹ is used throughout this work as a partner of tLap ('BtLap' XC scheme). Hence the post-SCF implementation is based on a KS potential that consists of two terms: (i) the Becke(88) exchange potential in a fully SCF manner and (ii) a local correlation potential obtained by differentiating the correlation energy in its gradientless limit, i.e., when eqs 28 and 29 are used for the wave vectors in place of eqs 32 and 33. In this local potential the two scaling parameters are set equal, $\alpha_p = \beta_p$, which gives one fitting parameter in the potential to optimize with respect to geometry estimates. Such a potential composition, even though not fully SCF, yields very good structure parameters, especially concerning weak

Table 1. Molecules Included in the Validation Tests

H ₂ , N ₂ , F ₂ , O ₂ , S ₂ , P ₂ , Cl ₂ , HF, CO, NO, PN, CN, NH, CS, CH, OH, HCl, SiO, NaCl, NaF, HCN, H ₂ O, H ₂ S, CO ₂ , NH ₃ , PH ₃ , N ₂ O, H ₂ O ₂ , SiH ₄ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , H ₂ CO, CH ₃ OH, C ₆ H ₆ , <i>trans</i> -butadiene (C ₄ H ₆), pyrrole (C ₄ H ₅ N), pyridine (C ₅ H ₅ N)

intermolecular and intramolecular hydrogen bonds.⁸ In the case of tLap the corresponding local correlation potential is a bit more complicated due to the presence of the density-dependent screening functions, eqs 30 and 31. Post-SCF implementation of meta-GGA functionals was recently adopted also in the code ADF based on BLYP as a SCF carrier (see ref 14). The improvement brought by the meta-GGA functionals is mostly in the relative energies. A post-SCF implementation allows for the benefit from this in an economic way (“get the most for the least”). Similar is the situation with the CCSD(T) post-Hartree–Fock method for example. Nevertheless, a SCF implementation of the BtLap functional has its merits. Having the true analytical energy gradient is very important for various applications. We present here SCF results with the BtLap functional within the Q-Chem code. In the MO-LCGTO representation the matrix elements of the XC potential ($V_{\mu\nu}^{\text{xc},\sigma}$) are determined by differentiating the XC energy matrix over the density matrix ($P_{\mu\nu}^{\sigma}$)

$$V_{\mu\nu}^{\text{xc},\sigma} = \frac{\partial E_{\text{xc}}}{\partial P_{\mu\nu}^{\sigma}} = \sum_i \frac{\partial f_{\text{xc}}}{\partial g_i} \frac{\partial g_i}{\partial P_{\mu\nu}^{\sigma}} \quad (34)$$

where f_{xc} is the exchange-correlation kernel that is a function of certain variables g_i :

$$E_{\text{xc}} = \int f_{\text{xc}}(g_1, g_2, \dots, g_i, \dots) d\mathbf{r} \quad (35)$$

This is equivalent to the integration by parts standard procedure of evaluating matrix elements of a XC potential without computing explicitly this potential.^{48,50} In the case of tLap, the functional variables to differentiate upon are n_{σ} , τ_{σ} , and $\nabla^2 n_{\sigma}$, $\sigma = \alpha, \beta$.

4. Results and Discussion

Detailed validation tests of the BtLap XC scheme are currently ongoing. Here we report some preliminary results following the wisdom that a careful selection of diverse test examples is more important than their number.⁵² We use in part the test set elaborated previously.^{7,8,51} It includes atomization energies and bond lengths for a variety of bonding situations that have proven to be difficult at least for the GGA functionals. The choice of the examples was based also on the availability of benchmark data. The set of molecules used in the present tests is listed in Table 1.

In addition to this, we include the dimerization energy and geometry of two weakly bound dimers (H₂O)₂ and (HF)₂ as examples of intermolecular hydrogen bonding.^{8,51}

The calculations with deMon-KS3 employ a TZVP2* orbital basis set of Gaussian-type functions that had been optimized specifically for KS-DFT calculations.⁵³ Auxiliary bases from the deMon library were used for fitting the charge density and the XC potential in order to avoid four-center

integrals and to facilitate the energy derivatives. Upon SCF convergence, one final extra-iteration is performed numerically (without fitting) on the grid to obtain more accurately the total energy.

