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## Note: Theoretical mixing coefficients for hybrid functionals

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The theoretical foundations of the double hybrid exchange-correlation functionals have been recently analyzed by Sharkas *et al.*,<sup>1</sup> and, successively, by Brémond and Adamo<sup>2</sup> and by Toulouse *et al.*<sup>3</sup> This analysis partially resulted in the introduction of a new class of double hybrids depending on just one parameter, the value of which was assumed to be 0.5 by Brémond and Adamo.<sup>2</sup> In this note, I will suggest that other values can be chosen and that all these choices can be justified using the same theoretical arguments. These values are also “theoretical” mixing coefficients for single-hybrids, i.e., functional where only the exchange is hybridized.

In a recent paper, Sharkas *et al.*<sup>1</sup> obtained, by a rigorous approach, the following expression for a one-parameter double-hybrid (1DH) exchange-correlation functional:

$$E_{xc}^{\text{DS1DH}} = \lambda E_x^{\text{HF}} + (1 - \lambda) E_x^{\text{DFA}}[n] + E_c^{\text{DFA}}[n] - \lambda^2 E_c^{\text{DFA}}[n_{1/\lambda}] + \lambda^2 E_c^{\text{MP2}}, \quad (1)$$

where  $E_x^{\text{HF}}$  is the Hartree-Fock exchange energy,  $E_c^{\text{MP2}}$  is the second-order Møller-Plesset correlation,  $E_x^{\text{DFA}}[n]$  and  $E_c^{\text{DFA}}[n]$  are semi-local density functionals, and “DS” recalls that the functional contains a dependence on the scaled electron density:  $n_{1/\lambda} = (1/\lambda^3)n(\mathbf{r}/\lambda)$ .

Sharkas *et al.* simplified Eq. (1) by assuming that  $E_c^{\text{DFA}}[n_{1/\lambda}] \approx E_c^{\text{DFA}}[n]$ , thus obtaining the following 1DH functional:

$$E_{xc}^{\text{1DH}} = \lambda E_x^{\text{HF}} + (1 - \lambda) E_x^{\text{DFA}}[n] + (1 - \lambda^2) E_c^{\text{DFA}}[n] + \lambda^2 E_c^{\text{MP2}}. \quad (2)$$

A different approximation of  $E_c^{\text{DFA}}[n_{1/\lambda}]$  was adopted by Brémond and Adamo,<sup>2</sup> who assumed that  $E_c^{\text{DFA}}[n_{1/\lambda}] \approx \lambda E_c^{\text{DFA}}[n]$ . By such an approximation, and consistently modifying the  $\lambda$  dependence of the MP2 term, they derived the following functional:

$$E_{xc}^{\text{1DH}} = \lambda E_x^{\text{HF}} + (1 - \lambda) E_x^{\text{DFA}}[n] + (1 - \lambda^3) E_c^{\text{DFA}}[n] + \lambda^3 E_c^{\text{MP2}}. \quad (3)$$

Successively, Toulouse *et al.*<sup>3</sup> showed that the same expression could also be derived starting from the Görling-Levy perturbation theory,<sup>4</sup> giving strong theoretical support to Eq. (3).

The value of the  $\lambda$  parameter can be determined by fitting some reference datasets, as it was done in Ref. 1, or it can be chosen on the basis of some theoretical arguments. Brémond and Adamo assumed  $\lambda = 0.5$ , which is the mixing parameter of the Becke half-and-half single-hybrid (SH) functional.<sup>5</sup>

This value was obtained by a two-point approximation of the integral describing the so-called adiabatic connection

$$E_{xc} = \int_0^1 U_{xc,\alpha} d\alpha, \quad (4)$$

where

$$U_{xc,\alpha} = \langle \Psi_\alpha | \hat{V}_{ee} | \Psi_\alpha \rangle - \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5)$$

and  $\Psi_\alpha = \text{Min}_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle$ .

