

# The electronic structure of AlF molecule

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Aluminum monofluoride (AlF) is an excellent molecule for ultracold experiments due to its high chemical stability and nearly diagonal Franck–Condon factors between the ground and selected excited states. However, the flawless design of cutting-edge experiments requires detailed knowledge of molecular properties, obtained either through spectroscopy or high-level electronic structure calculations. In this work, we provide a comprehensive characterization of the AlF molecule using state-of-the-art *ab initio* coupled cluster methods and extended basis sets.

We begin with a systematic analysis of AlF's electronic structure, covering singlet, triplet, and quintet states up to 70,000 cm<sup>-1</sup> above the ground state. We not only reproduced the position of experimentally known states but also identified previously unknown ones located at higher energies than those measured so far. Additionally, we obtained the potential energy curves for related ions.

The high-accuracy potential energy curves are presented for the  $X^1\Sigma^+$  and  $a^3\Pi$  states, with particular attention to non-adiabatic, relativistic, and quantum electrodynamic (QED) effects. We found that quantum electrodynamic and non-adiabatic effects are much larger than the resolution of a typical spectroscopic experiment. We assess the convergence of these calculations with basis set size, achieving an estimated uncertainty of 6 MHz for rotational constants and 0.6 cm<sup>-1</sup> for vibrational frequencies - illustrating the current precision limits of theoretical methods.

In addition, we compute hyperfine interaction parameters for both the  $X^1\Sigma^+$  and  $a^3\Pi$  states, demonstrating rapid convergence with respect to electronic wavefunction accuracy. Finally, we report the electric properties of AlF, including the permanent dipole moment and both static and dynamic polarizabilities.

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