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Modified Becke'05 method of nondynamic correlation in density functional theory with self-consistent implementation

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Abstract

Becke's B05 method for nondynamic correlation is simplified for self-consistent implementation. An alternative form is proposed for the nondynamic correlation factors that do not require solving a complicated nonlinear algebraic equation. The four linear parameters of B05 are re-optimized together with one extra parameter entering a modified expression for the second-order same-spin energy contribution. The latter is co-linear with the exact-exchange energy density and does not require higher moments of the relaxed exchange hole. Preliminary tests of this method show that it leads to a slight improvement over the resolution-of-identity B05 results reported previously for atomization energies, and to a definite improvement for reaction barriers of Hydrogen abstraction.

Systems with strong nondynamic (ND) electron correlation remain a major challenge for Density Functional Theory (DFT) [1–4]. Various solid state phenomena, reaction barriers, transition-metal compounds and others, manifest such a strong correlation. A significant breakthrough in DFT modeling of ND correlation is the post-LSD real-space correlation method of Becke: the B03 and B05 schemes [1, 5]. Another DFT model that includes ND correlation with full exact exchange, the PSTS functional, was suggested later on [2]. Other avenues to the ND correlation in DFT are also gaining steam [6–11].

The B05 results obtained in a post-local-spin-density (LSD) manner, were very promising [5], especially concerning barriers of “difficult” reactions [12], but the calculations turned out very costly. In our recent work [13], the B05 method was implemented self-consistently in the “SCF-RI-B05” scheme. To make the self-consistency feasible, important modifications of the method were made [13], dealing with intrinsic discontinuities in the ND correlation potential. The unbearable computational cost of B05 was dramatically reduced based on a resolution of identity (RI) technique. Still, the RI-B05 algorithm remains technically quite demanding. In this work we propose a simplification of the B05 method that makes the algorithm less demanding, easier to implement, and leads to somewhat faster SCF convergence in many cases. The accuracy of this scheme (“SCF-RI-mB05”) is on average about the same as the original SCF RI-B05, after re-optimizing all the functional parameters. For reaction barriers the new scheme is somewhat more accurate than SCF-RI-B05 [14].

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ND correlation can be understood and explained within a real-space analysis of the spin-resolved exchange-correlation (XC) hole ($h_{\sigma\sigma'}^{\text{xc}}$), cast as a sum of exact exchange hole and a model DFT correlation hole:

$$h_{\text{XC}\sigma\sigma'}(1, 2) = \delta_{\sigma\sigma'} h_{\text{X}\sigma}^{\text{ex}}(1, 2) + h_{\text{C}\sigma\sigma'}^{\text{DFT}}(1, 2) \quad (1)$$

where the electron coordinates ($\mathbf{r}_1, \mathbf{r}_2$) are denoted as '(1,2)', and σ, σ' are spin indices. The exact exchange hole depends solely on the electron density and the occupied KS molecular orbitals (MO):

$$h_{\text{X}\sigma}^{\text{ex}}(1, 2) = -\frac{1}{\rho_{\sigma}(1)} \sum_{i,j}^{\text{occ}} \psi_{i\sigma}^*(1) \psi_{i\sigma}(2) \psi_{j\sigma'}^*(2) \psi_{j\sigma'}(1) \quad (2)$$

For finite systems with boundary conditions at infinity, the following normalization sum rule holds true:

$$\int_{\infty^3} h_{\text{X}\sigma}^{\text{ex}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1, \quad \text{at each reference point } \mathbf{r}_1 \quad (3)$$

For a given open subdomain Ω of the system, a partial normalization of the exchange hole can be defined as [15]:

$$\int_{\Omega} h_{\text{X}\sigma}^{\text{ex}}(\mathbf{r}_1, \mathbf{s}) d\mathbf{s} = -N_{\sigma}^{\Omega}(\mathbf{r}), \quad N_{\sigma}^{\Omega}(\mathbf{r}) \leq 1. \quad (4)$$

