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Theoretical study of the low-lying electronic excited states for molecular aggregates

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We present here a brief summary of a National Natural Science Foundation Major Project entitled “Theoretical study of the low-lying electronic excited state for molecular aggregates”. The project focuses on theoretical investigation of the electronic structures and dynamic processes upon photo- and electric-excitation for molecules and aggregates. We aim to develop reliable methodology to predict the optoelectronic properties of molecular materials related to the electronic excitations and to apply in the experiments. We identify two essential scientific challenges: (i) nature of intramolecular and intermolecular electronic excited states; (ii) theoretical description of the dynamic processes of the coupled motion of electronic excitations and nucleus. We propose the following four subjects of research: (i) linear scaling time-dependent density-functional theory and its application to open shell system; (ii) computational method development of electronic excited state for molecular aggregates; (iii) theoretical investigation of the time evolution of the excited state dynamics; (iv) methods to predict the optoelectronic properties starting from electronic excited state investigation for organic materials and experimental verifications.

linear scaling TDDFT, relativistic TDDFT, excited-state dynamics theory, molecular aggregates, opto-electronic properties for organic materials, charge mobility and exciton diffusion

1 Introduction and background

There have increasing interests on the optoelectronic functional materials based on organic molecules [1–4]. The important properties of these materials are determined by the responses stimulated, upon optical or electrical excitations, through electronic excitations in molecular aggregates [5, 6], namely, through the basic physical chemistry processes including photovoltaic conversion, carrier transport, energy transfer *etc* [7–9]. Description for the excited state structure and dynamics in organic molecular aggregates constitute a major challenge for theoretical chemistry. It is essential to develop reliable theoretical methodologies to establish structure-property relationship and to eventually predict the opto-electronic property for organic materials. We identify the following three major challenges from theoretical perspectives:

1.1 Description of electronic excitation process constitutes one of the major challenges in theoretical chemistry

The basic law for microscopic world is quantum mechanics. Materials consist of large amounts of particles, obeying statistical mechanics. The basic target of theoretical chem-

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*Corresponding author (email: zgshuai@tsinghua.edu.cn) istry is to apply quantum mechanics and statistical mechanics to explain, to describe, and to predict chemical phenomena. As Paul Dirac [10] pointed out long back that: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble". As far as material design is concerned, ultimately we can simply specify chemical elements and property and enter into the computer to invent new materials without any inputs from experiments, in another word, at first-principles level. Great progresses have been made after half century as symbolized by the Nobel Prize 1998 awarded to John Pople and Walter Kohn for their developments in "computational methods in quantum chemistry" and in "density functional theory", respectively. Indeed, their ground-breaking progresses have achieved a big step forward toward the "ultimate goal", that is, designing materials with chemical elements and computers. We are still far from that. One major difficulty lies in our limited understanding and lack of method to deal with excited states. In an issue of science addressing "challenges in theoretical chemistry", six major challenges have been proposed: (a) limitations of DFT; (b) quantum dynamics of chemical reaction; (c) surface scattering; (d) modeling materials; (e) intermolecular potentials; and (f) large scale molecular dynamics simulations of self-assembling systems. As the authors claimed that the first 4 challenges are all related more or less to the excited state. For example, in DFT, the electron density is based on the ground state and the excited state is obtained through linear response theory. Due to the limitations of the exchange-correlation functional, the calculated energy gap is too small, the excited charge is too much delocalized, and the orderings of the low-lying excited states are wrong *etc* [11]. Even though great progresses have been made in understanding chemical reaction quantum dynamics, it is limited in one potential energy surface for small systems, say, four atoms. The challenge lies in either large molecule or more surfaces where non-adiabatic effects come to play [12]. Molecular scattering in a solid surface is the key process for catalysis. Great progresses have been made in modeling such process. However, for bond-breaking, when the high vibrational state is close in energy to the electronically excited state, there occurs inelastic scattering, which is beyond the reach of present-day theory [13]. In fact, even for the ground state, theory is still below the chemical accuracy. DFT is the workhorse for modeling materials. However, "predicting the behavior of molecular, soft, amorphous, or heterogeneous materials poses notable challenges" and the excited state related property is difficult to predict [14]. On word, excited state is at the core of challenges in theoretical chemistry.

