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DFT for excited states: time−dependent DFT, exact exchange, RPA correlation

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The feasibility of excited−state computations from Time−Dependent Density Functional Theory (TD−DFT) has been recently demonstrated for molecules and clusters.

In this talk, it is first shown how the knowledge of selected matrix elements of the TD−DFT exchange and correlation functional allows one to connect practical approaches to excited states, based either on DFT or on many−body perturbation theory. Of particular significance is the decomposition of the DFT functional in its exact−exchange contribution and its correlation contribution. The latter is given in principle exactly by the adiabatic−connection fluctuation−dissipation (ACFD) formula, that can be evaluated within the Random−Phase Approximation (RPA).

Then, the TD−DFT formalism is applied to the computation of excited−state potential−energy surfaces. For the $(HeH)^+$ system, the 5 lower−lying singlet and triplet $^1\Sigma$ states are obtained for a series of internuclear distances.

Finally, an implementation of the ground−state ACFD−RPA formalism is presented within the plane−wave pseudopotential method (ABINIT software). The binding energy of the H_2 and Be_2 dimers is analyzed, with special emphasis on the role of short−range correlations beyond the RPA.