The superexchange mechanism in trapped hole diffusion on semiconductor nanocrystals

Joel D. Eaves and Gordana Dukovic
Department of Chemistry
University of Colorado, Boulder
joel.eaves@colorado.edu and gordana.dukovic@colorado.edu

In Cd-chalcogenide nanoparticles, photogenerated holes readily trap to the surfaces. I will show evidence that the holes form small polarons on the surface and hop from site to site via phonon-assisted tunneling.[1] By including the superexchange mechanism in microscopic electronic structure calculations, where the hole visits a tier of virtual hole states in the bulk before trapping back to another surface atom, we can reproduce tunneling amplitudes measured in temperature-dependent transient absorption spectra quantitatively.[1-3] These calculations present some unique challenges—the number of atoms required to faithfully represent the particle's surface is large and perturbation theory for the hole tunneling matrix element breaks down. I will show how we use many-body Green's function theory to map the problem of computing the superexchange amplitude onto an exactly solvable quantum impurity problem, allowing the calculation of the superexchange matrix element to infinite order in perturbation theory.

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(2) Utterback, J. K.; Ruzicka, J. L.; Hamby, H.; Eaves, J. D.; Dukovic, G. Temperature-Dependent Transient Absorption Spectroscopy Elucidates Trapped-Hole Dynamics in CdS and CdSe Nanorods. *J Phys Chem Lett* **2019**, *10*, 2782-2787.

(3) Cline, R. P.; Eaves, J. D. Surface-Trapped Hole Diffusion in CdS and CdSe: The Superexchange Mechanism. *Journal of Physical Chemistry C* **2020**, *124*, 28244-28251.