Several different basis sets of Pople were tested within Q-Chem, ranging from 6-311G(d), and 6-311++G(d,p), to 6-311++G(f,d,p) up to the exhaustive G3LARGE available in Q-Chem. For each system we have used the largest basis set that still leads to a converged, stable SCF solution. Both Q-Chem and deMon-KS3 employ atom-centered grid for the numerical integrations. Becke’s relative weight scheme⁵⁴ is used to adjust the weights as the grid points originating from different atoms overlap in space. The radial part of the grid is treated by the Euler-Maclaurin scheme proposed by Murray et al.⁵⁵ and the angular part by Lebedev quadrature.⁵⁶ In Q-Chem the quadrature is pruned by removing angular points from regions where they are not necessary. We use here the pruned grid SG-1,⁵⁷ which has 50 radial and 194 angular points. In some cases a larger grid of 128 radial and 194 angular points was used. It has been shown recently⁵⁸ that auxiliary cubic grids can be used to reduce greatly the cost of the atom-centered grid. The calculations with deMon-KS3 employ an unpruned grid scheme as described in ref 46. The user defined number of grid points was 128 radial points and 194 Lebedev angular points. The optimization of the fitting parameters in tLap is completed so far within the deMon-KS3 code only. With Q-Chem we employ for the time being these parameter values. The optimization was done looping over a subset of 10 molecules (H₂, N₂, O₂, F₂, CO₂, N₂O, CH₄, C₂H₄, C₆H₆, (H₂O)₂) and comparing atomization energies and bond lengths. Atomic correlation energy tests are not used in the present fitting procedure. The following parameter values are obtained: (1) $\alpha_e = 2.53$ – optimizes the share of parallel-spin correlation and (2) $\beta_e = 1.087$ – optimizes the share of opposite-spin correlation. In the post-SCF implementation there is one additional parameter entering only in the local SCF correlation potential: (3) $\alpha_p = \beta_p = 0.786$ – optimizes the geometry performance.

The SCF implementation of the BtLap scheme in Q-Chem is based on eq 34. Special care should be taken to avoid negative values of the kinetic energy density t_s , eq 20, since the wave vectors are ill defined in such cases. We have verified the sign of t_s for each system studied at each grid point and SCF iteration. With no exception t_s as defined by eq 20 remained always positive after the first 4–5 SCF iterations. However, its sign often fluctuates at the beginning of the SCF, which may cause convergence problems. To avoid such situations we do the first 4 SCF iterations using the local correlation potential used in the post-SCF implementation of BtLap.

The atomization energy (E_{at}) is calculated as the difference between the molecular ground-state energy and the sum of ground-state energies of the constituent atoms. One problem here is that the atomic ground state is not unambiguously determined within the standard KS-DFT scheme based on a single KS determinant. Results from different codes may slightly differ depending on how atoms are handled. In both Q-Chem 3.0 and deMon-KS3, the single-determinantal atomic KS state is converged to integer orbital occupancies.

Table 2. Mean Absolute Deviations (kcal/mol) for Atomization Energies (without the ZPE Contribution)

functional	20 diatomics	19 polyatomics	all 39	12 difficult
XC with no HF Mixing				
BP(d) ^a	3.94	15.13	9.39	20.68
BP(Q)	5.97	16.40	10.85	22.37
BLYP(Q)	5.58	5.23	5.41	7.73
OCS1(d) ^b	4.36	3.16	3.78	4.82
BLap3(d) ^a	3.30	8.39	5.78	9.86
Bm τ 1(d) ^a	3.11	4.13	3.61	5.09
BtLap(d)	3.21	3.60	3.41	4.77
BtLap(Q)	3.08	3.81	3.44	5.67
Hybrid XC				
BMK(Q)	2.72	2.49	2.61	2.58
B3LYP(Q)	2.54	1.84	2.20	2.42

^a Result from ref 8. ^b Result from ref 51 where the OCS1 XC scheme of Handy and Cohen^{61,62} was implemented in deMon-KS3.

For open-shell atoms this means having one or several holes within a partly filled shell. The location of these holes is sensitive to the functional used and the way the SCF procedure is conducted. The two codes use different approaches in constructing the KS potential and conducting the SCF procedure. As it was mentioned before, deMon-KS3 uses auxiliary basis fitting. As a result, one may observe some differences in the atomization energies between the two codes. Using fractional orbital occupancies that maintain atomic spherical symmetry is another known way of handling atoms within the standard KS scheme. However, the physical meaning of such ‘spherical atoms’ is not so obvious.

Table 2 contains the calculated atomization energies in terms of mean absolute deviations (MAD) from the experimental values. The post-SCF BtLap results with deMon-KS3 are labeled ‘BtLap(d)’, while the SCF BtLap results with Q-Chem are labeled ‘BtLap(Q)’. Similarly are labeled other XC functionals used with either of the two codes for comparison. The deviations are with respect to experimental values deduced from refs 59 and 60 after removing the temperature and ZPE contributions.

