TUNNELING SPLITTINGS IN HYDROGEN-BONDED MOLECULES AND HYDROGEN TUNNELING IN CONDENSED PHASES

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A theory of tunneling splitting in hydrogen-bonded systems and hydrogen tunneling dynamics in condensed phases is presented. The theory is developed on a model of a fast-moving particle in an one-dimensional metastable or bistable potential coupled to a bath of lower-frequency harmonic oscillators. A power series expansion of the coupling terms up to a biquadratic one is included explicitly which accounts for all different coupling symmetries in the system. Analytical formulae are derived for the tunneling splitting or tunneling rate in terms of the normal modes of the system making the treatment applicable to systems of arbitrary size. For vibrational eigenvalue problems the treatment can be viewed as an extension of the normal mode treatment to incorporate small tunneling splittings. For dynamical problems, such as hydrogen-transfer reactions and hydrogen diffusion in solids or at surfaces, the method incorporates a precise definition of a transition state and can be viewed as a close quantum-mechanical analog of the classical transition-state theory. The method is tested on model multidimensional tunneling problems against numerical calculations from the literature with excellent results. Applications to calculations of tunneling splittings and isotope effects in hydrogen-bonded molecular systems and comparisons with experimental data are given.