

Force calculations within the Tamm–Dancoff approximation to TDDFT

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Electronic structure calculations of excited states based on linear response within time-dependent density functional theory (TDDFT) [1] have recently attracted a lot of interest. As for ground state DFT calculations, these methods provide in many cases accurate results comparable to high level wavefunction methods, for only a fraction of the cost.

We have implemented the Tamm–Dancoff approximation to TDDFT [2] into the pseudopotential/plane wave based *ab initio* molecular dynamics program CPMD [3]. In first applications we have investigated the excitation spectra of molecules and molecular condensed systems. The observation that many excitations only involve a small number of states leads to the proposal of subspace approximations, reducing the computational cost considerably. This made it possible to sample excitation spectra along molecular dynamics trajectories. The efficient implementation [4] of nuclear forces within the Tamm–Dancoff and its subspace approximations allows the optimization of structures, calculation of harmonic vibrational spectra and molecular dynamics simulations in excited states. Preliminary applications will be reported.

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