WHAT DO WE MEAN BY “ELECTRONIC STRUCTURE”? 

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A large and diverse set of spectroscopic data for the CaF molecule has been used to determine the parameters of an s-p-d-f quantum defect matrix and its derivatives with respect to energy and internuclear distance, μ(E,R). The result is a complete description of the 10 Rydberg series (four Σ, three Π, two Δ, and one Φ) of CaF, each consisting of an infinite number of discrete states plus an associated ionization continuum. The quantum defect matrix may be converted into ten R-dependent eigenquantum defect functions, which describe the infinite series of potential energy curves and all the nonadiabatic interactions among them. The E dependences of these eigenquantum defect functions describe how the potential curves evolve as one goes from the lowest member (terminus state) of the series, where the Rydberg electron interacts most strongly with the not-round and chemically inhomogeneous ion-core, to the nearly-bare ion-core, where the electron-ion interaction is of a predominantly long-range rather than chemical nature. The E-dependent shapes of the eigenquantum defect curves reveal global features of the electronic structure, such as direct and induced avoided crossings, that would not be evident in a state-by-state or even a series-by-series description. The principal irregularities appear to be due to exclusion of one Σ and one Π repulsive state, terminus states of series converging to excited states of the CaF+ ion core, from the quantum defect matrix fit model.