

## Excited-state properties calculations: Applications to biological systems

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**Summary.** — We present *ab initio* calculations of the excited-state properties of indole in water. Indole and water are first studied separately and then in solution. Calculations are performed within DFT and in the framework of many-body Green's function formalism. The geometries are determined by classical and mixed quantum-classical dynamics. The optical-absorption spectra with the inclusion of excitonic effects are calculated by solving the Bethe-Salpeter equation (BSE) after the Kohn and Sham eigenvalues have been corrected by using the GW method.

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### 1. – Introduction

Indole is the side chain of tryptophan (one of the twenty aminoacids existing in nature). It is composed by two aromatic rings. This particular chemical structure gives to indole the property to absorb and emit light in the near-ultraviolet region. Because of this peculiarity indole is largely used by biologists and biochemists as an optical probe in proteins. Its solvatochromic shift is measured in many proteins. The solvatochromic shift or solvatochromism is the shift induced on the spectral lines of a molecule by the chemical environment surrounding it. It gives important information on the conformation of the molecule in a particular chemical situation. A completely *ab initio*, free-parameter, determination of solvatochromism is thus very important for the interpretation of the experimental spectra and of the chemical features of the system. However, *ab initio* calculations of optical spectra of biological systems require sophisticated theoretical methods; they will be reviewed in the first section. Then we will present our study on the two subsystems (indole and water) and on the full system (indole in water solution).

## 2. – Methods

Density functional theory (DFT) [1] is powerful to study the ground-state properties of materials, and represents the starting point of several excited-states methods. DFT enables to treat systems of hundreds of atoms but biological systems are frequently much larger. Nevertheless, treating just small parts of the system at an accurate quantistic level, and the rest at a less-refined level, is often already sufficient to reproduce accurately the most important physical and chemical properties. Quantum-mechanics/molecular-mechanics (QM/MM) techniques [2] have been developed to manage this kind of systems and enable to separate them in two subsystems. In one of these the microscopic electronic properties are important and have great influence on the dynamics and the optical properties; therefore must be treated quantum mechanically. The second subsystem can instead be treated by a classical model where the atoms are replaced by point-charges and the interatomic interactions are modeled by harmonic forces.

Within a completely QM approach, the optical properties of materials can be accurately computed in the framework of many-body perturbation theory (MBPT). In particular MBPT can take into account the excitonic effects (namely the effect of the interaction between the electron and hole formed by the optical excitation) solving an effective two-body Hamiltonian, called excitonic Hamiltonian [3]. The excitonic Hamiltonian is not necessarily Hermitian, however in the calculations that we will present just its Hermitian part is taken into account, which in transition space is given by

$$(1) \quad H_{(vck)(v'c'k')}^{2p,exc} = (E_{ck} - E_{vk'})\delta_{vv'}\delta_{cc'}\delta_{kk'} + 2v_{vck}^{v'c'k'} - W_{vck}^{v'c'k'}.$$

Here  $E_{ck}, (E_{vk'})$  are the quasiparticle energies (calculated within the GW approximation [4]), of the states  $(ck)$  and  $(vk')$ ,  $v_{vck}^{v'c'k'}$  and  $-W_{vck}^{v'c'k'}$  are the matrix elements of the electron-hole exchange and attraction term, respectively. The macroscopic dielectric function can be expressed in terms of the eigenvalues and eigenvectors of this Hamiltonian. However its diagonalization not only can be very time consuming: in the case of large systems also the memory requirement can become prohibitive. However, methods exists<sup>(1)</sup> that allow to obtain the macroscopic dielectric function within an iterative scheme in a continued-fraction representation such as

$$(2) \quad \epsilon(\omega) = \text{Im} \left( \frac{1}{z - a_1 - \frac{b_1^2}{z - a_2 - \frac{b_2^2}{z - a_3 - \dots}}} \right).$$

The coefficients  $\{a_i, b_i\}$  are defined by repetitively applying the excitonic Hamiltonian to an initial state so that the only operation that has to be performed is a matrix-vector product, which requires the memory storage of only a matrix line at the time. The optical properties of liquid water that will be presented below are obtained using the Haydock algorithm.

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<sup>(1)</sup> This procedure is a generalisation of the Lanczos method [5] introduced by R. Haydock [6], and it has been used to compute the macroscopic dielectric function by L. X. Benedict and E. L. Shirley in ref. [7]. Nowadays the Haydock recursive method is commonly used and implemented for the solution of the BSE equation and can be generalised also to the case of non-Hermitian excitonic Hamiltonians.

