Nonadiabatic reactions and tunnelling: beyond the golden-rule approximation

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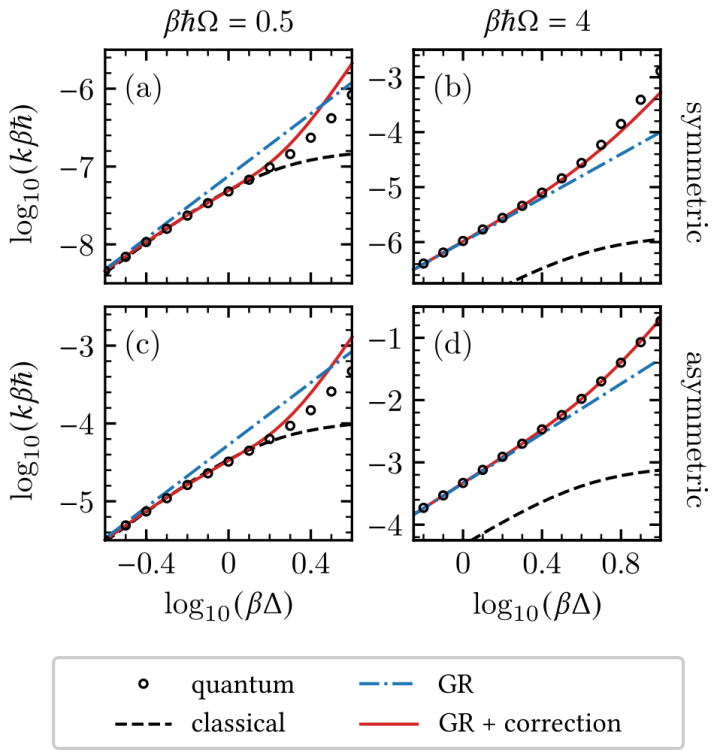
Fermi's golden rule (GR) [1] is commonly used to calculate the rates of nonadiabatic reactions. Treated exactly, it is only tractable for simple models, but several approximate formulations have been developed, whose accuracy and computational efficiency make them a valuable tool in the study of chemical systems. GR instanton theory is one such formulation that accurately accounts for zero-point energy effects and multidimensional nuclear tunnelling in polyatomic systems [2-4]. However, not all nonadiabatic reactions are adequately described by Fermi's golden rule, and it has long been known that it can be improved with the help of perturbation theory. Much like the golden rule itself, exact perturbative corrections are too expensive for practical applications, and so we have developed a corresponding practical instanton formulation [5]. Our findings reveal how nonadiabatic effects can either suppress or enhance reaction rates, giving new mechanistic insight into the interplay of electronic transitions and nuclear tunnelling. We discuss how our new theory can be used to easily test and improve the accuracy of previous instanton calculations. We also present a novel procedure that uses our theory to find the optimal diabatic nuclear Hamiltonian for golden-rule calculations, expanding the scope of reactions that can be tackled with instanton techniques.



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