Ab Initio Calculation of Optical Spectra of Liquids: Many-Body Effects in the Electronic Excitations of Water

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We present *ab initio* calculations of the excited state properties of liquid water in the framework of many-body Green's function formalism. Snapshots taken from molecular dynamics simulations are used as input geometries to calculate electronic and optical spectra, and the results are averaged over the different configurations. The optical absorption spectra with the inclusion of excitonic effects are calculated by solving the Bethe-Salpeter equation. The insensitivity of screening effects to a particular configuration make these calculations feasible. The resulting spectra, which are strongly modified by many-body effects, are in good agreement with experiments.

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The electronic structure of liquid water is still not fully elucidated, even though it is essential to understand the properties of many biochemical and industrial processes that occur in solution, where it is crucial to include the role of the solvent in the reactions. Water is also essential for the survival of living organisms and for biological systems in general. For these reasons the study of the excited state properties of water is fundamental for advancement in many research fields. However, in recent years, theoretical studies of water [1–10] have mostly focused on its structure and ground state properties whereas less effort has been dedicated to its electronic structure and optical absorption spectrum. As a consequence, experimental data about excited states are poorly understood. One of the purposes of the present work is to solve these issues by carrying out *ab initio* many-body calculations of the electronic structure and optical spectra of water.

Here, we generalize the application of the many-body perturbation theory (MBPT) [11] to liquid systems, and present a calculation of the optical absorption spectrum of water from first principles, including both self-energy effects and the electron-hole interaction. We show the occurrence of important excitonic effects, which are crucial for a good description and interpretation of experimental data.

The main problem concerning the study of water relies on the fact that, in order to simulate a complex disordered system, one should use a very large unit cell, with a prohibitive computational cost. In order to avoid this, we used a smaller unit cell but exploiting several molecular dynamics (MD) snapshots of water as input geometries. Averaging the resulting electronic and optical spectra over many configurations should give a good approximation for the excited states properties of the real system. We used 20 configurations of 17 water molecules in a cubic box with 15 a.u. side and 8 special k points. This is a quite low number of molecules [10]; still, the computational effort of the many-body calculations for all the configurations would have been almost prohibitive. However, we will show in the following that one can restrict the calculation of certain ingredients, in particular, of the screening, to a single configuration. In this way the calculations become feasible with a reasonable effort. Already the results obtained for 17 molecules, averaged over several snapshots, compare well with experiments.

The water configurations have been obtained by sampling every 2 ns a 40 ns long classical MD simulation trajectory. A TIP3P water model potential [12] has been used to represent the water molecules in our simulation box. Equations of motion have been integrated numerically using a time step of 1 fs. The MD run has been done in the NVT ensemble, where thermal equilibrium at 298 K has been achieved applying a Nosé-Hoover thermostat [13]. Electrostatic interactions were treated using Particle-Mesh-Ewald; all van der Waals interactions between nonbonded atom pairs were included. Despite the small size of our system, the resulting radial distribution functions are in very good agreement with the experimental ones [14], as it is shown in Fig. 1. This confirms that we are using good input geometries for the excited state calculations.

We performed the electronic and spectroscopic calculations on three levels: we started with density functional theory (DFT) [15,16] within the local density approximation (LDA) and within the generalized gradient approximation (GGA) to obtain the Kohn-Sham (KS) eigenvalues and eigenvectors, and the DFT independent-particle absorption spectrum. As expected, it shows strong discrepancies with respect to experiment. These could not be cured by moving to time-dependent (TD) DFT, in the adiabatic local density approximation (ALDA)

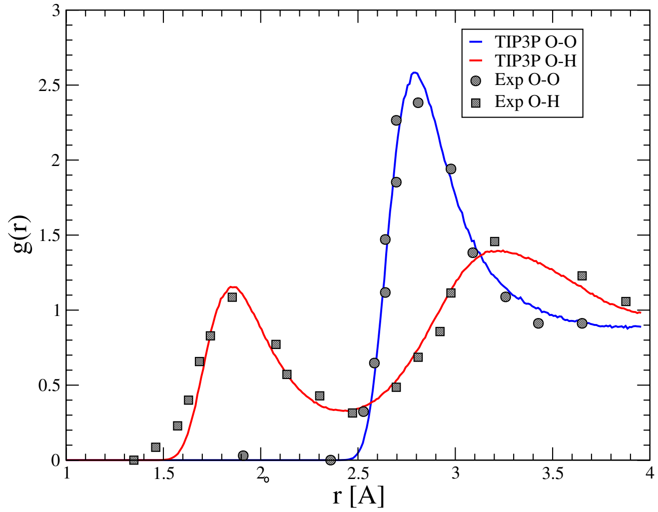

FIG. 1 (color online). Oxygen-oxygen (blue line) and oxygen-hydrogen (red line) radial distribution functions averaged over the 20 molecular dynamics snapshots compared to experimental data [14] (● and ■).

