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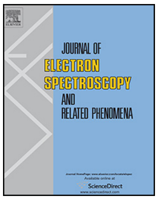

Theoretical optical spectroscopy of complex systems

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ABSTRACT

We review here some of the most reliable and efficient computational theoretical ab initio techniques for the prediction of optical and electronic spectroscopic properties and show some important applications to molecules, surfaces, and solids. We investigate the role of the solvent in the optical absorption spectrum of indole molecule. We study the excited-state properties of a photo-active minimal model molecule for the retinal of rhodopsin, responsible for vision mechanism in animals. We then show a study about spectroscopic properties of Si(1 1 1) surface. Finally we simulate a bulk system: paper, that is mainly made of cellulose, a pseudo-crystalline material representing 40% of annual biomass production in the Earth.

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1. Introduction

Ab initio computational simulations have contributed, in the last two decades, in understanding the physical behavior of molecules and solids, as witnessed by the extensive number of publications. The importance of these investigation methods was also rewarded by the scientific community by assigning the Nobel prize to Kohn in 1998, for the Density Functional Theory [1], one of the most used approach in theoretical condensed matter simulations. First principles, parameter-free simulations have reached by now a high degree of predictivity. Another great advantage of ab initio theoretical simulations with respect to phenomenological approaches is the possibility to investigate systems that have not been yet realized [2,3], or whose properties are not measurable in some particular conditions, or that are simply not experimentally achievable, but that can give important information about physical properties of real systems.

In the first section we briefly review some of the most modern techniques for the calculation of optical and excited-state properties. These techniques are based on quantum mechanics, and their high computational cost reduces their range of application to small systems of few hundred atoms. In this same section we show that this range of application can be extended to systems with hundred of thousand of atoms by a Quantum Mechanics/Molecular Mechanics (QM/MM) approach. In the second section we show a simple application to an indole molecule in water solution where the solvent is simulated with more than 1300 water molecules. Here we show all the potentialities of QM/MM approaches that enable to apply sophisticated methods based on Many-Body Perturbation Theory (MBPT) to this large system, and to understand the causes of the solvent shift of indole optical absorption spectrum. In the third section we investigate a photo-active molecule, the *tZt-penta-3,5-dieniminium* cation ($C_5H_6NH_2^+$), that is the Protonated Schiff Base Minimal Model (PSBMM) of the retinal of the rhodopsin. Beside its biological interest, our calculations allow to relate its optical properties to its geometry, with interesting possible applications to photovoltaic organic cells. In the fourth section we calculate electronic and optical properties of one of the most studied surfaces: the Si(1 1 1)2 × 1 surface. Some aspects of its reconstruction are still debated and we give a contribution to this discussion with theoretical calculation of its electronic and optical properties for the two known isomers. In the last section, finally, we study a bulk system: paper. In particular we investigate the role of oxidation in

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paper induced by aging. This is an example of how the combination of experimental and theoretical spectroscopic techniques can give information on optical, structural, and chemical properties of a complex system such as paper, and how the results provided by these combination can go beyond their pure scientific interest, and could be of interest also for the preservation of our cultural heritage.

2. Methods

Most of condensed matter simulations are performed within the Born–Oppenheimer approximation, where the total Hamiltonian is separated in an Hamiltonian for the nuclei, and one for the electrons. Ions contribution appears also in the electron Hamiltonian H through the ion-electron Coulomb interaction V_{ext}:

$$H = \sum_i -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + V_{ext}(\mathbf{r}_i) + \frac{e^2}{2}\sum_{i \neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = T + V_{ext} + V_{e-e}. \quad (1)$$

The 3 terms in Eq. (1) represent respectively the electron kinetic energy, the ion-electron interaction, and the electron–electron interaction. A direct diagonalization of this Hamiltonian is impossible even for modern computers for most of condensed matter systems. A different approach is therefore necessary. A successful method for the calculation of ground-state properties, such as for example the geometry of the material, or its total energy, makes use of Density Functional Theory (DFT). DFT is based on the Hohenberg and Kohn theorem [1], that states that the ground-state energy of an interacting-electron system is a unique functional of the electronic ground state density $n(\mathbf{r})$. As a consequence, DFT enables to focus the attention on the electronic density $n(\mathbf{r})$ rather than on the more complex many body wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The Hohenberg and Kohn theorem is valid also for non-interacting electron systems. Kohn and Sham used this fact to demonstrate that the interacting-electron problem can in principle be solved by finding the solutions of a single-particle Schroedinger-like equation [4]

$$\left[-\frac{\nabla^2_{\mathbf{r}}}{2} + V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\phi_j(\mathbf{r}) = \varepsilon_j\phi_j(\mathbf{r}). \quad (2)$$

This is the so-called Kohn–Sham (KS) equation. The exchange-correlation potential $V_{xc}(\mathbf{r})$ is a functional of the density, but its analytical expression is unknown. Many approximations (LDA, GGA, ...) [4–6] have been developed for V_{xc}. The Kohn–Sham (KS) equation allows to calculate the charge density n,

$$n(r) = \sum_j f_j|\phi_j(\mathbf{r})|^2, \quad (3)$$

where f_j are the occupation numbers, and ϕ_j are the solutions of the KS equation, and derive from it all the other ground-state quantities.

