Core multipoles and polarization effects affect the term values and spectroscopy of Rydberg states, and, conversely, Rydberg state spectroscopy provides a window into the nature of ground electronic state charge distributions, and into polarization due to configuration interaction. As experimental resolution continues to increase through the introduction of techniques like chirped mm-wave techniques for Rydberg systems, more details about the core electronic structure as a function of Rydberg state quantum numbers \((n,\ell)\) and internuclear separation, \(R\), will become available. Existing modeling of the CaF Rydberg spectrum, although extensive, is not ready for the challenge of higher resolution measurements. Even for the existing data, MQDT calculations (based on a two center effective potential with limited atomic polarization) show reasonable agreement at equilibrium \(R\), but deviates from the phenomenological QDT fit with \(R\).

We have performed a series of all-electron calculations for CaF\(^{+}\) itself, and for CaF\(^{+}\) with a test negative charge fixed at distances and angular positions around the core with a range of \(R\), with a goal of improving our understanding of the nature and magnitude of polarization effects for polar diatomics like CaF. In analyzing these results, we have considered core moments through the octupole, and polarizabilities and hyperpolarizabilities defined in perturbation theory to 4\(^{th}\) order that contribute to the \(e^{-}\)-core energy in first and second order. Polarization contributes to \textit{ab-initio} energies with characteristic \((r, \theta)\) dependence that allows the contributions to be identified by type and as a function of \(R\). Terms describing asymmetric polarization like dipole-dipole and dipole-octopole are found to contribute more strongly than symmetric terms like quadrupole-quadrupole. The fields present in the \(e^{-}\)-core interaction are so high that the F- anion polarizability is approaching saturation at \(R = R_{eq} = 3.54a_0\), while the Ca\(^{2+}\) polarizability is still independent of \(R\).

We will describe the energy expression in the simple effective potential, describe the more complete form including multipolar and polarization terms in Cartesian and spherical coordinates, present two methods for determining polarizabilities, and compare these \textit{ab-initio} results with the limited experimental information currently available.