1.2 Excited state is at the heart of predicting opto-electronic property of molecular materials

Upon external stimulations like electric, magnetic, thermal, optical, or mechanical, the properties in molecular materials are dictated by the electronic responses. Taking example or photovoltaic phenomena, except inorganic semiconductors which have been well described band structure theory, for either organic/polymeric materials [15] or dye-sensitized materials [16], the intra- and intermolecular electronic excited states followed by energy transfer, charge separation, charge transfer and diffusion, charge recombination and charge dissociation at interface are essential for the photovoltaic conversion. At each process, the electronic excitations are strongly coupled with the nuclear degrees of freedom, leading to a complicated electron dynamics.

Undoubtedly, silicon is the most important element for the 20th century, constituting the foundation of modern electronics and information technology. Solid state band structure theory is the basic description for the inorganic semiconductors, where electrons and/or holes move in the delocalized bands. Carbon is the most important element in Earth vital for living subjects. Like silicon, carbon atom has 4 valence electrons, namely possessing equal capability for electron donating or accepting. Carbon is the lightest element for the same valence structure. Carbon based organic materials doom to be flexible much as protein, where the functions are realized by the flexible folding. Carbon becomes naturally the most important element for the 21st century, especially with the discoveries of fullerene, nanotube, and graphene. Light element manifests stronger electron-nucleus coupling. In another word, the non-Born-Oppenheimer effect is more pronounced for organic materials. It has been shown that electronic excitations can be trapped by lattice motion resulting in localized exciton or polaron and the delocalized band structure is no more appropriate [5, 6, 9]. The coupled electron-nucleus dynamics for complex system relies on both electronic excited state theory and the chemical dynamics for large degrees of freedom, which become more and more important, and essential towards predicting property of molecular materials.

1.3 Developing predictive methodology brings about challenges and opportunity for theoretical chemistry

Energy gap engineering is essential for designing semiconductors with the advances in computational physics. For molecular materials, the concept of energy level such as frontier molecular orbitals plays similar role in designing functional materials and devices. Nevertheless, the charge, spin and exciton dynamics are closely related to the opto-electronic functions, which well distinguishes from inorganic semiconductors. First, the inter-molecular interaction is weak, often with van der Waals type bonding instead covalent. The band width is narrow and both static and dynamic disorders are severe. The narrow bandwidth is comparable with the electron correlation at the frontier orbital, the latter becoming important [17]. The motion of electron in organic and carbon materials is always strongly coupled with the nuclear degrees of freedom. In the language of solid state physics, the electron-phonon coupling is big [9]. Combining prominent disorders, electron correlation, and electron-phonon, organic solids consist of complicated system for theoretical modeling.

Targeting the excited states and their dynamics in molecular aggregates, through developing theoretical methodologies, aiming at molecular design of high performance functional materials, this project is expected to obtain original results with combining theoretical and experimental efforts.

2 Objectives and tasks

The major objective of this project is to develop theoretical methodologies for dealing with electronic excited states, both intra- and inter-molecular excitations, as well as their dynamic processes, which consist of the core challenges for modern theoretical chemistry. The focus is on the theoretical design of functional optoelectronic materials with high performance through applying the originally developed methods in close collaboration with experiments. At the same time, undertaking these challenging problems, our younger generation of theoretical chemists can get profound training for solving the difficult while important problems. The project contains the following tasks:

2.1 Low-scaling computational method for excited state of large molecules

As the size of molecule increases, the complexity of accurate computation increases exponentially, consisting of a formidable task in quantum chemistry. The current trend has been directed either through efficient low-scaling algorithm or through combining quantum mechanics with classical mechanics (QM/MM) to lower the computational efforts while keeping sufficient accuracy. Linear scaling algorithm has been progressed greatly by virtue of sparcity and locality of the density matrix. The development in multipole expansion allows efficient computation for the Coulomb interaction. Due to the locality or short-sightedness of electron correlation, the extended canonical molecular orbitals are transformed to local orbitals. With proper cutoff, the computational scaling can be reduced toward linear scaling. So far, these have been successfully implemented for ground state as well as for excited state at the level of equation of motion in coupled cluster theory. For large molecules, time-dependent DFT is the most popular approach for the low-lying excited state structure. At the real time framework with the reduced density matrix formalism, linear scaling has been demonstrated by Liang and Chen *et al.* [18]. Analytical derivatives for the excited state energy with respect to the nuclear coordinates or to the external strength field are highly desirable for geometry optimization and property evaluations. Thus, one of our tasks is to develop linear scaling TDDFT and the analytical derivatives for the excited states.