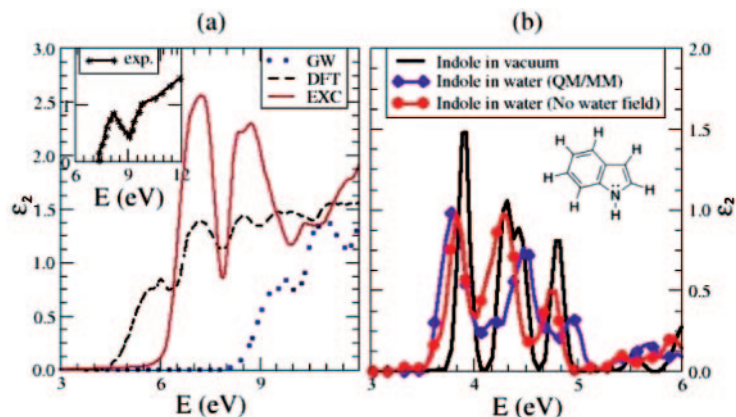


Fig. 1. – (Colour online) a) Optical absorption spectrum of liquid water calculated within DFT (dashed black line), GW approximation (dotted blue line) and by solving the Bethe-Salpeter equation (straight red line) [10]; inset: experimental optical absorption spectrum of liquid water, from ref. [9]. b) DFT IP-RPA spectrum of indole in vacuum and in water solution.

### 3. – Application to liquid water and indole

The excited state properties of “pure” liquid water are particularly important since, as a solvent, it influences many biological bio-chemical reactions. These properties have been studied in several works and are reviewed, for example, in [8].

The most recent experimental measure of the absorption spectrum of water has been performed by [9] using a synchrotron radiation light source. We calculated the optical properties of liquid water in a previous work [10] using DFT as a preliminary step and, on top of this calculations, many-body perturbation theory (MBPT); the disorder in the liquid system has been modeled by averaging the results over many classical Molecular Dynamics (MD) configurations.

The resulting DFT, GW and BSE spectra are shown in fig. 1(a), together with the experimental spectrum in the inset [9]. As expected, the BSE spectrum (red continuous line) is in better agreement with experiment.

Let us now turn to the Tryptophan (Trp) side chain (an indole ring, reported in the inset of fig. 1 (b)). This molecule is very relevant biologically, as the indole ring has been exploited as a spectroscopic tool to monitor changes in proteins and to yield information about local structure and dynamics. In fact, its spectral signatures allow it to be used as a structural probe in proteins [11].

We calculate the indole absolute value of absorbance in water solution as well as in the gas phase. 20 ps hybrid QM/MM Car-Parrinello simulations [12,2] as implemented in the Car-Parrinello code CPMD3.11.1 [13] are used for indole in water. We consider one indole molecule (QM-part) surrounded by 2000 classical water molecules. Indole in vapor phase is obtained by performing calculations for an isolated indole molecule surrounded by vacuum.

For ten snapshots of the QM/MM dynamics (one every two ps) we compute the optical spectra at the independent particle level (IP-RPA). The final spectrum is obtained by an average over the snapshots (see fig. 1 (b)). The optical gap of liquid water (7 eV [10]) is larger than the gap of the indole molecule (4.3 eV [14]). As a consequence, under 7 eV

the spectra of indole and water do not overlap. In fig. 1 (b) we report the spectra of indole in water (violet line) and in vapor phase (black line) calculated by DFT. From experimental observations we know that the most intense peak of the lower part of the optical spectrum is at 4.77 eV ( $^1L_a$ ). This peak is visible at 3.9 eV in the DFT spectrum, the discrepancy with experiment being due to the neglect of many-body effects.

Finally, we investigate the effect of solvation and solvent shift. We find, in agreement with experiments [14-16], a redshift of the optical spectrum when going from vapor phase to solution. The value of the theoretical solvent shift obtained is 0.15 eV in good agreement with the experimental value of 0.18 eV [15] (see fig. 1).

Moreover we calculate the spectrum of indole for 8 snapshots without water field (but with the geometry distorted as if water was present). The average spectrum is red-shifted of about 0.1 eV compared to the spectrum of indole in vapor phase (see fig. 1). This is a strong indication that both the geometrical and electrostatic effect induced by the solvent are equally important to obtain the correct solvatochromic shift.

In conclusion, we have studied the optical properties of liquid water and of indole in liquid water. Our results reproduce satisfactorily the redshift induced by the solvent. More accurate calculations with the inclusion of excitonic effects are needed to get a quantitative agreement with the experiments [17]. Moreover we have shown that this shift is a consequence of both the geometry distortion and of the electrostatic interaction with the solvent.

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