PROPENSITY RULES FOR SURFACE-JUMPING BETWEEN MULTIDIMENSIONAL OSCILLATORS: MATHEMATICAL ASPECTS OF THE PHASE-SPACE APPROACH

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We consider radiationless vibronic relaxation: a transition without loss of energy from the bottom of an upper vibrational potential energy surface of an electronically excited donor state to one of vibrationally excited states on a lower surface of the ground electronic state. The recently developed phase-space distribution approach to propensity rules for surface jumping gives a general prescription for finding the leakage point of energy-transfer between two Born-Oppenheimer surfaces. We focus here on the mathematical aspects of this approach and on its application to multidimensional harmonic and anharmonic oscillator surfaces. By approximating the Wigner function of the acceptor by its classical limit $\delta\left(E - H_{cl}(p,q)\right)$, the problem reduces to finding a maximum of the Wigner function of the donor on the accepting surface $H_{cl}(p,q) = E$ that can be easily solved algebraically. We have defined auxiliary transitional variables to describe the jump between the two surfaces and found that the Franck-Condon phase-space integrand is maximal at a point in phase space near the eigenvector corresponding to the smallest eigenvalue of an auxiliary matrix equation. The relation between the auxiliary transitional variables and the traditional normal modes is discussed, and the dependence of the propensity rules on the energy gap and on the displacement of the potential minima is formally studied.