The closer the partial normalization $N_{\sigma}^{\Omega}(\mathbf{r})$ to 1 at a given point, the larger the depth of the exchange hole (the minimum of the spherically averaged hole as a function of the electron-electron distance s) about that point (due to Eq.(3)) and a larger portion of the hole remains localized within Ω . The exact exchange hole alone is artificially too delocalized in multi-center systems. Model DFT XC holes at GGA and meta-GGA levels are on the contrary, well localized but the depth of the hole is not large enough. In the B05 model, the spherically averaged exact-exchange hole of spin σ , $\bar{h}_{\text{X}\sigma}^{\text{ex}}$, is deepened in a physically motivated manner by the exact exchange hole of opposite spin β and by a second order same-spin correction ($\bar{h}_{\text{C}\sigma\sigma}$):

$$\bar{h}_{\text{XC}\sigma}^{\text{nd}}(\mathbf{r}, s) = \bar{h}_{\text{X}\sigma}^{\text{ex}}(\mathbf{r}, s) + \left[f(\mathbf{r}) \bar{h}_{\text{X}\sigma'}^{\text{ex}}(\mathbf{r}, s) + \bar{h}_{\text{C}\sigma\sigma}(\mathbf{r}, s) \right]. \quad (5)$$

The function $f(\mathbf{r})$ is a complicated, position-dependent function ("correlation factor") that probes at each point the strength of opposite-spin ND correlation [1]. The ND correlation energy is obtained by integrating the Coulomb potential of the ND XC hole. The opposite-spin ND energy component reads:

$$E_c^{\text{nd-op}} = \frac{1}{2} \int f(\mathbf{r}) \left[\rho_{\alpha}(\mathbf{r}) U_{\text{X}\beta}^{\text{ex}}(\mathbf{r}) + \rho_{\beta}(\mathbf{r}) U_{\text{X}\alpha}^{\text{ex}}(\mathbf{r}) \right] d\mathbf{r}, \quad (6)$$

where $U_{\text{X}\sigma}^{\text{ex}}$ is the spin-resolved Slater exact exchange potential [1, 5]. In the present work, the opposite-spin ND correlation energy, Eq.(6), has formally the same form as in B05, while

we propose a different model for the spin-resolved components of the correlation factor $f(\mathbf{r})$, namely:

$$f(\mathbf{r}) = \min(f_\alpha(\mathbf{r}), f_\beta(\mathbf{r}), 1), \quad 0 \leq f(\mathbf{r}) \leq 1, \quad (7)$$

$$f_\alpha(\mathbf{r}) = \frac{[1 - T_\alpha(\mathbf{r})]}{T_\beta(\mathbf{r})}; \quad f_\beta(\mathbf{r}) = \frac{[1 - T_\alpha(\mathbf{r})]}{T_\beta(\mathbf{r})}, \quad (8)$$

$$T_\sigma(\mathbf{r}) = \frac{V_{X\sigma}^{\text{ex}}(\mathbf{r})}{2\varepsilon_{X\sigma}^{\text{BR89}}(\mathbf{r})}, \quad (9)$$

where $V_{X\sigma}^{\text{ex}}(\mathbf{r})$ is the exact-exchange energy density as defined and evaluated in refs.[13–14]:

$$V_{X\sigma}^{\text{ex}}(\mathbf{r}) \equiv \rho_\sigma(\mathbf{r})U_{X\sigma}^{\text{ex}}(\mathbf{r}) = - \sum_{i,j}^{\text{occ}} \rho_{ij\sigma}(\mathbf{r})v_{ij\sigma}(\mathbf{r}), \quad v_{ij\sigma}(\mathbf{r}) \equiv \int \frac{\rho_{ij\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad (10)$$

and $\varepsilon_{X\sigma}^{\text{BR89}}(\mathbf{r})$ is the exchange energy density of the original (unrelaxed) Becke-Rousel exchange functional [16]. The $T_\sigma(\mathbf{r})$ factors in Eqs.(8), (9) are alternatively replacing the relaxed-hole normalization $N_{X\sigma}^{\text{eff}}$ used in B05 to measure the extra-delocalization of the exact exchange hole. The more localized a given exchange hole is about a reference point, the larger and narrower is the depth of this hole there (due to Eq.(3)), which reflects in more negative exchange energy density at that reference point [2]. The larger the value of $T_\sigma(\mathbf{r})$ as defined by Eq.(9), the smaller the extra-delocalization of the exact-exchange hole, and the larger would be the relaxed-hole normalization $N_{X\sigma}^{\text{eff}}$ used in B05 in place of $T_\sigma(\mathbf{r})$. There is a physically motivated one-to-one correspondence between $T_\sigma(\mathbf{r})$ and $N_{X\sigma}^{\text{eff}}$. The factor of 2 in the denominator on the r.h.s of Eq.(9) is introduced to make compatible the two, otherwise defined differently, exchange energy densities.

