

Weak Bonds from a Semilocal Density Functional

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Weak or van der Waals bonds are important for soft and biological matter. While the computationally-efficient semilocal density functionals for the exchange-correlation energy necessarily miss the long-range part [1] of the van der Waals interaction, some heavily-parametrized empirical meta-generalized gradient approximations capture an important intermediate-range part around equilibrium. Here we show that the right meta-GGA ingredient is $\alpha = (\tau - \tau_w) / \tau^{unif}$, where τ is the positive kinetic energy density of the Kohn-Sham orbitals that create the density n , $\tau_w = |\nabla n|^2 / 8n$ is its Weizsaecker approximation, and τ^{unif} is its Thomas-Fermi approximation. Unlike other widely-used dimensionless ingredients, α can recognize all degrees of orbital overlap: $\alpha \approx 0$ in single bonds, $\alpha \approx 1$ in metallic and multiple bonds, and $\alpha \gg 1$ in weak bonds. Meta-GGA's that use α as the only kinetic-energy ingredient can describe all these bonds usefully, with few or no empirical parameters. Examples are given: graphene on a nickel surface, the argon dimer, and the interaction between stacked nucleobase pairs.

[1] A. Ruzsinszky et al., van der Waals Interactions between Nanostructures: Fullerenes Defy Conventional Wisdom, talk at this meeting.