On the calculation of quantum mechanical electron transfer rates

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We present a simple interpolation formula for the rate of an electron transfer reaction as a function of the electronic coupling strength. The formula only requires the calculation of Fermi Golden Rule and Born-Oppenheimer rates and so can be combined with any methods that are able to calculate these rates. We first demonstrate the accuracy of the formula by applying it to a one dimensional scattering problem for which the exact quantum mechanical, Fermi Golden Rule, and Born-Oppenheimer rates are straightforward to evaluate. We then describe how the formula can be combined with the Wolynes theory approximation to the Golden Rule rate [1], and the ring polymer molecular dynamics (RPMD) approximation to the Born-Oppenheimer rate [2], to capture the effects of nuclear tunnelling, zero point energy, and solvent friction on condensed phase electron transfer reactions. Comparison with exact hierarchical equations of motion (HEOM) [3] results for a demanding set of spin-boson models shows that the interpolation formula has an error comparable to that of RPMD rate theory in the adiabatic limit, and that of Wolynes theory in non-adiabatic limit, and is therefore as accurate as any method could possibly be that attempts to generalise these methods to arbitrary electronic coupling strengths.

References

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