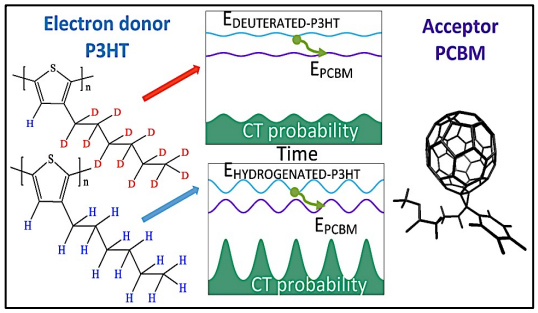
How Isotopes Tune Energy Conversion in Polymers

Achievement: Protonic and deuteronic wavefunctions expose how isotopic substitution attenuates the energy gaps relevant to charge transfer between donor and acceptor electronic states in an active layer of a solar cell.



Schematic illustrating the basic mechanism for the isotope effect in side chain deuterated (SD) poly(3-hexylthiophene) (P3HT). The middle panel show the probability of charge transfer to the acceptor molecule (PCBM) and corresponding energy levels; SD-P3HT show shallower fluctuations in probability for charge transfer.

Significance and Impact: Tuning the efficiency of polymer-based active layers in photovoltaic cells (OPVs) requires a delicate balance of competing processes, including those dominated by interactions within (intra) and between (Inter) polymer chains. Isotopic substitution can directly modulate these interactions and thus provides a new modality to tune the efficiencies of OPVs.

Research Details:

- Quantum trajectory-electronic structure with nonlinear corrections to the quantum forces
- Protonic and deutronic time-dependent wavefunctions combined with a 4-state diabatic Hamiltonian for full analysis of charge transfer processes

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Overview:

This work describes the development and application of a quantum dynamics methodology for multiple quantum nuclei that is suitable for simulations of the isotope effect in conducting polymers. In particular, focus is on an unexpected nuclear quantum effect (NQE) is caused by side-chain H/D substitution in a P3HT/PCBM blend where there is a substantial decrease in the open circuit voltage. The computational approach includes a quadratic basis quantum force correction to account for non-linear contributions of the CH/D anharmonic vibrations. Extensive simulations strongly suggest that isotope-dependent fluctuations may account for the observed NQE by promoting charge transfer via tunneling in P3HT compared to side chain deutrated-P3HT (SD-P3HT)and increasing carrier loss. With this information and the ability to accurately model the isotope effect, specific design of optimally deutrated polymers for OPVs can in principle be achieved.