Concerning the same-spin correction to the ND correlation energy, we propose here a somewhat different expression that is compatible with the present model of $f(\mathbf{r})$:

$$E_c^{\text{ND}\sigma\sigma} = \frac{1}{2} \int U_{c\sigma\sigma}^{\text{ND}}(\mathbf{r}) d^3\mathbf{r}, \quad (11)$$

$$U_{c\sigma\sigma}^{\text{ND}}(\mathbf{r}) = Q_{\sigma\sigma}^{\text{ND}}(\mathbf{r})V_{X\sigma}^{\text{ex}}(\mathbf{r}), \quad (12)$$

$$Q_{\sigma\sigma}^{\text{ND}}(\mathbf{r}) = \min(A_\sigma(\mathbf{r}), D_\sigma(\mathbf{r})), \quad D_\sigma = \frac{D_{s\sigma}}{(3\rho_\sigma^{5/3})}, \quad D_{s\sigma} = \tau_\sigma - \frac{(\nabla\rho_\sigma)^2}{4\rho_\sigma}, \quad (13)$$

$$A_\sigma(\mathbf{r}) = \frac{1}{kT_\sigma(\mathbf{r})} (1 - T_\sigma(\mathbf{r}) - f(\mathbf{r})T_{(\sigma')}(\mathbf{r})), \quad \sigma' \neq \sigma, \quad (14)$$

The shifted kinetic-energy density $D_{s\sigma}$ in Eq.(13) is the same as the one used in the original B05 model, but the related function D_σ is not the same. This is because the present same-spin ND correlation factor A_σ , Eqs.(13), (14), is dimensionless. It is constructed *ad-hoc*, following some analogy with the original B05 model. The numerator in Eq.(14) is formally

the same as in the B05 expression for A_σ , taking into account the correspondence between our T_σ factors and the relaxed-hole normalization $N_{X\sigma}^{\text{eff}}$. Since the present model does not involve the B05 relaxed exchange hole explicitly, we do not dispose with its higher moments either. Instead, we use a scaled T_σ factor (kT_σ) in the denominator of A_σ in place of the second order moment $M_\sigma^{(2)}$ of the B05 relaxed exchange hole (k being here an adjustable parameter). Because the present A_σ function is dimensionless, the same-spin ND-correlation energy density $U_{\text{corr}\sigma}^{\text{ND}}(\mathbf{r})$, Eq.(12), appears naturally as co-linear to the exact-exchange energy density of spin σ . This is a major difference from the original B05 model, where the first, and the second moments of the B05 relaxed exchange hole are employed in obtaining $U_{\text{corr}\sigma}^{\text{ND}}(\mathbf{r})$. The latter originates in B05 from a second order correction to the relaxed exchange hole as the distance from the reference electron s tends to zero. In our model this feature holds only approximately, to the extent to which the scaled factor (kT_σ) approximates the second order moment $M_\sigma^{(2)}$ of the B05 relaxed exchange hole.

In order to adjust the present same-spin ND model to reality, the new fitting parameter k in Eq.(14) was optimized from a get-go, making sure before all that the binding energies of open-shell diatomics like O_2 , S_2 , Si_2 , SO , are obtained about right. Concerning the SCF potential, it has now a simpler form compared to the SCF-RI-B05 potential derived in ref. [14], mainly because the notorious $x(y)$ function is no longer present. This leads to a faster SCF convergence in many cases, which lowers the computational cost. The required smoothening of the $\min()$ functions in Eqs.(7),(13) is achieved using the same technique as in ref.[13]. The four linear parameters are re-optimized in the present context, together with the new parameter k , using the same procedure and test samples as in ref.[13]. The following parameter values are found to provide a balanced performance of the new “SCF-RI-mB05” scheme:

$$a_c^{\text{nd-opp}}=0.7950; a_c^{\text{nd-par}}=0.6426; a_c^{\text{d-opp}}=1.033; a_c^{\text{d-par}}=0.9854; k=1.119.$$

Similar to the SCF-RI-B05 scheme [13], the SCF convergence is quite sensitive to the quality of the initial guess used. We found that the best initial guess for SCF-RI-mB05 is provided by a converged Hartree-Fock solution at the same fixed geometry.