2.2 Excited states of molecular aggregate at multiscale/multilayer level

The above-mentioned approach is targeted for single molecule. For molecular aggregate, first-principles method is not yet ready to be applicable for the excited state. We propose here the following tasks: model Hamiltonian, density matrix cutoff, fragmentation, QM/MM hybridization etc. For example, by starting with excited state at a single molecule, the aggregates are treated classically as providing an electrostatic environment, and the aggregation effects on light-emitting have been accounted with success [19]. Large molecules can be divided into fragments. Molecular aggregate is naturally divided into fragment with each molecule being one. Fragment orbital approach including inter-fragment charge transfer excitation is promising for dealing with molecular aggregates with linear scaling.

2.3 Excited state electron dynamics

The opto-electronic property does not only depend on the electronic structure, but also on the electron dynamics of the excited state. As a starting point, we proposed to treat nuclear motion classically and the electron dynamics can be treated through either Ehrenfest mean-field or surface hopping dynamics as applied to either the singly charged specie or the excited states for the temporal evolution. Average over the trajectories statistically can give rise to optoelectronic property such as charge mobility or non-radiative decay rate. In order to avoid the difficulty of constructing potential energy surfaces for the ground state and the excited state, the excitation energy and its gradient as well as non-adiabatic coupling between the surfaces are going to be calculated on-the-fly in the dynamics simulation, for which fast computational approach for the electronic structure of excited state is essential. We will start with semiempirical Hamiltonian to demonstrate the principle of work.

2.4 Effective Hamiltonian approach to electron dynamics

For electron dynamics in molecular aggregate, there have been established several model Hamiltonians dealing with Frenkel exciton or charge transfer exciton, coupled with harmonic bath. The challenges lie in going beyond the perturbative treatment and the Markovian approximation. The recently proposed quantum hierarchical equations of motion approach has been shown to overcome the conventional

Redfield theory or Haken-Strobl model, promising in treating strong system-environment interaction and large degrees of freedom. Nevertheless, the computational efficiency should be further improved. In that aspect, mixed quantum-classical dynamics will lead to effective inclusion of the quantum effect of the nuclear motion, beyond either the Ehrenfest or surface hopping dynamics.

2.5 Assessment of optoelectronic properties through excited state theory

It is a long-standing dilemma for theoretical chemistry: methodology development or application to tackle essential scientific issue. We try to conciliate such situation, namely, we think that the reason for the scientific issues remain unsolved is due to lack of proper method. Developing predictive method is central to the project. The test ground for the theory is the optoelectronic properties for organic and carbon materials, which attracted much effort in China and has become one of the important research areas. We propose to apply the methodology developed here to assess the light-emitting efficiency and emission spectrum, including but not limited to narrow bang gap materials and organometallic materials. The non-adiabatic coupling is more pronounced in low band gap systems, and the spin-orbit coupling is essential for the organometallics. Theory should properly take these effects into account for the excited state dynamics. We are also interested in carrier transport phenomena in organic and carbon based materials. It concerns dynamics of electric-excitation in aggregates. The charge transport mechanism has been debated for decades and is still far from clear as to which extent the charge is trapped by nuclear motion and how dynamic disorder can affect the charge transport. In a traditional inorganic semiconductor, charge state is described by delocalized band and the transport is described by the scattering-relaxation process with phonons or impurities. In another extreme, charge is self-trapped by a single molecule and the transport is carried on from one site to another via hopping. Organic materials cover both and most of them fall between the two extreme ends.

3 Scientific issues and the proposed methodologies applicable

The essential scientific issues are summarized as following (Figure 1):

(i) the electronic structures of the low-lying excited states for both intra- and inter-molecular excitations;

(ii) electron dynamics for the low-lying excited state;

(iii) relationship between the microscopic electronic excitation and the macroscopic opto-electronic property.

We propose to tackle the scientific issues through developing original methodology in excited state theory, from linear scaling, analytical gradient, hierarchical equation, mixed quantum-classical dynamics, to the global assessment of opto-electronic properties for functional materials.

