Optimal orbitals from a quantum information perspective

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Treating simultaneously static and dynamic correlations in strongly-correlated systems in a balanced way is a very challenging task of crucial importance. We examine this problem at one of the very first steps in electronic structure theories, namely the optimization of orbitals. While the latter affects subsequent steps in a significant way, this problem is often not systematically investigated: According to the common paradigm one typically optimizes the orbitals in the presence of static correlations, such as in complete active space self-consistent field theory (CASSCF), and only then takes dynamic correlations into account by some other means, without further systematically optimizing the orbitals. Recently, it was demonstrated that quantum information-theoretical concepts, such as the orbital entanglement entropy, can be used to optimize active space orbitals to a quality that is on par of CASSCF. Based on this work, we will show that a generalized framework can be devised to optimize orbitals in the presence of both kinds of correlations, using tailored coupled cluster theory as an example. The resulting orbitals are termed quantum information orbitals (QIOs). We demonstrate that QIOs can reduce errors in the total energy by as large as 20 mHa in certain cases compared to the CASSCF orbitals. Further evidence of the improved many-body wavefunction in QIOs is shown by the reduction of errors in the 2-RDM and by the information gained evident by the increase of the total entanglement entropy. We only touch the tip of the iceberg of the quantum information tools that can be used for challenging quantum chemical problems and hope to inspire more explorations along this direction.