Alchemical derivatives of reaction energetics.

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Based on molecular grand canonical ensemble density functional theory, we present a theoretical description of how reaction barriers and enthalpies change as atoms in the system are subjected to alchemical transformations, from one element into another. The change in the energy barrier for the umbrella inversion of ammonia is calculated along an alchemical path in which the molecule is transformed into water, and the change in the enthalpy of protonation for methane is calculated as the molecule is transformed into a neon atom via ammonia, water, and hydrogen fluoride. Alchemical derivatives are calculated analytically from the electrostatic potential in the unperturbed system, and compared to numerical derivatives calculated with finite difference interpolation of the pseudopotentials for the atoms being transformed. Good agreement is found between the analytical and numerical derivatives. Alchemical derivatives are also shown to be predictive for integer changes in atomic numbers for oxygen binding to a 79 atom palladium nanoparticle, illustrating their potential use in gradient-based optimization algorithms for the rational design of catalysts.

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