

## Time-Dependent Density-Functional Theory Kernels From Many-Body Perturbation Theory

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RPA-like methods based upon time-dependent density-functional theory (TDDFT) [1] in its linear response formulation [2] have become a method of choice in the study of excited state properties of medium- and large-sized molecules. Though successful in many cases, TDDFT is not a black box method.[3, 4] The origin of the difficulty lies in the adiabatic approximation of the exchange-correlation kernel,

$$f_{Hxc}(\mathbf{r}, \mathbf{r}', t - t') \approx \delta(t - t') \frac{\delta^2 E_{xc}[\rho_t]}{\delta \rho_t(\mathbf{r}) \delta \rho_t(\mathbf{r}')}, \quad (1)$$

which assumes that the self-consistent (Hxc) field responds instantaneously and without memory to any temporal changes in the external perturbation. As a consequence of this approximation, one-electron excitations are essentially decoupled from higher-order excitations. This is too crude an approximation for many problems, including organic chromophores with conjugated  $\pi$  systems, describing bond rupture in photochemistry, and representing the spectra of open-shell molecules. The analytical form of a post-adiabatic approximation of the kernel is obtained by extracting  $f_{Hxc}(\omega)$  from an exact Dyson-like equation for the kernel,

$$f_{Hxc}(\mathbf{r}, \mathbf{r}'; \omega) = \chi_s^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - \chi^{-1}(\mathbf{r}, \mathbf{r}'; \omega), \quad (2)$$

in which we apply many-body perturbation theory (MBPT) techniques.[5] The kernel has a similar structure to the dressed-TDDFT kernel.[6, 7] Some preliminary computational results with the non-adiabatic kernel will also be presented.

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