Analytic continuation of Wolynes' theory into the Marcus inverted regime

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Poster Abstract

Wolynes' theory of electronically nonadiabatic reaction rates [P. G. Wolynes, J. Chem. Phys. **87**, 6559 (1987)] is based on a saddle point approximation to the time integral of a reactive flux autocorrelation function in the nonadiabatic (Fermi Golden Rule) limit. The dominant saddle point is on the imaginary time axis at $t = i\lambda\hbar$, and provided λ lies in the range $-\beta/2 \leq \lambda \leq \beta/2$, it is straightforward to find the saddle point and evaluate the rate constant using information obtained from an imaginary time path integral calculation. However, if λ lies outside this range, as it does for the spin-boson model of electron transfer in the Marcus inverted regime, the path integral diverges. This has led to claims in the literature that Wolynes' theory cannot describe the correct behaviour in the inverted regime. Here we show how the imaginary time correlation function obtained from a path integral calculation can be analytically continued to $\lambda < -\beta/2$ and the continuation used to evaluate the rate in the inverted regime. Comparison with exact Fermi Golden Rule results for a spin-boson model and a model of electronic predissociation show that the theory it is just as accurate in the inverted regime as it is in the normal regime.