Aperiodic fragments in periodic solids: Eliminating the need for supercells and background charges in mean-field-embedded electronic structure calculations

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Sites in solids with strong electron correlation are difficult to characterize computationally due to the high expense of suitable methods and the large size and periodicity of the system. Various "embedding" schemes have been formulated to treat the majority of the solid with an inexpensive, mean-field method such as Hartree-Fock (HF) and then perform highly accurate calculations on the correlated site with mean-field surroundings. Thus far, however, all embedding methods rely on periodic supercells in which the correlated site, such as a defect, is far enough from its repeated image such that it can be assumed to be non-interacting. Furthermore, to avoid divergence of the periodic electrostatics, a compensating background charge must be introduced if the site is charged. This is a source of unquantifiable error and, in some cases, renders total energies and energy differences useless. Here, we introduce embedding within a periodic mean field formulated such that a pristine, primitive unit cell may be used for the periodic HF, after which atoms may be moved or charged for the embedded, correlated calculation. By eliminating the need for compensating background charges and large supercells, we reduce both error and computational expense in embedded electronic structure calculations, as demonstrated by bond-breaking in fluorographane and excitation energies of the nitrogen-vacancy anion center in diamond.