

Revisiting and Revising Rungs of Jacob's Ladder of Density Functional Theory, with Application to Problems of Molecular Adsorption on Metal Surfaces

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Kohn-Sham (KS) density-functional theory (DFT), where only the exchange-correlation energy needs to be approximated, is one of the most frequently applied methods in many-body theory. On the Jacob's ladder for the exchange-correlation energy of density functional approximations, higher rungs are usually built on and thus improve accuracy over lower ones. However, climbing from the lowest three semilocal rungs (local spin density approximation (LSDA), generalized gradient approximation (GGA), and meta-GGA (MGGA)) to the higher fully-nonlocal rungs increases the computational cost dramatically. Due to the efficiency of the semilocal approximations, there are still efforts to refine the widely used semilocal approximations.

To make a firmer base for the higher rungs, a new model called density parameter interpolation is designed for the correlation energy per electron, $e_c(r_s, \zeta)$, of the uniform electron gas for LSDA. It shows that known or knowable information about the high- ($r_s \rightarrow 0$) and low-density ($r_s \rightarrow \infty$) asymptotes can be used to predict the correlation energy per electron, $e_c(r_s, \zeta)$, of the three-dimensional (3D) uniform electron gas over the whole range of the density parameter ($0 \leq r_s \leq \infty$) and relative spin polarization ($0 \leq \zeta \leq 1$), without Quantum Monte Carlo or other input.

At the MGGA level, The Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA and its revised version, the newly proposed revTPSS, are implemented self-consistently within the framework of project augmented wavefunction (PAW) in the Vienna Ab-initio Simulation Package (VASP). revTPSS yields not only accurate atomization energies of molecules, but also lattice constants and bulk moduli of solids, which are comparable on average to those of Perdew-Burke-Ernzerhof (PBE)sol and Armiento-Mattsson (AM)05, the two GGA's designed for solids. As for the magnetic properties, revTPSS predicts for Fe the right ground-state solid phase, the ferromagnetic (FM) body-centered-cubic (bcc) structure, with an accurate magnetic moment. The application on the problem of CO adsorbed on transition metals (111) surfaces shows that although revTPSS still fails to predict the right adsorption sites for some metals, e.g. Pt, it produces more accurate lattice constants for the transition metals as well as better adsorption energies than PBE, which so far hasn't been achieved by any functional at the GGA level.