Double Hybrid Functionals Based on the Adiabatic Connection Formalism

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For the purpose of approximating the exchange and correlation energies, doubly hybrid (DH) functionals present a new class of density functional approximations (DFAs). Different types of DH functionals have been proposed according to different philosophies.

Truhlar and co-workers coined, for the first time, the name 'doubly hybrid' and proposed the MC3BB method:

$$E_{tot}^{MC3BB} = e_2 \left(E_{tot}^{HF} + e_1 E_c^{MP2} \right) + \left(1 - e_2 \right) E_{tot}^{BBX} \tag{1}$$

It is a multi-coefficient (MC) method that mixes the total energy from the second-order Møller-Plesset (MP2) method with that of a conventional DFA (i.e. BBX, a hybrid on top of B88 and B95 for exchange and correlation, respectively). Two separate self-consistent-filed (SCF) calculations are carried out, leading to two sets of orbitals and densities, one from Hartree-Fock (HF) and the other from BBX.

Grimme proposed B2PLYP:

$$E_{xc}^{SCF} = a_1 E_x^{HF} + \left(1 - a_1 \right) E_x^{B88} + a_2 E_c^{LYP} \tag{2}$$

$$E_{tot}^{B2PLYP} = E_{tot}^{SCF} + \left(1 - a_2 \right) E_c^{MP2} \tag{3}$$

where the SCF calculation is first carried out using a hybrid DFA defined in eq. 2, and the orbitals and orbital eigenvalues thus obtained are subsequently used in the same way as in MP2 for a perturbative correlation energy evaluation, leading to the full expression for the total energy as defined in eq. 3. Note that B2PLYP reduces to the conventional MP2 if {a1=1, a2=0}, while B2PLYP deduces to BLYP if {a1=0, a2=1}. Hence, B2PLYP was also constructed as a mixture between MP2 and a DFA. The mix is at the orbital or density level in B2PLYP, while the mix is at the energy level in MC3BB.

We proposed another type of the DH functional, coined as XYG3:

$$E_{xc}^{B3LYP} = c_1 E_x^{HF} + \left(1 - c_1 \right) E_x^{S} + c_2 \Delta E_x^{B88} + c_3 E_c^{VWN} + \left(1 - c_3 \right) E_c^{LYP} \tag{4}$$

$$E_{xc}^{XYG3} = b_1 E_x^{HF} + \left(1 - b_1 \right) E_x^{S} + b_2 \Delta E_x^{B88} + \left(1 - b_3 \right) E_c^{LYP} + b_3 E_c^{MP2} \tag{5}$$

where the SCF calculation is first carried out using a conventional DFA (e.g. B3LYP as in eq. 4), and the final energy is evaluated on top of the as obtained orbitals and orbital eigenvalues based on a DH functional (e.g. XYG3 as in eq. 5).

In this talk, we will present a detailed reasoning/derivation for the XYG3 type of DH functionals based on the adiabatic connection formalism.