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Many-body frozen-orbital embedding and downfolding with auxiliary-field quantum Monte Carlo (AFQMC)

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While quantum Monte Carlo (QMC) electronic structure calculations have favorable scaling as a low order polynomial with increasing system size [similar to density functional theory (DFT) and hybrid-DFT], routine use of QMC for large systems remains challenging due to its large prefactor compared to DFT. Many strategies, including embedding and downfolding approaches, have been actively explored to address this problem. In these approaches, the expensive many-body calculations are done on a much smaller subsystem, which is locally embedded in a spatially larger host system, where the latter is treated using a less expensive and lower-level theory. In many systems of interest, strong correlated-electron effects are spatially localized, so such embedding is naturally suggested. Examples include molecular catalysts with a small subcluster of *d*-shell atoms and surface adsorbates of *d*- or *f*-atoms. We previously used quantum mechanical embedding [1, 2] to calculate adsorption site energetics of Co/graphene using AFQMC. There, the occupied Hartree-Fock orbitals were unitarily transformed to local orbitals, freezing the most distant from the Co atom to obtain an effective Hamiltonian for a small active region (analogous to the frozen-core approximation for atoms). Here we will describe recent developments in extending this approach to reducing the Hilbert space of the effective Hamiltonian by also localizing the unoccupied orbitals. The approximation in our approach is controlled by two localization radii, for the occupied and virtual sectors, respectively, and its accuracy can be systematically dialed up to the results of full many-body treatment. The systematic dependence on these localization radii is first illustrated for a simple one-dimensional atomic chain system. We then show that similar systematics are obtained for a Co atom adsorbed onto a large graphitic molecular substrate.

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[1] W. Purwanto, S. Zhang, and H. Krakauer. *Frozen-Orbital and Downfolding Calculations with Auxiliary-Field Quantum Monte Carlo*, J. Chem. Th. and Comput. **11**, 4825 (2013).

[2] Y. Virgus, W. Purwanto, H. Krakauer, and S. Zhang. *Stability, Energetics, and Magnetic States of Cobalt Adatoms on Graphene.* Physical Review Letters **113**, 175502 (2014).