

# Efficient determination of excitation energies and absorption spectra of nanoclusters

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## Abstract

Despite the available powerful computing resources, accurate ab-initio methods are still compute-intensive and sometimes prohibitive for nanomaterials. In this research, a computationally cheap method capable of producing accurate excitation energies and absorption spectra for nanoclusters was developed. The method involves parameterizing intermediate neglect of differential overlap for spectroscopy (INDO/s) Hamiltonian with benchmark excitation energies from Equation-Of-Motion Coupled-Cluster Singles Doubles (EOM-CCSD) for diatomics at different interatomic separations. The optimized model was validated and then used to compute excitation energies and absorption spectra for large clusters and nanoclusters. This method was tested with silicon, sulphur, zinc and cadmium.

A fit of the INDO/s model to EOM-CCSD was obtained with mean absolute error (MAE) 0.25 eV. The obtained optimized model was found to be transferable to atomic clusters (Si, Zn, Cd, S, ZnS, and CdS) not included in the training geometries. It produced vertical excitation energies with MAE 0.27 eV as compared to EOM-CCSD. For larger clusters for which EOM-CCSD is prohibitively expensive, comparisons were made with Time-Dependent Density Functional Theory (TDDFT) and MAE 0.29 eV was obtained. Also, though absorption spectra were not included in the training data, the optimized model produced absorption spectra that agree qualitatively with those from EOM-CCSD.

The optimized model was employed to compute excitation energies and UV-absorption spectra for Si, S, Zn, Cd, ZnS, and CdS nanoclusters. It predicted Si, Zn, and Cd nanoclusters to be metallic.