For a molecule with a closed-shell core, high-$I$ Rydberg states tend to belong to Hund’s angular momentum coupling case (d) or (e), while lower-$I$ states may be in any of the cases (a)–(e). For an open-shell core, the coupling case of both the core and the Rydberg electron must be considered. Typical core cases are (a)–(c), because a Rydberg state with a case (d) or (e) core is better regarded as a state with two Rydberg electrons. This gives fifteen possible coupling cases, (a±a), (a±b), ..., (c±e), for the core and a single Rydberg electron, and there are a number of sub-cases corresponding to different schemes for coupling the core and Rydberg angular momenta. The good quantum numbers for the different cases will be discussed, together with approximate values for the matrix elements of some of the terms of the Hamiltonian in the case (d) or (e) limit for the Rydberg electron.