Results of \textit{ab-initio} R-matrix calculations \cite{Altunata2005} indicate the presence of a broad shape resonance in electron-CaF$^+$ scattering for the $^2\Sigma^+$ electronic symmetry near the ionization threshold. The properties of this shape resonance are analyzed using the adiabatic partial-wave expansion of the scattered electron wavefunction introduced by Le Dourneuf et. al. \cite{LeDourneuf1982} The qualitative aspects of the shape resonance are explained by an adiabatic approximation on the electronic motion. Mulliken’s rule for the structure of Rydberg state wavefunctions \cite{Mulliken1964} specifies that, except for an $(n^*)^{-3/2}$ scale factor, every excited state wavefunction within a Rydberg series is build on an innermost lobe that remains invariant in shape and nodal position as a function of excitation energy. Mulliken’s rule implies a weak energy dependence of the quantum defects for an unperturbed molecular Rydberg series, which is given by the Rydberg-Ritz formula.

This zero-order picture is violated by a single $^2\Sigma^+$ CaF Rydberg series at all Rydberg state energies ($n^* \geq 5$, increasingly with $n^*$) below the ionization threshold, under the broad width of the shape resonance. Such a violation is diagnostic of a global “scarring” of the Rydberg spectrum, which is distinct from more familiar local level perturbations.

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