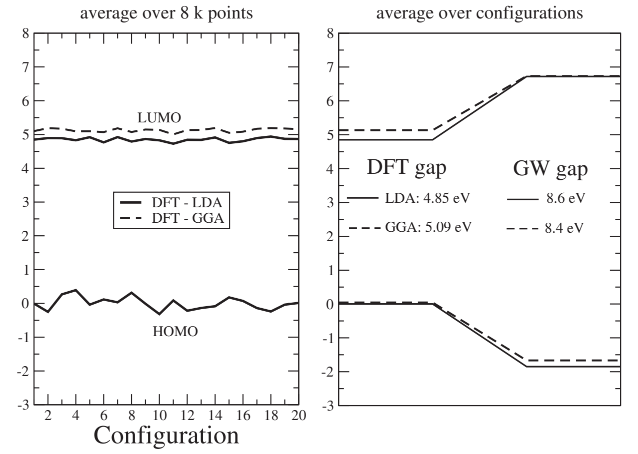

FIG. 2. Left: DFT HOMO and LUMO energies, averaged over the $8k$ points, for the 20 MD configurations. Right: schematic DFT and GW HOMO-LUMO gaps, calculated within LDA (continuous lines) and GGA (dashed lines) approximations, averaged over the 20 MD configurations.

[17]. Therefore, we corrected the Kohn-Sham energy levels using the Green's function perturbation approach, with the exchange-correlation self-energy Σ calculated within the GW approximation $\Sigma = iGW$ [11,18] (G is the one-particle Green's function and $W = \epsilon^{-1}v$ the screened Coulomb interaction). The quasiparticle (QP) energies (that is, the electronic "band structure" of water), were calculated in first order perturbation theory:

$$\varepsilon_n^{\mathrm{QP}} = \varepsilon_n^{\mathrm{DFT}} + \Delta\varepsilon_n^{\mathrm{QP}} = \varepsilon_n^{\mathrm{DFT}} + \langle n|\Sigma - V_{xc}^{\mathrm{DFT}}|n\rangle, \quad (1)$$

where V_{xc}^{DFT} is the exchange and correlation KS potential and the self-energy is evaluated at the quasiparticle energy. The optical absorption spectrum was then calculated by solving the Bethe-Salpeter equation [11], fully including local-field effects and the electron-hole interaction [19].

DFT-KS results for the electronic and spectroscopic properties of water (obtained averaging over the $8k$ points for each of the 20 configurations) are shown in Figs. 2 and 3(a). The configuration-averaged HOMO-LUMO gap (where HOMO stands for highest occupied molecular orbital and LUMO for lowest unoccupied molecular orbital) turned out to be 5.09 in GGA and 4.85 eV within LDA, in good agreement with previous DFT calculations [1] but strongly underestimating the experimental gap (8.7 ± 0.5 eV [20]), as expected in DFT. Also optical absorption spectra at the DFT independent-particle level obtained for the 20 MD snapshots and, more importantly, their average [Fig. 3(a)] do not compare in a satisfactory way with the experimental absorption spectrum [21,22] reported in the inset of Fig. 5.

We have therefore performed calculations of the optical absorption spectrum within TDDFT [17]. In principle, this represents an exact way to calculate optical spectra, but the quality of the results depends on the approximation that is used to describe exchange-correlation effects. A widely used and computationally most efficient approximation is ALDA. Unfortunately our results, shown in Fig. 4(a), show no improvement with respect to the static DFT independent-particle result. Long-range and/or dynamical effects that are missing in the ALDA kernel should hence be important for the absorption spectrum of water, and one has to resort to more elaborate (hence time-consuming) TDDFT approximations [23], or to work in a different framework. We have adopted the latter choice in this work, since many-body perturbation theory offers a well-

