Local Excitations in Nitrogen Vacancies in Diamond with Multireference Density Matrix Embedding Theory

Soumi Haldar[†], **Abhishek Mitra**[†]**, Matthew R. Hermes**[†]**, and Laura Gagliardi**[*†‡¶]

[†]*Department of Chemistry, Chicago Center for Theoretical Chemistry, University of Chicago, Chicago, IL 60637, USA.*
[‡] *Pritzker School of Molecular Engineering, James Franck Institute, Chicago Center for Theoretical Chemistry, University of Chicago, Chicago, IL 60637, USA.*
[¶]*Argonne National Laboratory 9700 S. Cass Avenue Lemont, IL 60439, USA.*

Localized spin defects in wide band-gap semiconductors have emerged as excellent qubit candidates. The accurate prediction of the electronic structure and characters of these spin defects demand first principles simulations. Density functional theory (DFT) which is most widely used for solids is not accurate enough to describe spin defects having strongly correlated excited states. On the other hand, multireference methods are computationally impractical for solid-state defects that are modelled by periodic supercells containing several atoms. Quantum embedding theories offer an appealing solution to this, providing a trade-off between the computational cost and accuracy. We investigate the ground and excited states of the negatively charged nitrogen-vacancy centre in diamond with periodic density matrix embedding theory (pDMET). To account for the strongly correlated defect excited states, the complete active space self-consistent field (CASSCF) and n-electron valence state second-order perturbation theory (NEVPT2) were employed as impurity solvers. The electronic excitation energies obtained using CAS-pDMET are almost unaffected by the size of the embedding subspace. On the other hand, a linear dependence on the inverse of the size of embedding subspace is observed for the NEVPT2-pDMET energies. Based on this observation we performed an extrapolation of the excitation energies to the non-embedding limit using linear regression. The extrapolated first triplet-triplet excitation energy is 2.31 eV and that for the optically inactive singlet-singlet transition is 1.02 eV. Both values agree with the experimentally observed vertical excitation energies of 2.18 eV and 1.26 eV, respectively. Our observation suggests that the localized defect excitation is largely influenced by dynamic correlation in the crystal – which cannot be entirely captured by CASSCF. Such an extrapolation scheme can be employed in the future for an accurate description of the electronic structure of extended materials.