

QUASICLASSICAL VERSUS PHASE SPACE APPROACHES TO RADIATIONLESS TRANSITIONS IN MOLECULES

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We study a radiationless transition in a polyatomic molecule when the electronic energy of an excited electronic state is transferred to vibrational degrees of freedom of the nuclei, and when some nuclear coordinates change abruptly. The rate of the transition is proportional to the square of the Frank – Condon integral, or an overlap integral between the nuclear components of the wavefunctions.

In the quasiclassical approximation, the bulk of the overlap integral goes from a vicinity of the point \vec{q}_L in the coordinate space where the classical momentum on the donor Born – Oppenheimer surface is opposite to the momentum on the acceptor surface. In the Wigner representation, the bulk of the phase space overlap integral goes from a region near the point (\vec{q}_*, \vec{p}_*) on the surface of constant energy where the Wigner function is maximal. For illustration, these two approaches in different regimes are compared for two models with Morse or Poeschl– Teller oscillators.

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