Automated Hubbard parameters in LCAO DFT+U with SIESTA

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Standard Density Functional Theory (DFT) is known to over-delocalize charge, leading to an inaccurate description of strongly correlated systems such as metal oxides [1]. This failure originates from the violation of the piecewise-linear constraint with respect to the electron number in approximate exchange–correlation functionals [2]. Twenty years ago, a linear-response methodology was proposed to determine the Hubbard parameter U in DFT+U such that this constraint is satisfied [3]. With this approach, +U ceases to be an empirical parameter, restoring the ab initio character of the simulations. The method was implemented in the plane-wave DFT package Quantum ESPRESSO [4] and has improved standard DFT results for many systems, later being extended to DFT+U+V [5]. To date, Quantum ESPRESSO has effectively monopolized this linear-response procedure for obtaining Hubbard parameters [1]. Here we implement this methodology in the DFT code SIESTA [6], which employs a Linear Combination of Atomic Orbitals (LCAO) basis instead of plane waves. This framework offers advantages such as a more natural localized basis description, faster calculations in systems with large vacuum regions, and improved scaling with system size [6]. Additionally, the resulting real-space Hamiltonian can be directly reused as a tight-binding model, for example in quantum-transport simulations. Our implementation follows the original formalism and uses utilities from the AiiDA-SIESTA [7] plugin. The obtained U values are of the same order of magnitude as those from Quantum ESPRESSO U($CrCl_3$) = 4.03 eV, U($CrBr_3$) = 4.31 eV, U(CrI_3) = 4.83 and reproduce the trend U($CrCl_3$)<U($CrBr_3$)<U(CrI_3) [8]. Ongoing work benchmarks the approach across several systems against Quantum ESPRESSO. The implementation can also compute the intersite Hubbard V with only a marginal additional cost. Making this capability available in a public SIESTA release would remove the current dependence on Quantum ESPRESSO and enable LCAO-based simulations with automatically computed Hubbard parameters.

References

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