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### Hybrid Density Functionals Tuned towards Fulfillment of Fundamental DFT Conditions

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Hybrid exchange-correlation functionals (XC), e.g. PBE0 and HSE, have significantly improved the theoretical description of molecules and solids. Their degree of exact-exchange admixture ( $\alpha$ ) is in principle a functional of the electron density, but the functional form is not known. In this talk, I will discuss *fundamental conditions* of exact density-functional theory (DFT) that enable us to find the optimal choice of  $\alpha$  for ground-state calculations. In particular, I will discuss the fact that the highest occupied Kohn-Sham level of an  $N$ -electron system ( $\varepsilon_{\text{HOMO}}(N)$ ) should be constant for fractional particle numbers between  $N$  and  $N-1$  [1,2] and equals the ionization potential (IP) [3, 4], as given by the total-energy difference. In practice, we realize this in three different ways. XC( $\alpha$ ) will be optimized (opt-XC) until it (i) fulfills the condition:  $\varepsilon_{\text{HOMO}}(N) = \varepsilon_{\text{HOMO}}(N-1/2)$  or the Kohn-Sham HOMO agrees with the ionization potential computed in a more sophisticated approach  $\varepsilon_{\text{HOMO}}(N) = \text{IP}$  such as (ii) the  $G_0W_0$ @opt-XC method [5,6] or (iii) CCSD(T) or full CI [6]. Using such an opt-XC is essential for describing electron transfer between (organic) molecules, as exemplified by the TTF/TCNQ dimer [5]. It also yields vertical ionization energies of the G2 test set of quantum chemistry with a mean absolute percentage error of only  $\approx 3\%$ . Furthermore, our approach removes the starting-point uncertainty of  $GW$  calculations [5] and thus bears some resemblance to the consistent starting point scheme [7] and quasiparticle self-consistent  $GW$  [8]. While our opt-XC approach yields large  $\alpha$  values for small molecules in the gas phase [5], we find that  $\alpha$  needs to be 0.25 or less for organic molecules adsorbed on metals [9].

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