

# Multiconfigurational Pair Density Functional Theory within a Periodic Density Matrix Embedding Framework

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Understanding the electronic structure of localized perturbations in crystalline materials, such as solid-state defects and adsorbate molecules on solid surfaces, often requires accurate and cost-effective correlated wave function-based methods. These perturbations break translational symmetry, which can make traditional correlated wave function-based methods expensive to use in large supercells. In order to address this issue, we have recently developed strongly correlated electronic structure solvers, including complete active space self-consistent field (CASSCF) and *n*-electron valence state second-order perturbation theory (NEVPT2) within a periodic density matrix embedding theory (pDMET) algorithm.<sup>1</sup> These methods allow us to study electronic excitations in solid-state defects and binding energies of gas molecules on solid surfaces. However, even though NEVPT2-DMET is cheaper than NEVPT2, it scales poorly with the active space size and the parameter space. A significantly more affordable option for capturing dynamical electron correlation at the post-SCF level is multiconfigurational pair density functional theory (MC-PDFT)<sup>2</sup> and hybrid MC-PDFT (h-MC-PDFT).<sup>3</sup> In this study, we present a method for calculating the correlation energy using MC-PDFT and h-MC-PDFT as effective high-level methods within the framework of pDMET. We apply this method to investigate local excitations and spin state gaps in an oxygen vacancy (OV) and an oxygen di-vacancy (OOV) on a magnesium oxide (100) surface and find that the absolute deviations between pDMET using MC-PDFT/h-MC-PDFT (DME-PDFT/h-DME-PDFT) and the non-embedded MC-PDFT/h-MC-PDFT approach are within 0.05 eV. We also use DME-PDFT and h-DME-PDFT to calculate local excitations and spin state gaps in larger supercells for the OV defect, where the use of non-embedded MC-PDFT or h-MC-PDFT is not practical.

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(3) Pandharkar, R.; Hermes, M. R.; Truhlar, D. G.; Gagliardi, L. A New Mixing of Nonlocal Exchange and Nonlocal Correlation with Multiconfiguration Pair-Density Functional Theory. *J. Phys. Chem. Lett.* **2020**, *11* (23), 10158–10163.