**A TD-DFT Method for the Prediction of Electronic Response to Electron Beam Irradiation.**

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In this presentation, I will discuss our recent development efforts in the area of *ab initio* modeling of materials under electron beam irradiation. [1] The use of scanning transmission electron microscopes to manipulate substitutional defects in graphene has recently been demonstrated and modeled using ground state *ab initio* molecular dynamics, but the role of electronic excitations induced through inelastic electron scattering in promoting these transformations has so-far remained unexplored. Our recently developed methods have been applied to resolve the effects of electronic excitation on the structural dynamics of graphene quantum dots of differing edge morphologies that have been substitutionally doped with silicon or phosphorous. [2] The potential energy barriers for pyramidal inversion of these nonplanar doped species in ground and excited electronic states were evaluated using (time-dependent) density functional theory. Excited states in which the barrier is decreased are identified in the low energy region of the electronic spectrum, and the degree of barrier lowering in a given excited state is found to correlate with the extent of charge transfer away from the defect site. Transitions to these states are optically allowed, suggesting that photoexcitation can modulate the reactivity of defects in graphene under electron beam irradiation. Coupling matrix elements due to external point-source electric fields evaluated between these inversion-favoring excited states and the ground state, as well as real-time simulations of the material's response to a point charge impulse enacted immediately above the defect, indicate that focusing an electron beam near the defect can promote the population of these states. This result suggests that beam electrons incident on a defect can simultaneously excite the material to an inversion-favoring state through inelastic (beam electrons- material electrons) scattering and transfer momentum to the defect to initiate the inversion through the elastic (beam electrons-material nuclei) scattering, highlighting the importance of considering electronically non-adiabatic reaction pathways for materials under electron beam irradiation.

[1] Lingerfelt, David B., Panchapakesan Ganesh, Jacek Jakowski, and Bobby Sumpter. First Principles Determination of Electronic Excitations Induced by Charged Particles. **2019**, *ChemRxiv*: 7726139

[2] Lingerfelt, David B., Panchapakesan Ganesh, Jacek Jakowski, and Bobby Sumpter. Electronically Nonadiabatic Structural Transformations Promoted by Electron Beams. **2019**, *Adv. Funct. Mater.* (In review)

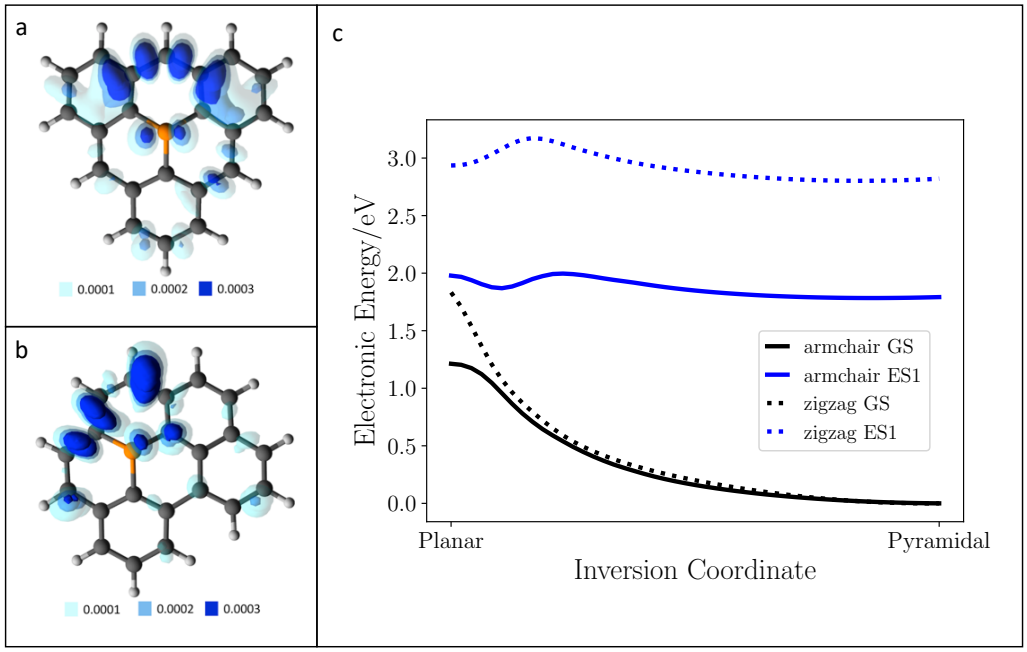


Figure 1. Potential energy surfaces for ground and first excited state along the ground state minimum energy reaction coordinate for pyramidal inversion of substitutional phosphorous defect in zigzag and armchair graphene fragments (c), and point charge locations associated with high probability for promoting transitions between ground and excited states visualized as isosurfaces of the position-dependent transition rates (a,b).