Let me assume, as it was done by Brémond and Adamo,<sup>2</sup> that  $\lambda$  can be identified with the mixing parameter of standard SHs. The most famous “theoretical” mixing coefficient is the one (1/4) proposed by Perdew *et al.*<sup>6</sup> on the basis of the following argument. They performed a series expansion of  $U_{xc,\alpha}$  and supposed that a realistic description of the exact  $U_{xc,\alpha}$  is provided by the first  $m+1$  terms of that series:

$$U_{xc,\alpha} = c_0 + c_1\alpha + \dots + c_m\alpha^m. \quad (6)$$

Then, they considered the following model of the  $U_{xc,\alpha}$  dependence on  $\alpha$ :

$$U_{xc,\alpha}^{\text{1SH}} = U_{xc,\alpha}^{\text{DFA}} + (E_x^{\text{HF}} - E_x^{\text{DFA}})(1 - \alpha)^m. \quad (7)$$

In Eq. (7), the exponent of  $(1 - \alpha)$  is equal to the maximum exponent of  $\alpha$  in Eq. (6). The resulting 1SH functional is

$$E_{xc}^{\text{1SH}} = E_{xc}^{\text{DFA}} + \frac{1}{m+1} (E_x^{\text{HF}} - E_x^{\text{DFA}}). \quad (8)$$

Finally, they argued that  $m+1$  could be identified with the smallest order of the perturbation theory, which provides a good description of the systems in which one is interested. As for the atomization energies of the molecules of the G1 dataset the fourth-order Møller-Plesset perturbation theory is adequate, they suggested to choose  $m+1 = 4$ . Thus  $\lambda = \frac{1}{m+1} = \frac{1}{4}$ .

A different value can be obtained by using a slightly different approach. According to Perdew and co-workers, let me assume the validity of Eqs. (6)–(8). In order to determine  $m$ , suppose to develop the wave function  $\Psi_\alpha$  entering in Eq. (5) in power series of  $\alpha$ . Stopping the series at the order  $n$ , one has  $m = 2n$  and  $\lambda = \frac{1}{2n+1}$ . Thus, at zero-order

$$E_{xc}^{\text{1SH}} = E_x^{\text{HF}} + E_c^{\text{DFA}}, \quad (9)$$

while  $\lambda = \frac{1}{3}$  at the first order

$$E_{xc}^{\text{1SH}} = \frac{1}{3} E_x^{\text{HF}} + \frac{2}{3} E_x^{\text{DFA}} + E_c^{\text{DFA}}. \quad (10)$$

This value of  $\lambda$  works very well if the semi-local functional entering in Eq. (10) is the nTCA functional introduced in Ref. 7. Good results are also obtained if this value is inserted in the Brémond and Adamo 1DH given in Eq. (3). This can be verified in Fig. 1 of Ref. 2: the results for the atomization energies of the G2 dataset are as good as, or even better of, those obtained by taking  $\lambda = 0.5$ .

Concerning this approach, some remarks are in order. First, as  $U_{xc,\alpha}$  is defined in terms of  $\Psi_\alpha$ , a development in power series of the latter implies an analogous development of the former, while the opposite is not true. In particular, there are no reasons for using an odd value of  $m$  in Eq. (6). Second, using a second-order approximation of  $\Psi_\alpha$ , one obtains  $\lambda = 0.2$ , which is the optimum value<sup>8</sup> if the semi-local functional is the RevTCA one proposed in Ref. 7. Third, the values  $\lambda = 0.5$  and  $\lambda = 0.25$  are obtained at the first- and second-order, respectively, if the exponent of  $(1 - \alpha)$  in Eq. (7) is assumed to be  $m - 1$  instead of  $m$ . This can be a reasonable choice if  $n \geq 1$ , that is,  $m \geq 2$ . In such a case,  $m - 1$  could provide a better description of the global dependence of the exact  $U_{xc,\alpha}$  on  $\alpha$  (Eq. (6)). In conclusion, there are four values of the SH mixing parameter: 1/2, 1/3, 1/4, 1/5, which actually have the same theoretical basis. It is quite interesting that all these values are (almost) the optimal ones for SHs based

on different semi-local functionals. Two of these values, 1/2 and 1/3, also work if they are inserted in the 1DH expression given in Eq. (3) and the semi-local functional is chosen to be the Perdew-Burke-Ernzerhof (PBE) one.<sup>9</sup> However, the other values could be a better choice for 1DH based on other semi-local parameter-free functionals, such as those belonging to the TCA family.<sup>7,10</sup>

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