

Electronic Excitations in the Condensed Phase

The interaction of electromagnetic radiation (visible light, UV and IR radiation, X-rays, etc.) with matter is governed by the rules of quantum mechanics. When a photon incident on a sample is absorbed, one or more electrons are excited from their equilibrium state in normal conditions, the ground state Ψ_0 , to one of the system's electronically excited states Ψ_n . The character of the excited state can be quite different from the ground state, e.g. in the way atoms are

arranged or in its response to external perturbations. The ability to account quantitatively for the physics of electronic excitations is important for the interpretation of experimental spectroscopic data and for the prediction of complex phenomena occurring in catalytic processes, solar energy conversion and radiation damage in materials and biological systems, like proteins and DNA in living cells.

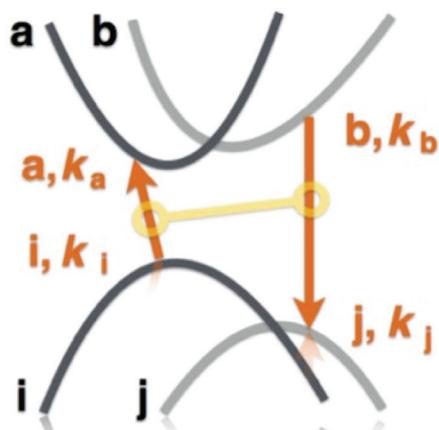


Figure 1 The exciton problem in TD-DFT. Electron-hole pairs (red) created by excitations from occupied (i, j) to unoccupied (a, b) one-electron bands in a crystal couple via a generalised eigenvalue equation (Casida's equation). This coupling creates bound states lower in energy than the empty bands. The number of electron-hole pairs determines the size of the matrices A and B and it can grow prohibitively large in calculations on infinite periodic systems.

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

There are two fundamental challenges in the physics of excited states than need to be addressed:

1. the mechanism through which an excited electron interacts with the positive hole created by the absorption of a photon (the *exciton* problem);
2. the atomic relaxation following the creation of the excited state Ψ_n .

These two classes of phenomena can manifest themselves differently in finite systems (molecules, small atomic clusters, etc.) and in condensed phase samples (e.g. crystals, surfaces, polymers, nanostructures, liquids and large biological molecules). The formation of excitons is particularly important in infinite crystals, e.g. the crystalline semiconductors used in various classes of photovoltaic devices, as well as at crystal surfaces and in polymers.

An exciton can be represented as an electron-hole pair, in which the electron and the hole carry a negative and a positive charge respectively. Effectively, this system

is an exotic atom created by photoexcitation within a crystal lattice, similar to a hydrogen atom in which the nucleus is replaced by the positive hole. Excitons are the quasi-particles responsible for the transfer of energy in solar cells, LEDs and semiconductor circuits and they are involved in various natural processes, including photosynthesis.

The formation of an exciton is a quantum many-body process, in which virtual electron-hole pairs screen the bare excited electron and hole (Figure 1). The screened electron-hole pair is held together by Coulomb interactions. The development of methods capable of describing these phenomena fully from first principles, i.e. with no need of external empirical parameters, has been the focus of work carried within the Theoretical and Computational Physics group over several years. One of the successes of this effort has been the development of an original and powerful method for computing electronic excitations in solids based on the time-dependent density-functional theory (TD-DFT) framework. [1] This approach exploits a mathematical

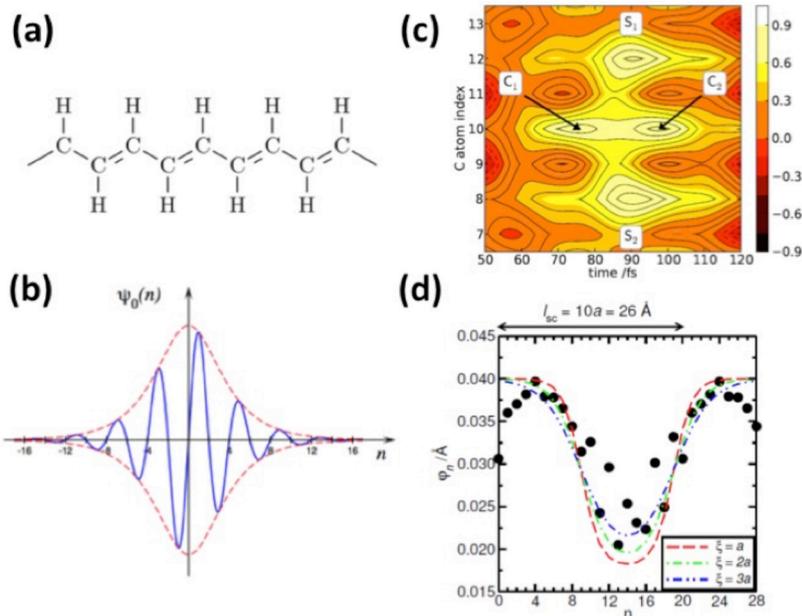


Figure 2 Photoexcited dynamics in trans-polyacetylene. (a) The structure of polyacetylene. (b) A soliton wavefunction. (c) Soliton collision at room temperature: electronic correlation determines the appearance of non-linearity in the soliton dynamics; the figure shows a 2-bounce resonance of a soliton and an antisoliton, an intriguing phenomenon observed in certain classes of non-fully integrable partial differential equations with chaotic solutions. (d) Condensation of solitons at zero temperature: a soliton and an antisoliton form a bound pair stabilized by electronic correlation.

procedure to recast the direct diagonalisation of large matrices describing the electron-hole screening into a more manageable self-consistent field (SCF) minimization of a suitable functional. Effectively, the SCF avoids the complexity of the direct coupling of elementary excitations, and allows calculations to be carried accurately and efficiently on three-dimensional infinite crystals. This method has been implemented in the CRYSTAL software, one of the most advanced electronic structure codes for extended systems currently available, whose development has been actively supported by STFC/CCLRC for almost 40 years, and it has been applied successfully to several problems including optical absorption in semiconductors, [1-2] the design of new materials for photovoltaics [3] and the nature of low-energy excitations in alkali halide crystals. [4]

The second challenge, the nuclear relaxation following photoexcitation, is currently an open problem, with important implications in photochemistry, solar energy production (exciton transport in a crystal lattice) and biology (exciton trapping and energy transfer, photoinduced defect formation in macromolecules). Once a system is excited to Ψ_n , the forces acting on

each atom change relative to the ground state, and the atoms rearrange to reach new equilibrium positions. The nuclear relaxation may induce the population of excited states other than Ψ_n , and the forces acquire multi-state (non-adiabatic) character. The inclusion of non-adiabatic effects for excited state relaxation in extended systems within the TD-DFT framework requires substantial methodological and algorithmic developments. Our preliminary work in this field has been focussing on polymeric quasi-1D systems, in which hopping between excited states occurs relatively infrequently. An interesting example is trans-polyacetylene (PA), an important prototype material for applications in photovoltaics, optoelectronics, nonlinear optics and electromagnetic shielding. We have used TD-DFT excited-state dynamics to examine the photoinduced formation of topological defects (solitons) in PA and their dynamics at room temperature (Figure 2). [5] Our work shows that electron-electron correlation in excited states affects profoundly the properties of the solitons, and brings about exotic non-linear effects in their dynamics. This work is currently being extended to biological macromolecular crystals, in collaboration the Diamond Light Source.

Authors

L. Bernasconi, Rutherford Appleton Laboratory

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