

Variational Excited States in DFT, QMC, and Quantum Chemistry

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We will discuss uses for excited state variational principles across a wide range of electronic structure contexts, including mean field theory,¹ density functional theory,² multi-reference theory,³ and quantum Monte Carlo.⁴ In all of these areas, variational approaches allow excited states to be modeled without the need for additional approximations beyond those present in the ground state theory. For example, this approach avoids (a) the need for the adiabatic approximation in density functional theory,² (b) the need to use ground state orbitals in correlated quantum chemistry methods,¹ and (c) the need for state averaging in multi-reference methods.³ Remarkably, in all of these cases, the variational excited state approach achieves a cost scaling equivalent to the corresponding ground state method.¹⁻⁴ In addition to discussing the formalism behind these developments, we will present preliminary results showing how the removal of common excited state approximations leads to improved predictive power in difficult cases like charge transfer excitations^{1,2} and double excitations.³

References

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