VIOLATION OF MULLIKEN'S RULE FOR RYDBERG STATES

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The results of *ab-initio* $\mathbf{R}$-matrix calculations display profound deviations from Mulliken's rule in the continuum electronic structure of CaF. In the $1-D$ effective potential for the electronic motion, a shape resonance induces a crossover from short-range Mulliken-type dynamics to long-range dipole-mediated dynamics. This effect is visible in the scattering matrix as well as the photoionization cross-sections and photoelectron anisotropies. The non-Mulliken behavior can be exploited by l-selective detection of Rydberg dynamics and spectra, revealing the l-decomposition of molecular eigenstates.