Comparing the BtLap(d) results with BLap3(d), a visible improvement is seen with BtLap(d). To note in particular the decrease of MAD for polyatomics from 8.39 kcal/mol with BLap3(d) to 3.6 kcal/mol with BtLap(d) and the decrease of MAD for the selected 12 ‘difficult’ molecules from 9.86 kcal/mol with BLap3(d) to 4.77 with BtLap(d). The latter are cases where the GGA scheme BP shows MAD bigger than 0.5 eV: O₂, CO₂, N₂O, H₂O₂, CH₄, C₂H₄, C₂H₆, CH₃OH, C₆H₆, C₄H₆, C₄H₅N, C₅H₅N. Among the functionals with no HF mixing in Table 2, BtLap(d) shows the smallest MAD. The MAD of the self-consistent version BtLap(Q) is slightly smaller than that of BtLap(d) for diatomic atomization energies and slightly bigger in the polyatomic case, Table 2. The latter is mainly due to the somewhat bigger MAD for the considered 12 difficult cases. This will be kept in mind during the reoptimization of the two fitting parameters in BtLap(Q). We expect that using the new form of the correlation wave vectors in other similar functionals, as for example Bm τ 1, may bring some relative improvement there as well (work in progress).

Table 3. Mean Absolute Deviations (Å) for Bond Lengths of 36 Molecules (45 Bonds)

functional	diatomics	polyatomics	all
XC with no HF Mixing			
BP(d) ^a	0.0242	0.0136	0.0183
BP(Q)	0.0230	0.0132	0.0176
OCS1(d) ^b	0.0271	0.0231	0.0249
BLYP(Q)	0.0174	0.0112	0.0140
BLap3(d) ^a	0.0189	0.0080	0.0132
Bm τ 1(d) ^a	0.0198	0.0084	0.0128
BtLap(Q)	0.0155	0.0105	0.0127
BtLap(d)	0.0133	0.0084	0.0106
Hybrid XC			
BMK(Q)	0.0112	0.0081	0.0095
B3LYP(Q)	0.0073	0.0046	0.0058

^a Result from ref 8. ^b Result from ref 51.

It is interesting to compare the atomization energies with one and the same GGA scheme, say BP, Becke(88)⁴⁹ exchange plus Perdew(86)^{63,64} correlation, with each of the two codes (Table 2). In deMon-KS3 BP is implemented self-consistently using analytical functional derivatives for the SCF XC-potential but fitting its numerical values using an auxiliary basis set. In Q-Chem the BP XC scheme is implemented using the integration by parts procedure to evaluate the matrix elements of the SCF potential with no auxiliary basis fitting. This leads to some differences in the BP results obtained with the two codes.

We compare also the results with the OCS1 and BLYP functionals, following up the discussion on the same in ref 62. Keeping in mind the different codes and test sets used, the present results seem to confirm that OCS1 yields on average better atomization energies than BLYP. While being not strictly speaking GGA functionals, both OCS1 and BLYP are performing better than BP, at least on the test set used here.

Concerning the two hybrid functionals, B3LYP and BMK, both yield MAD of atomization energies below 3 kcal/mol on this test set, B3LYP doing slightly better than BMK. The latter was particularly optimized for thermochemical kinetics.²⁰ Maintaining at the same time very good performance on atomization energies is a plus for the BMK scheme.

Next we consider the functional performance for bond lengths. The reference bond lengths are from the experimental data in refs 66 and 67 corrected for rovibrational effects⁶⁵ when necessary. The obtained MAD values with different functionals are listed in Table 3. Comparing again BtLap(d) with BLap3(d), some improvement is seen with BtLap(d) yielding MAD close to that of BMK(Q). To keep in mind here that BtLap(d) and BLap3(d) are post-SCF schemes, and these bond lengths are a merit of the respective local correlation potential as explained in the preceding section. The MAD with the SCF version BtLap(Q) are somewhat bigger than that of BtLap(d) due to some more or less systematic elongation of the bond lengths.

The hybrid schemes BMK, and especially B3LYP, yield rather good bond lengths on this test set.

It is seen that the selected set of test examples, even though not large in number, allows for the assessment of the

Table 4. BSSE Corrected Dimerization Energy (kcal/mol) and Distances (Å) in the Water Dimer and HF Dimer

functional	(H ₂ O) ₂		(HF) ₂	
	E _b	R(OO)	E _d	R(FF)
Pure DFT XC with no HF Mixing				
BP(d) ^a	4.69	2.885	4.56	2.705
BP(Q)	4.06	2.900	4.06	2.737
BLYP(Q)	4.08	2.944	4.22	2.774
BLap3(d) ^a	4.63	2.979	4.68	2.793
Bm τ 1(d) ^a	4.79	2.982	4.54	2.793
BtLap(d)	4.91	2.941	4.87	2.760
Hybrid XC				
BMK(Q)	4.13	2.936	4.27	2.728
B3LYP(Q)	4.37	2.919	4.53	2.745
experiment ^b	4.7–5.0	2.95–2.97	4.5–4.7	2.74–2.78

^a Reference 8. ^d References 68 and 69 for (H₂O)₂, ref 70 for (HF)₂.

functional performance. We agree with the conclusions of ref 52 that a huge number of tests is not necessary. The situation is similar to the pre-election polls. These can yield reliable predictions and statistics even though only a small fraction of the electorate is questioned. Including cases that are difficult for at least GGA helps the analysis more when they are not immersed in a very large number of other tests.⁴⁰

Our last test example is on the weakly bound water dimer and HF dimer held by a hydrogen bond (Table 4). The BLap3, BP, and Bm τ 1 results have been reported previously⁸ and are given here for comparison.