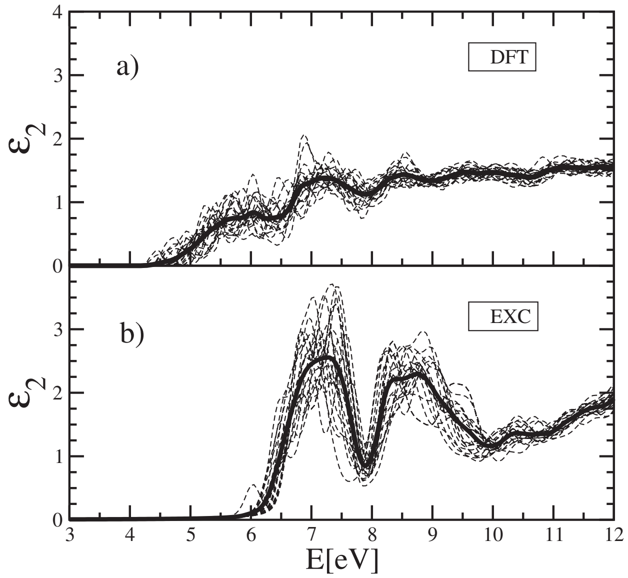

FIG. 3. Optical absorption spectra of the 20 configurations (thin lines) and their average (thick lines). (a) DFT single particle calculation; (b) with the inclusion of the electron-hole interaction.

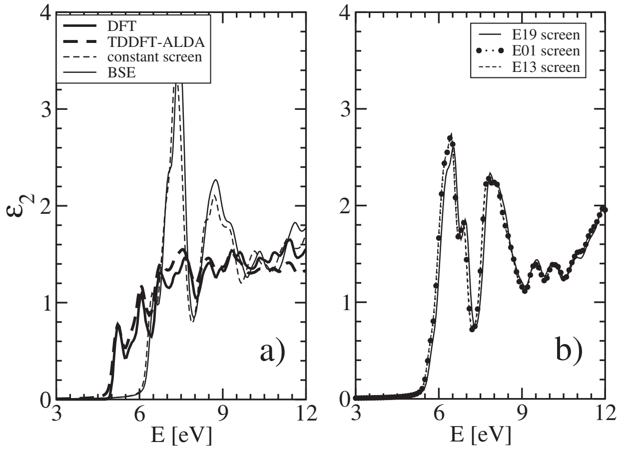

FIG. 4. Optical absorption spectrum for one MD configuration. (a) Thick lines: time-dependent DFT within the adiabatic LDA vs single particle Kohn-Sham DFT spectrum. Thin lines: BSE spectrum calculated using the full screened electron-hole interaction and using for W a constant dielectric function $\epsilon^{-1} = 1/1.7$. (b) BSE spectrum for configuration E19, calculated using its own screening, and the screening of configurations E01 and E13.

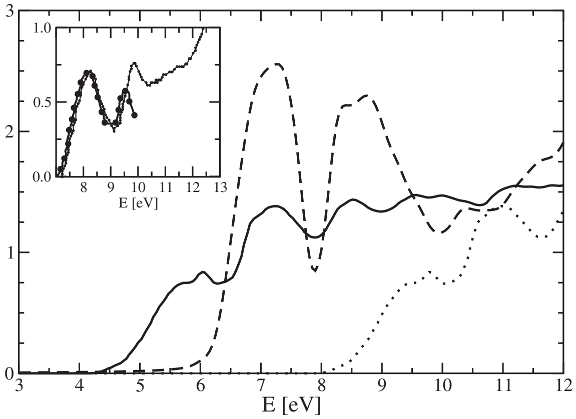

FIG. 5. Calculated optical absorption spectra averaged over 20 configurations. Solid line: single particle DFT spectrum; dotted line: spectrum obtained with the inclusion of the GW corrections; dashed line: spectrum obtained with the inclusion of the electron-hole interaction. Inset: experimental optical absorption spectrum of water (line: [21]; ●: [22]).

established way to compute and analyze optical spectra of extended systems.

In order to correct the KS electronic gap and optical spectra, one can calculate the GW corrections $\Delta\varepsilon_n^{\mathrm{QP}}$ to the KS energies. This should be done for *all* the 20 MD configurations, followed by an average. In particular, the calculation of the screened Coulomb interaction for 20 configurations constitutes a true bottleneck. Instead, one can expect that, changing the position in space of an occupied orbital also moves the region of strong screening in the same direction. Hence GW corrections $\Delta\varepsilon_n^{\mathrm{QP}}$ might be quite stable with respect to the configuration.

This is indeed the case in our calculations. In other words, the difference between DFT and GW, $\Delta GW = \varepsilon_n^{\mathrm{QP}} - \varepsilon_n^{\mathrm{DFT}}$, was practically constant going from one snapshot to another. This is explicitly shown in Table I for three different configurations. We could, hence, use the same GW corrections for all the DFT configurations.

