ANALYSIS OF THE EXTENDED COUPLED-CLUSTER METHOD IN QUANTUM CHEMISTRY

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The mathematical foundation of the so-called extended coupled-cluster method for the solution of the many-fermion Schrödinger equation is here developed. We prove an existence and uniqueness result, both in the full infinite-dimensional amplitude space as well as for discretized versions of it. The extended coupled-cluster method is formulated as a critical point of an energy function using a generalization of the Rayleigh–Ritz principle: the bivariational principle. This gives a quadratic bound for the energy error in the discretized case. The existence and uniqueness results are proved using a type of monotonicity property for the flipped gradient of the energy function. A comparison to the analysis of the standard coupled-cluster method is made, and it is argued that the bivariational principle is a useful tool, both for studying coupled-cluster type methods, and for developing new computational schemes in general.

Keywords: quantum chemistry; coupled-cluster method; extended coupled-cluster method; bivariational principle; uniqueness and existence; error estimates

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