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Optical Absorbance by Doped Si Quantum Dots Calculated by Time-Dependent DFT with Electronic Self-Interaction Corrections

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The optical absorbance spectra of Si quantum dots (QDs) with P and Al dopants have been calculated with the recently tested HSE/PBE density functionals [1] to ascertain the effect of functional corrections to electronic self-interaction. New results have been obtained for both crystalline and amorphous structures of Si_{29} and Si_{35} quantum dots and are compared to our previous results obtained using the PW91/PW91 functionals [2]. Quantitative comparisons show the absorbances to be greater in magnitude and shifted to higher energies in HSE calculations compared to PW91 calculations. Nevertheless, trends in the shifts of absorbances due to doping are similar for both sets of calculations, with doped QDs absorbing at lower photon energies than undoped QDs. The molecular orbitals involved in the transitions of the largest oscillator strengths have also been analyzed, with qualitative comparisons showing that the electron density moves from one side of the quantum dot to the other as the structure is excited. The lifetimes of excited states were found to differ substantially between the two functionals due to their sensitivity to the overlaps of initial and final orbitals in photoinduced electron transitions. Comparison with available experimental [3] and independent theoretical results [4,5] support the theory that generalized gradient approximations tend to underestimate band gap energies, and that hybrid functionals such as HSE better match experimental results due to the inclusion of exact Hartree-Fock exchange.

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