Calculation of Electronic Absorption Spectra with Account of Thermal Geometry Fluctuations

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Abstract. An influence of thermal fluctuations of molecule's geometry on calculated electronic-absorption Vis/Uv spectra is considered. Paper presents the quantum chemical modeling of the electronic-absorption spectra for the collection of graphene samples (44, 56, 60, 68 atoms). The calculations were performed by time dependent density functional theory (TDDFT) method in combination with molecular dynamics (MD) simulation at T=300 K. The noticeable changing of spectra relative to single point TDDFT calculation was discovered for two of four structures. We associate achieved results with perturbation of hydrogen and carbon atoms on the edges of the structures. We believe that suggested methodology will be useful in application engineering researches of novel molecules and molecular complexes.

1. Introduction

Quantum chemistry (QC) calculations is a powerful tool in basic researches and applications engineering of novel molecules and complexes. Many distinctive features in electronic structure and optical properties of graphene nanostructures were explored by first-principles or semi-emperical QC calculations. There is significant research interest on the optical properties of graphene related to highly selective adsorption spectrum and its dependences on size, shape and structure of the edges of the graphene samples.

Band gap engineering by varying structure of graphene edge has been an exciting area of research and was studied extensively [1, 2]. Strong adsorption and high oscillator strengths of electronic transitions are as well of paramount importance in such studies. Osella et al. [3] described it in respect with the optical properties of graphenenanoribbons (GNR). Denk et al. [4] studied the exciton optical response of GNRs with zigzag edge and its precursor. Chopra et al. [5] investigated small graphene samples of various form and found the highest oscillator strength for the rectangle one. Cocchi [6] denoted the growth of oscillator strength with the length of GNRs.

At the present time graphene structures attract a lot of interest for practical application; educated features were explored properly. The great interest is arisen to the research of particular engineering applications of graphene in photonics and optoelectronics. In spite of augmentation of experimental studies, method of QC is still high evaluated, though some auxiliary aspects have to be taken into account regarding practical side of investigation.

We consider an influence of thermal fluctuations on the QC calculated graphene absorption spectra. Most part of the recent QC studies are usually based on single point calculations for ground state optimized geometries [4-7]. At the same time the relation between geometrical deformations of graphene samples and their electronic properties was shown previously [7]. Thus we suppose that single-point methodology of studies is challenging for the practical aspect of graphene engineering.
In this study the methodology of ab-initio calculations of absorption spectra with account of thermal fluctuations based on combination of time dependent density functional theory (TDDFT) and molecular dynamics (MD) is presented. The set of graphene samples described in [5] was considered. We believe that suggested methodology will be advantageous in application engineering researches of novel molecules and molecular complexes and will provide better agreement between the calculated and measured spectra.

2. Methodology

It should be noted that the similar issues were discussed before [8, 9], however an account of only metastable geometries of molecules was considered. The question about an influence of thermal geometry fluctuations of graphene samples has not been systematically examined previously.

The range of considered graphene samples was taken from the study [5] by S. Chopra and L. Maidich. Primary parameters of QC calculations are the same as in [5]. The similarity of objects and parameters of calculations was kept of the verification considerations. The proposed graphene structures are also very useful for discussion of noticed hypothesis about influence of fluctuation of graphene edge on the obtained spectra. Two triangle structures, depicted on the figure 1 (b, d) produce larger contribution of edge that rectangle (a, b) samples. The highest oscillator strengths were obtained by Chopra for rectangle samples as well, moreover the question about an influence of thermal fluctuations on the strongest electronic transition is of special interest.

![Figure 1. Four considered samples of graphene (blue balls denote carbon atoms, red - hydrogen): a) C_36H_{14}; b) C_{33}H_{24}; c) C_{40}H_{16}; d) C_{46}H_{22}](image)

We considered the temperature T = 300K. Suggested method of account of thermal fluctuations is implemented by four-step workflow:

1. Obtaining of optimized geometry of a molecule;
2. Producing the set of fluctuated geometries by MD simulation;
3. QC calculations of spectrum of electronic transitions for each geometry form the set;
4. Averaging of spectrum with Boltzmann weights \( \exp\left[\frac{(U_0 - U)}{kT}\right] \) (\( k \) is a Boltzmann constant). Estimation of distribution and etc.

The workflow was implemented based on CLAVIRE program platform [10].
The optimized geometries of graphene samples were obtained by HF/6-31G(d) calculations. Energies $U_0$ and $U$ were estimated as QC total energy values and thus the details of MD simulation are not so important. It was performed by NAMD package with CHARMM22 force field [11] during 100ps with 1ps output period that is enough to avoid correlation among the states. Remarkable revelation is that we had to decrease the temperature of MD ensemble to 200K since the value of 300K provided many low probability states. The UV-visible absorption spectrum were calculated at TDDFT/B3LYP approach using 6-31G (d) basis set with 50 singlet excited states. All calculations have been performed with the Firefly package, v.8.1.1 [12].

Though we believe that this QC method is substantially preferable for molecules of carbon and hydrogen atoms [13], we note that the same workflow can be implemented with another QC approaches.

3. Results and discussion

The passivation of edges by hydrogen structure as it is depicted at the figure 1 provides good convergence of SCF procedure. We have not observed any discrepancies in rate of convergence for optimized and fluctuated geometries.

3.1.1. Rectangle samples

The calculated spectrum of electronic transitions for rectangle samples (figure 1) are depicted at the figure 2. At the upper two charts the transparency of red bars is referred to probability of the related fluctuated geometry, so the distribution is visible.

![Figure 2](image1.png)

**Figure 2.** The spectrum of electronic transitions for a) C$_{30}$H$_{14}$ and b) C$_{40}$H$_{16}$ graphene samples. The transitions for optimised geometries are depicted by black bars, the transitions for fluctuated geometries, T=300K (upper), and average spectra (lower) are depicted by red bars.

We distinguished restricted shift of spectrum and small variations of oscillator strengths due to thermal fluctuations. The intensity of strongest electronic transitions did not change considerably and look even more stable for the larger molecule.
3.1.2. Triangle samples

The different results were obtained for triangle graphene samples (figure 3). We can see the significant shift of transition energies (for the C46H22 especially) and that is more interesting – appearance of more intensive transitions during the fluctuations (however they are still lower than for the rectangle samples).

\[\text{Figure 3. The spectrum of electronic transitions for a) C}_{33}\text{H}_{24} \text{ and b) C}_{46}\text{H}_{22} \text{ graphene samples. The transitions for optimised geometries are depicted by black bars, the transitions for fluctuated geometries, T=300K (upper), and average spectra (lower) are depicted by red bars}\]

\[\text{Figure 4. LUMO for a) optimized and b) fluctuated geometries; cyan – isovalue 0.005, orange – isovalue -0.005}\]
This is in agreement with our hypothesis of fluctuation of edge atoms influence since one is considerable for triangle structures then for the rectangle. The figure 4 illustrates the altering in electronic structure (LUMO) and the localization of electron density with fluctuations can be perceived.

4. Conclusion
Two main purposes were fulfilled in the present study: to show the necessity of account of thermal fluctuation of the geometry in QC modelling and a methodology for it; to examine the stability of most intensive electronic transitions in graphene samples. Study presents high tolerance of the spectrum of rectangle graphene samples and its growth with the size of the structure. It allows to assume the stability of the optical response of large GNRs, engineering application of which is implied. On the other hand QC calculation for triangle samples demonstrates the case that the thermal fluctuations have an essential influence. This indicates the necessity in account of thermal fluctuations and supports the suggested combination of MD and QC for modeling in engineer application.

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