2.1. Dynamics

Dynamical processes of insulators and molecules at room temperature, can be considered with good approximation as occurring by maintaining the electrons in the ground state in all the geometrical configurations visited, since the electronic transition to excited states requires an energy of the order of some eV, that is much larger than k_BT, where k_B is the Boltzmann constant. Since DFT is conceived to calculate ground-state properties, it is particularly suited to simulate the dynamics of a condensed matter system.

In the Born–Oppenheimer (BO) molecular dynamics, the ionic degrees of freedom are propagated by Newtonian laws in which forces acting on the atoms are calculated at each iteration as the derivative of the total energy with respect to the ionic coordinates. This implies that the DFT electronic problem must be solved with conventional matrix diagonalization methods for each step of the dynamics. In contrast, in the most used Car–Parrinello method [7] the electronic degrees of freedom are explicitly introduced as (fictitious) dynamical variables. This is done by writing an extended Lagrangian for the system which leads to coupled equations of motion for both ions and electrons. In this way an explicit electronic minimization at each iteration is not needed: after an initial standard electronic minimization, the fictitious dynamics of the electrons is conceived to keep them near the BO surface for each new ionic configuration visited along the dynamics.

2.2. Excited-state properties

In order to calculate excited state properties, we used two different approaches. The first one is based on Time-Dependent Density Functional Theory (TDDFT) [8,9] that is an extension of DFT to time-dependent domain, and is conceived for example to study optical properties. TDDFT is based on the Runge and Gross theorem [8] that is the analogous of the Hohenberg and Kohn theorem of DFT. The excited states energies can be computed, in linear response regime, as the poles of the response function of the interacting-electron system (the functional derivative of the density charge with respect to the external potential) that can be calculated by a Dyson-like equation:

$$\chi = \chi_{KS} + \chi_{KS}(v + f_{xc})\chi, \quad (4)$$

where χ_{KS} is the independent particle response function calculated using KS-equation solutions, v is the Coulomb potential, and f_{xc} is the exchange and correlation kernel, that is the functional derivative of the exchange-correlation potential with respect to the density. The microscopic dielectric matrix can be easily calculated from the response function. The macroscopic dielectric function is then obtained from the microscopic one [10–13].

TDDFT is formally an exact theory, but, since the analytical form of the exchange-correlation kernel, as well as the exchange-correlation potential, is unknown, some approximations are required. Most of these approximations are local and do not describe the long range part of the exchange-correlation interaction. Therefore TDDFT usually works well for isolated systems (such as molecules, see for example [14]), and special care has to be used in its applications to infinite systems [15], where the electron–electron and electron–hole long range interaction are important. Nevertheless, with appropriate kernels, also surfaces [16] and bulk [17,18] have been recently studied.

The second approach is a combination of two quantum Many-Body Perturbation Theory (MBPT) techniques based on Green's Function Theory: the GW method [10–13], and the Bethe–Salpeter equation (BSE) [19]. The GW method enables to calculate the quasi-particle energies, that are related to the electronic band structure. The GW approximation is derived by setting the vertex in the Hedin equations [20,11] equal to a delta function. Under this condition, the time-Fourier transform of the self energy $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$, becomes a convolution of the Green's function $G(\mathbf{r}, \mathbf{r}', \omega)$ with the screened Coulomb potential $W(\mathbf{r}, \mathbf{r}', \omega)$. The electronic bands can be obtained by solving the following eigenproblem:

$$\left[-\frac{\hbar^2\nabla^2_{\mathbf{r}}}{2m} + V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r})\right]\phi_j(\mathbf{r}) + \int d^3\mathrm{r}'\,\Sigma(\mathbf{r}, \mathrm{r}', \varepsilon_j^{QP})\phi_j(\mathrm{r}') = \varepsilon_j^{QP}\phi_j(\mathbf{r}), \quad (5)$$

where ε^{QP} are the quasi-particle energies (the electronic energy levels) and, as a first approximation for ϕ_j, the Kohn–Sham eigenfunctions can be usually used [21]. The GW method provides a way

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