Electronic and optical properties of nanostructures and biomolecules from first-principles

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Overview

Theoretical understanding of electronic properties and light-matter interactions from **first principle**

Fundamental processes occurring in biosystems and new technological devices

Quantum mechanical description is needed

\[ i\hbar \frac{\partial \Psi (r, t)}{\partial t} = H \Psi (r, t) \]

\( \Psi (r, t) \)  very complicate object
Theoretical approach

**Density Functional Theory (DFT)** (W. Kohn Nobel Prize 1998)

- **Density instead of wave function as fundamental variable.**
- Correlation effects approximated by effective potentials

**Ground state properties:** Electronic structure, reliable geometries

**Time Dependent Density Functional Theory (TDDFT)** (Runge, Gross 1984)

- Extension of DFT for time-varying external potential
- **Excited state properties:** Absorption spectrum
- **Very good compromise between computational efficiency and accuracy.**
- Approximations of correlation effects can be critical

**Many Body Perturbation Theory** (Hedin 1965)

- Perturbation theory around non interacting Hamiltonian
- Green function as a fundamental variable
- Quasi-particle energies (GW)
- **Absorption spectra:** inclusion of electrons-holes interaction (BSE)
- Accurate but computationally demanding

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TDDFT and MBPT permits the study of excited state properties of matter.

Computational ab-initio spectroscopy

Interpretation and theoretical assistance to experiments

GFP Nobel Prize (2008)


Exciton confinement in molecular chains

Role played by electron-hole attraction is not captured by TDDFT in simple approximations.

Excitonic effects in graphene nanostructures (nanoribbons)

Graphene

Graphene nano-ribbon

Modulated GNR

Binding energy depends on ribbon family: tunable optoelectronic features

addition or removal of single dimeric line permits confinement of electrons and holes

Son et al. PRL 97, 216803 (2006)

DNA for biomolecular electronics

DNA molecule presents great properties of structuring and recognition but poor conductivity for long (>40nm) molecules deposited on substrates.

• Improve measurement setup:
• Exploring DNA derivatives that could improve intrinsic conductivity:


Hole transfer in DNA

\[ k = \frac{2\pi}{\hbar} \left| \frac{V_{IF}}{4k_B T\lambda} \right|^2 \]

<table>
<thead>
<tr>
<th>xGC-xGC</th>
<th>GC-GC</th>
<th>xAT-xAT</th>
<th>AT-AT</th>
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<tr>
<td>0.205</td>
<td>0.075</td>
<td>0.054</td>
<td>0.008</td>
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Net increase upon size expansion
Importance of structural fluctuations

Larger diameter
Reduced inter-stacking distance
Enhanced inter-stacking interaction
Hypochromism


Optical activity in DNA nucleotides and base pairs

Development of a first principle scheme based on real time TDDFT for calculation of circular dichroism
D. Varsano et al. PCCP 11, 4481 (2009)

Natural CD in RT-TDDFT

Magnetic CD in RT-TDDFT

A-tracts have smaller bp/turns and axial rise than random DNA and alternating (AT:TA)_n

Significant role in translational and rotational positioning of DNA in nucleosomes.

Experimental Details

The hydrogen atoms were extracted from X-ray data (1d89 pdb file). The WC structure was constructed with the 3DNA builder. Bi- and tri-stranded DNA structures of Watson-Crick and cross-strand AT base pairs, (AT), (AT)_(2-9), (A)_(15-18), (AT), (AT), (A)_(27), and (AT)_(38) were extracted from X-ray experimental data, files 1d89 and 1bdn for (Ade)C-(Thy)O-2 (middle) and (Ade)N-6, (A)_(8-10), (T)_(8-10), (A)_(8-10), (T)_(8-10), (A)_(8-10). Bi- and tri-stranded DNA structures were used with a time step of 0.0079 fs and a total time of 15 fs.

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Significant role in translational and rotational positioning of DNA in nucleosomes.

The CS structures were obtained using a gradient minimization method. The CS structures were obtained using a gradient minimization method. All dihedrals were constrained to 180° except for the one between the DNA backbone and the sugar ring. When calculating the Hamiltonian, both CS and WC structures were used for the X-ray data (1d89 pdb file).

The CD spectra for this isolated adenosine is shown in Figure 2, where the spectra were averaged, baseline subtracted, and slightly smoothed with a Savitzky-Golay filter using the CD data for all the pure DNA strands.


**Optical properties and structural effects on DNA derivatives**

**DNA-Triplex:**

agents for alter gene expression sequence specific tool for potential gene therapy

- Stability by classical MD
- Fingerprint of Hoogsteen H-bonding in optical spectra

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**G4/porphyrins intercalation**

compound that stabilize G4 in DNA telomers can be potential candidates for anti-tumor drugs

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Optical properties of natural dyes

Cyanin: Natural dye in plants and fruits

Food industry, pharmaceutical, solar cell applications

what makes things look the color they have

TDDFT (PBE) gas-phase spectrum

stimulus = illuminant \times transmission \times sensitivity

Reasonable agreement of absorption peaks with experiments, but:
What about the color?

A. Calzolari, D. Varsano et al.

Current Research
Optical properties of natural dyes

Solvation effect - implicit solvent (PCM)

Explicit solvent: CP molecular dynamics

Optical effect of the solvent and intramolecular motion


Current Research
Future Research

Understanding fundamental processes in new generation photovoltaic hybrid materials by first principle techniques

Multiscale approach to optical properties of biological chromophores
Understanding fundamental processes in new generation photovoltaic hybrid materials by first principle techniques

The principal mechanism affecting the efficiency of excitonic solar cell: **Photoabsorption** of visible light by the dye and the subsequent **charge transfer** of the photoelectron to the semiconductor.

**Electronic and excitonic properties by first principle calculations of the molecule (polymer)/semiconductor interfaces**

- Nanoscale modeling of the dye(polymer)/semiconductor interfaces.
- Optical and electronic properties of the interfaces.
  *Many Body Perturbation Theory* can provide accurate quasiparticle energy levels, exciton binding energy, excitation character
- Charge dynamic of the electron-hole excitation

Future Research
Optical properties of biological chromophores in photoactive proteins

Specific interaction of the surrounding protein environment determines functionality and efficiency of the chromophores

The Peridinin-Chlorophyll-Protein (PCP) complex

a light harvesting complex that feeds energy to PSII in dinoflagellates.

Exploration of the optical properties of biological chromophores in their natural environment, by high accuracy quantum mechanical first principle methods focusing on a reliable description of the environment

- Mixed QM/MM methods: Many Body Perturbation Theory for optics and QMC for structural optimization (in collaboration with L. Guidoni, L’Aquila)
- Distinguish between geometry and external field effects: e.g. the role of the bond length alternation in the excitation of polyene chains
- Systems of interests: PCP, GFP, Rhodopsin:
Conclusion

• First-principle calculations: a powerful and predictive tool for nanoscale system characterization and interpretation and guidance of experiments

• My research combines different ab-initio methods for the study of electronic and optical properties with application in

★ Biological systems
★ Energy conversion materials
★ Molecular electronics