The GW corrections increase the electronic HOMO-LUMO gap to 8.4 eV starting from GGA (8.6 eV starting from LDA) (see Fig. 2) [24], well within the experimental range [20]. (Note that a larger gap, ~9.5 eV, is obtained in hexagonal ice [25]. This gap reduction is probably due to the disordered structure of liquid water [26].) Since the calculated GW shift is almost constant for all the bands, GW optical spectra show line shapes very similar to DFT ones, but shifted to higher energies, as shown in Fig. 5. The agreement with the experimental $\epsilon_2(\omega)$ is hence not at all improved, since the relative intensities of the two absorption structures (seen in experiments at 8.3 and 9.6 eV) are still not reproduced, and their position, from being redshifted in DFT calculations (Fig. 5, solid line), are now strongly blueshifted in GW (Fig. 5, dotted line).

We have hence clear hints that it is necessary to include the electron-hole interaction to describe the optical properties of water. To this end we had to solve the Bethe-Salpeter equation, where electrons and holes interact through the screened Coulomb potential W, for all the 20 MD configurations.

Our results are shown in Fig. 3(b) for all the 20 MD configurations and in Fig. 5, where their average is reported (dashed line). Dramatic many-body effects are evident. Agreement with experiment both in energy peak positions and onset, as well as in the relative intensities of the first two peaks, is significantly improved. The main remaining discrepancy is an overall redshift that might be due to a residual error arising from the limited size of our cell, and, in particular, to the fact that our GW calculations are not self-consistent but use DFT wave functions and energies (see, for instance, Ref. [27]).

The first peak in the spectrum turns out to be a bound exciton with a binding energy of 2.4 eV and large oscillator strength. These are a consequence of the weak electronic dielectric screening of water ($\epsilon_\infty \sim 1.8$). The second peak results from an excitonic enhancement of the oscillator

TABLE I. GW corrections to the HOMO and LUMO energy levels and to the GGA electronic gap, for three different water configurations (E19, E02, E9) [24]. Energies in eV.

	DFTgap	ΔGW HOMO	ΔGW LUMO	ΔGW gap
E19	5.09	−1.67	1.61	3.28
E8	4.71	−1.64	1.60	3.24
E2	5.29	−1.70	1.60	3.30

strength of interband transitions with respect to the single quasiparticle case. The binding energy of the lower exciton, although quite large, is smaller than the value $E_b = 3.2$ eV found in hexagonal ice [25]. In fact, one can expect that the mixing of electron-hole pairs of different energy, which leads to the bound exciton, partially counterbalances the disorder effect on the quasiparticle gap [26] (namely the gap shrinking that is determined by a local increase of occupied state energies, and a local decrease of unoccupied state energies). Moreover, the higher density in the liquid phase with respect to ice (around 7%), may also play a role in reducing the exciton binding energy, by allowing a greater mobility of electrons and holes.

It is of fundamental importance to explore also to which extent a detailed calculation of each single configuration is mandatory. In fact, the effect of the electron-hole interaction does not depend significantly on details of the screened Coulomb interaction $W = \epsilon^{-1}v$ [11], but rather on macroscopic averages. Therefore, the optical spectra of the various MD configurations can be calculated using the same static screening, $\epsilon^{-1}(r, r\prime)$, obtained for any of the independent MD snapshots. This is explicitly proven in Fig. 4(b). Moreover, test calculations done using a *constant* value for ϵ^{-1} have shown that a good agreement can also be obtained using a value for $\epsilon^{-1} = 1/1.7$ (very near to the experimental macroscopic electronic value $1/1.8$) as shown in Fig. 4(a).

In conclusion, we have presented an *ab initio* many-body calculation of the electronic structure and optical properties of water obtained averaging the results of snapshots taken from molecular dynamics simulation. We have found that the *GW* corrections are almost independent of the particular snapshot considered and give an average HOMO-LUMO electronic gap of 8.4 eV, and that the effect of the electron-hole screening is the same for all the configurations. This result implies a huge reduction of the computational effort, and opens a pathway to low cost calculations on other disordered systems.

Absorption spectra calculated with the inclusion of excitonic effects show important structures related to the electron-hole interaction which are essential to obtain a good description of experimental data. The onset position and the relative intensities of the first two peaks are well reproduced *only if* the electron-hole interaction is fully taken into account.

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