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Orbitals and orbital energies in DFT and TDDFT

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The status and meaning of orbitals and orbital energies in the Kohn-Sham one-electron model of DFT has been controversial, in contrast to Hartree-Fock orbitals and orbital energies. We will argue the opposite: the exact Kohn-Sham orbitals of DFT are "better" than HF orbitals and their orbital energies are much closer to ionization energies than HF orbital energies are. This follows from the relation between the KS potential and the wavefunction, which can be cast in the form $v_s = v_{c,kin} + v_H + v_{xc}^{hole} + v^{resp}$ ¹, where each term depends on the KS orbitals and the wavefunction (the one- or two-particle density matrices). The response potential

$$v^{resp}(r) = \sum_j \frac{|d_j(r)|^2}{\rho(r)} I_j - \sum_i^H \frac{|\psi_{s,i}(r)|^2}{\rho(r)} (-\epsilon_i) \quad (1)$$

(d_j is the Dyson orbital corresponding to ion state Ψ_j^{N-1} , $\psi_{s,i}$ is a Kohn-Sham orbital) enables the connection between ionization energies I_i and orbital energies ϵ_i to be made². For virtual orbitals and orbital energies similar statements can be made: the shapes and energies of the (exact) KS orbitals are much more realistic than those of the Hartree-Fock model or hybrid functionals³. The HOMO-LUMO gap in molecules is very close to the optical gap, and very different from the fundamental gap. In solids the situation is very different, which is the well-known "KS gap problem". Again the response potential v^{resp} (a good approximation to it) helps to solve this problem, affording a straightforward correction method of the KS gap to the fundamental gap⁴.

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