Regarding the water dimer, BtLap(d) and BLap3(d) yield comparable dimerization energies, both within the experimental margin. With an exception of BP(d), the rest of the results included in Table 4 are slightly below the lower end of the experimental range. Turning to the dimerization energy of (HF)₂, the BLap3(d) estimate is within the experimental margin, while the BtLap(d) energy is slightly above it. B3LYP(Q) and BP(d) yield for this dimer an accurate estimate, BMK(Q), BLYP(Q) and BP(Q) hit again somewhat lower. For both dimers the largest margin between the various energy estimates is less than 0.85 kcal/mol. More diverse are the results for the long O–O and F–F distances. These are known as difficult to reproduce characteristics. The BtLap(d) scheme is doing slightly better than BLap3(d) in both cases. Again to keep in mind that these distances are not a merit of the nonlocal tLap correlation functional per se but of the associated local potential in the post-SCF implementation of BtLap(d). The BtLap(Q) SCF version still meets some accuracy problems here, and the results will be reported elsewhere.

The considered hybrid methods have some problems in reproducing the O–O distance in the water dimer, tending to underestimate it: B3LYP by about 0.03 Å from the lower end of the experimental margin, BMK by about 0.015 Å. According to our data, the simpler BLYP scheme seems to perform better than either B3LYP or BMK in this case. B3LYP is doing very well for the F–F distance in the HF dimer, while BMK slightly underestimates it.

Concerning other tests from the set package considered in refs 8 and 51, the calculations are completed with BtLap-

(d), the results being of about the same quality as those with BLap3(d). The optimization of the SCF scheme BtLap(Q) within Q-Chem is work in progress. The improvement over BLap3 achieved with the BtLap functional is mainly in the calculated thermochemical and structural data, Tables 2 and 3.

One final remark about the importance of the correlation energy in KS-DFT: the exchange energy is usually about 10–20 times bigger than the correlation energy. This may produce the illusion that correlation functional is not that important and all we need is a good exchange functional. The present results clearly illustrate among other things that using the same exchange functional with various correlation counterparts leads to a dramatic alteration of the DFT accuracy. Both components of the XC functional are equally important since their separate definition and treatment is only virtual.

5. Conclusions

This work explores a way of improving further correlation functionals of the Lap series that were developed in the 1990s in the research group of Professor Dennis Salahub. Recent study⁴⁰ has shown, based on uniform electron gas tests, that the correlation wave vectors used in this type of functionals are still missing something. Corrections in terms of density dependent screening functions are proposed that yield a new functional starting from the Lap3 formulation. Compared to the latter, noticeable improvement for atomization energies is achieved, while two of the previous fitting parameters inherited from Lap3 are no longer necessary. One explanation for this is that the employed local screening functions seem to provide (after some uniform scaling) a reasonable transition between the high-density and low-density limits even in finite systems. This may suggest that the similarity hypothesis discussed above (which is close in spirit to the short-wavelength hypothesis³¹) has some reasoning. Interpolations of similar kind based on precise analysis of the uniform electron gas in the two density limits and real space cut-offs and splines were the keys in constructing nonempirical GGA and meta-GGA functionals (see ref 19 and references therein). The tLap model uses an alternative approach toward a similar goal in the context of a fully nonlocal functional. It would become nonempirical when the scaling parameters α_e and β_e in eqs 32 and 33 are equal to 1.00. The value of the opposite-spin scaling parameter β_e used now (1.087) is close to its theoretical value of 1.00. A better parallel-spin correlation model is needed to complete the goal.

The screening functions were obtained in ref 40 based on an interpolation to benchmark values of the spin-resolved correlation energy of the uniform electron gas. Two different forms of these functions were reported corresponding to two different benchmark energy data. The form used here conforms to the data of refs 41–43. We have tried also the second form of the screening functions that matches the energy estimates of refs 44 and 45. The two reference energy sources differ in the dependence of the separate spin components of the correlation energy on the density parameter. We were not able to find a suitable parametrization of

the tLap functional that would yield improvement using the second type of screening functions.

The BtLap scheme is implemented in two different codes, Q-Chem 3.0 and deMon-KS3. In spite of the program differences, the results obtained with BtLap(d) /deMon-KS3 and BtLap(Q) /Q-Chem so far agree reasonably. The optimization of the SCF version BtLap(Q) is in progress.

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