Coupled-Cluster Theory and Born-Oppenheimer Breakdown

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Breakdown of the Born-Oppenheimer approximation is commonly observed in molecular physics, often with immediate consequences to spectroscopy, quantum dynamics, and kinetics. A general way to deal with such systems is to work in a diabatic representation in which the electronic Hamiltonian is not diagonal, but the corresponding electronic states are relatively simple. Several successful models of this type have been advanced, perhaps the most successful of which is that due to Köppel, Domcke and Cederbaum. This brief talk emphasizes the considerable merits of coupled-cluster theory – especially in its equation-of-motion variant – for providing the required information to these models.