

MAR12-2011-007864

Abstract for an Invited Paper
for the MAR12 Meeting of
the American Physical Society

Towards the ab-initio description of photo-induced processes

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Excitons are prominent features in the optical spectra of periodic solids and molecular aggregates. Time-dependent density functional theory should, in principle, be able to describe excitonic effects. However, with standard functionals for the exchange-correlation (xc) kernel f_{xc} , such as adiabatic LDA and adiabatic GGA, excitonic features are completely absent. The construction of improved functionals for f_{xc} yielding excitons has a long history. Here we propose a new parameter-free approximation for the xc kernel through an algorithm in which the exact Dyson equation for the response is solved self-consistently with an approximate expression for the kernel in terms of the dielectric function [PRL **107**, 186401 (2011)]. We apply this to the calculation of optical spectra for various small bandgap (Ge, Si, GaAs, AlN, TiO₂, SiC), large bandgap (C, LiF, Ar, Ne) and magnetic (NiO) insulators. The calculated spectra are in very good agreement with experiment for this diverse set of materials, highlighting the universal applicability of the new kernel. These optical spectra are calculated with clamped nuclei. However, in a variety of optical phenomena, the coupling between electronic and nuclear motion plays an important role. Prominent examples are the process of vision and photo-synthesis. Standard approximations such as Ehrenfest dynamics, surface hopping, or nuclear wave-packet dynamics only partially capture the occurring non-adiabatic effects. As a first step towards a full ab-initio treatment of the coupled electron-nuclear system, we deduce an exact factorization of the complete wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration. We derive formally exact equations of motion for the nuclear and electronic wavefunction [PRL **105**, 123002 (2010)]. These exact equations lead to a rigorous definition of time-dependent potential energy surfaces as well as time-dependent geometric phases.