

Quantized time correlation function approach to non-adiabatic decay rates in condensed phase: Application to solvated electrons in water and methanol

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A new, alternative form of the Golden rule formula yielding the non-adiabatic transition rate between two quantum states in condensed phase is proposed. The formula involved quantum time correlation functions which can be inferred from their classical analogs. It is applied to the problem of solvated electrons in water and methanol and the lifetime of the equilibrated excited state electron can be estimated in both cases. For water we find that this lifetime is extremely short, below 10 fs, in agreement with the recent pump-probe experiments of Wiersma and collaborators using 5-fs pulses, and in contrast with all previous experimental or theoretical estimations.