Tables 1–3 contain some preliminary validation results with the SCF-RI-mB05 scheme. Results from a few other XC functionals, including the preceding pert-RI-B05 and SCF-RI-B05 schemes, are also included for comparison. The validation tests are the same as the ones used in ref.[14] and include atomization energies (Table 1), difficult reaction barriers (Table 2), and the energetic properties of the NO dimer, a system with an exceptionally strong ND correlation (Table 3). It is seen that SCF-RI-mB05 leads to a slightly improved atomization energies (Table 1), and to a definitively improved reaction barriers (Table 2) compared to both pert-RI-B05 and SCF-RI-B05. This is encouraging, given the fact that the present scheme is somewhat simpler. Of course, the extra parameter in it should also be given a credit for this improvement. Concerning the energetic of the NO dimer, the performance of SCF-RI-mB05 is about the same as SCF-RI-B05 for the dimerization energy. The singlet-triplet gap with SCF-RI-mB05 is slightly overshoot, but still remains a very good estimate of it. To our knowledge, no other DFT method has been reported in the literature that would yield the correct ground state multiplicity and dimerization energy of this strongly correlated system.

In conclusion, the B05 method of describing systems with strong nondynamic correlation within DFT is modified to make it simpler to implement and use in a fully SCF algorithm. The effective normalization of the B05 relaxed exchange hole is replaced with a physically

motivated *ad-hoc* form that does not require resolution in terms of a complicated nonlinear algebraic function. The four linear B05 parameters are re-optimized together with one extra parameter introduced in the new expression for the second-order same-spin ND energy component. The present SCF-RI-mB05 scheme leads to some improvement over the preceding pert-RI-B05 and SCF-RI-B05 schemes for atomization energies, and to a definitive improvement for reaction barriers of Hydrogen abstraction. A re-optimization of the original four linear parameters in conjunction with the new parameter k in mB05 (Eq. (14)) was a pre-requisite. Both SCF-RI-mB05 and SCF-RI-B05 are so far the only reported DFT methods that yield a correct ground state multiplicity and binding of the NO dimer.

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Highlights

- The B05 method for nondynamic correlation is made simpler.
- An alternative form is proposed for the B05 correlation factors.
- Improved results are reported for atomization energies, and reaction barriers.

Table 1

. Mean absolute errors (MAE) for atomization energies D_e (kcal/mol) on 69 molecules from Truhlar's 105AE test set at fixed geometries [14]. For these molecules the suggested data-base benchmarks for D_e and the equilibrium geometries, are comparable to other benchmark sources.

XC	MAE for D_e^a		
	26 diatomic	43 polyatomic	All 69 molecules
B3LYP	2.24	3.44	2.99
B3Lap	2.41	2.34	2.37
pert-RI-B05	2.77	2.21	2.42
SCF-RI-B05	2.56	2.29	2.39
SCF-RI-mB05 ^b	2.00	2.34	2.21
M06-2X	1.56	2.23	1.98

^aThe reference D_e values are from refs.[17–18].

^bResults of the present SCF-RI-mB05 scheme.

. The 18 most difficult barriers of Hydrogen abstraction reactions from Truhlar's data base (f = forward, r = reverse). The reference values are from the Truhlar's online data base (<http://comp.chem.umn.edu/database>).

Table 2

Reaction $V_f^{\ddagger}V_r$	pert-RI-B05	SCF-RI-B05	SCF-RI-mB05	M06-2X	B3LYP
MAE on 18 reactions of Hydrogen abstraction	1.3	1.8	1.2	1.5	2.9

. Singlet-triplet split Δ_{T-S} (kcal/mol), dimerization energy D_e (kcal/mol, BSSE corrected), and geometry (R_{N-N} and R_{N-O} in Å, \angle NNO in degree) of *cis* NO dimer ONNO.

Table 3

	B3LYP	B3Lap	M06-2X	RI-B05 SCF ^b	RI-mB05 SCF ^b	MRCI	Expt ^e
Δ_{T-S}	-2.3	+0.3	+4.0	+6.4	+7.2	+6.3 ^d	
D_e	-3.1	-0.9	-6.7	+5.4	+5.5	3.3 ^c	2.9–3.3
R_{N-N}	1.972	1.982	1.828	1.994	1.994	2.284 ^c	2.263
R_{N-O}	1.147	1.149	1.143	1.149	1.149	1.149 ^c	1.152
\angle NNO	101.5	102.4	104.4	101.3	101.3	96.1 ^c	97.17

^b SCF calculations at optimized 'by hand' geometry of the NO dimer.

^c Results of ref. [19];

^d $\Delta_{T-S} = E(^3B_1) - E(^1A_1)$ from ref.[20]. Positive Δ_{T-S} means the singlet is more stable.

^e Data from refs.[21–22].