

Coupled Cluster Theory and Full Configuration Interaction for electrons, photons and vibrations

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The Coupled-Cluster (CC) method is nowadays almost universally used as the preferred tool for introducing electron correlation effects into first-principles molecular electronic structure computations. Its effectiveness in converging towards the full configuration interaction (FCI) limit has been established through numerous studies, and its performance is almost always excellent when the Hartree-Fock reference is a good starting point. When there is strong static electron correlation, extensions and generalisations, including variational and extended CC and approximations to them, completely-renormalised approaches, and the distinguishable cluster approach, can also give accurate ground-state energies.

Less well known is whether there is always a unique physical solution to the equations that define the cluster amplitudes. The evidence from very many examples with weak correlation is that an obviously physical unique solution is nearly always found; but when static correlation is strong, it is less clear. We here investigate the possible existence of multiple solutions, and analyse their nature when they occur.

The underpinning of the standard Born-Oppenheimer approximation proves insufficient for describing many physical situations, particularly when potential energy surfaces cross, become close, or exhibit conical intersections. Physical contexts where nonadiabaticity plays a key role include photochemistry, electrochemistry and proton-coupled electron transfer. A huge amount of effort has been invested in theoretical and computational frameworks that model the non-adiabatic behaviour via a small number of Born-Oppenheimer states that are allowed to interact through the nuclear kinetic energy operator. The Born-Oppenheimer approximation starts by transforming a two-body Hamiltonian (describing the single-particle kinetic energies, and the pairwise interactions of charged particles) into a Hamiltonian with many-body potential-energy surfaces, in which all nuclear degrees of freedom are coupled together. This leads to exponential scaling of complexity with molecular size. As an alternative approach, we develop a theory for the quantum mechanics of electrons and nuclei together, without reference to the eigensolutions of the clamped nucleus hamiltonian.