

The constant A_y appears in the derivation of the local spin density approximation in DFT, and is defined as

$$A_y = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} \quad (1)$$

The reduced gradient of the density ρ with spin σ is

$$y = \frac{|\nabla \rho_\sigma|}{(\rho_\sigma)^{4/3}} \quad (2)$$

The gradient-corrected enhancement factor for the mPW density functional is defined as

$$F[y] = \frac{by^2 - (b - \beta)y^2 \exp(-cy^2) - 10^{-6} y^d}{1 + 6by \sinh^{-1} y - \frac{10^{-6} y^d}{A_y}} \quad (3)$$

where b , β , c , and d are constants. The pure gradient-corrected density functional is then

$$F^{pure} = (A_y - F[y]) \rho_\sigma^{1/3} \quad (4)$$

The DFT portion of the hybrid density functional introduces the scaling factors for the local and gradient-corrected portions of the exchange, $(1-x/100)$ and f_{GCF} , respectively, where x is the percentage of HF exchange. The form of the functional is then

$$F^{hybrid} = \left(\left(1 - \frac{x}{100} \right) A_y - f_{GCF} F[y] \right) \rho_\sigma^{1/3} \quad (5)$$

If we substitute $F[y]$ in Eq. 5 by using Eq. 3 we obtain the correct hybrid form for the mPW exchange energy:

$$E_y^{GGA-hybrid} = \sum_{\sigma} \int \left(\left(1 - \frac{x}{100}\right) A_y - f_{GCF} \frac{by^2 - (b - \beta)y^2 \exp(-cy^2) - 10^{-6} y^d}{1 + 6by \sinh^{-1} y - \frac{10^{-6} y^d}{A_y}} \right) \rho_{\sigma}^{4/3} d^3 r \quad (6)$$

However, the mPW energy in all versions of GAUSSIAN98 through the present version (GAUSSIAN98 Rev.A.11) is evaluated using the following incorrect form

$$E_y^{GGA-hybrid} = \sum_{\sigma} \int \left(\left(1 - \frac{x}{100}\right) A_y - f_{GCF} \frac{by^2 - (b - \beta)y^2 \exp(-cy^2) - 10^{-6} y^d}{1 + 6by \sinh^{-1} y - \frac{10^{-6} y^d}{\left(1 - \frac{x}{100}\right) A_y}} \right) \rho_{\sigma}^{4/3} d^3 r \quad (7)$$

The coefficient, $(1 - x/100)$, used to scale the local density exchange has snuck its way into the denominator of the gradient corrected portion of the functional in Eq. 7, making the density functional itself dependent on the fraction of DFT exchange used in the hybrid method. The typical error introduced by this error is less than a 0.1 kcal/mol for energies of reaction or bond strengths.