Vibrational Siegert states of anharmonic systems via curvilinear mean-field techniques

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Reaction probabilities, vibrational pre-dissociation, and other scattering phenomena are encoded by the S-matrix, whose pole structure is characterized by Siegert states (quasi-stationary states with complex energy eigenvalues). Calculating Siegert states is made difficult, however, by their non-Hermitian nature and the intrinsic anharmonicity of potential energy surfaces that contain reactive barriers. We address these problems with complex-scaled modifications of curvilinear vibrational mean-field techniques. These tools efficiently access the Siegert states associated with barrier transition states and quasi-bound resonances. We discuss the performance of perturbative and quasi-variational methods, as well as their application to reaction rate calculations and other scattering problems.