Looking at the world from a coupled-cluster perspective

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In this talk we will address the broader context of coupled-cluster (CC) theory in chemistry. The theory offers an approach to a new correlated orbital theory (COT) that has similar computational demands to density functional theory (DFT) but is built upon the premise that the one-particle spectrum of a molecule, its principal ionization potentials and electron affinities should be right. Approximations to these equations can be made to provide the computational advantages of an effective one-particle theory.

A related topic is the role of the random phase approximation (RPA) in defining a correlation potential for DFT. We introduce the concept of ‘coulomb attenuation” as a way to better treat the correlation problem, by first solving for Coulomb-only interactions, leaving the exchange and subsequent correlation to simpler, perturbative treatments. This new division of the correlation problem depends upon the close correspondence between CC theory and its RPA approximation limited to the sum of ring diagrams.