Non-Hermitian Quantum Chemistry: Connecting Excited States through the Complex Plane

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Electronic excited states are central to processes across many areas of science. In principle, excited-state energies are given by the discrete solutions of full configuration interaction (FCI) in a complete basis set, however accurately determining these energies remains a major challenge in theoretical chemistry. Alternatively, higher energy stationary states of approximate methods — including non-linear self-consistent field (SCF) approaches and truncated configuration interaction (CI) — can themselves be interpreted as approximations to excited states, although our general understanding into the nature of these solutions remains surprisingly limited. In this work, we present an entirely novel approach for exploring excited stationary states across quantum chemistry that exploits the properties of non-Hermitian Hamiltonians. Our key idea centres on performing complex analytic continuations of conventional methods that reveal rich and diverse behaviours in the complex plane. For example, by analytically continuing the electron-electron interaction in holomorphic Hartree–Fock theory,[1–3] we expose a hidden connectivity of multiple solutions across the complex plane.[4] In doing so, we reveal that Coulson–Fischer points (where real Hartree–Fock solutions coalesce) behave more generally as non-Hermitian "exceptional point" degeneracies. Finally, we demonstrate how one can exploit this complex topology to naturally evolve a ground-state wave function into an excited-state wave function using a well-defined complex adiabatic connection.

References

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