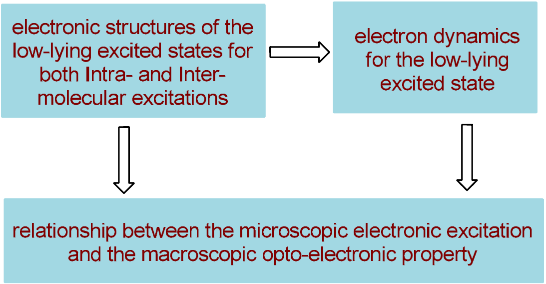

Figure 1 The essential scientific issues of the project.

First, we will try to employ density matrix truncation, localized molecular orbital, and fragment molecular orbitals, *etc* to realize low-scaling algorithm. For molecular aggregates, simplified models instead of first-principles tend to be more appropriate. For example, if the separation between molecules is large, the excitation can be regarded as a combination of excitations in single molecule and the inter-molecular interaction is through Coulomb potential. For more closely packed aggregates, for example, the π-π stacking in some organic semiconductors can reach 3.4 Å, which result in frontier molecular orbital overlap and make the charge transfer excitation stabilized in aggregate. Thus, the model should consist of both Frenkel and CT types. And it is also imperial to derive the model from first-principles.

Secondly, as far as the electron dynamics is concerned, we mostly rely on model Hamiltonian through extracting only the relevant degrees of freedom, namely, the electron-phonon couplings and exciton-phonon couplings. The dynamics is reduced to a system-bath problem. In this respect, once the system-bath couplings are strong, the usual perturbative and Markovian treatments fail. Through developing quantum hierarchical equation and the mixed quantum-classic approaches, more generally valid solutions to the carrier and exciton dynamics are expected to be available, providing an effective while efficient methodology for electron excitation problem in molecular aggregates.

Lastly, with these at hand, we are going to test for organic molecular and aggregates for the opto-electronic properties such as light-emitting efficiency and emission spectrum, carrier transport dynamics, energy transfer and exciton diffusion processes etc. This part will be carried out with experimental groups on organic and carbon materials synthesis and device fabrication for characterization to consolidate the theoretical results.

Accordingly, the tasks of the project are organized into the following four work units (WU) and Figure 2:

(i) WU1, theoretical developments on low-scaling TDDFT;

(ii) WU2, excited states for molecular aggregates;

(iii) WU3, electron dynamics for excited states;

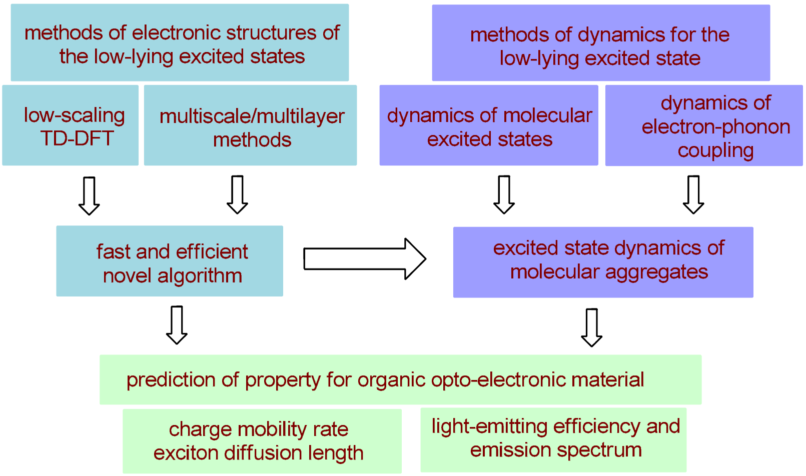

Figure 2 The main tasks of the project.

(iv) WU4, from excited states to opto-electronic property prediction.

Each of the WUs will be described in the subsequent articles, by Liu and Ma [20], Liang and Wu [21], Shi and Chen [22], and Shuai *et al*. [23].

4 Summary

To summarize, we present here an introduction to a Major Research Project from the National Natural Science Foundation. It focuses on the theoretical chemistry for the electronic excited states in molecular aggregates. This project covers four aspects, namely, (i) quantum chemical theory for excited state in a single molecule; (ii) theoretical modeling for excited state in molecular aggregates; (iii) electron dynamics for excited states in molecules and aggregate; (iv) towards predictive methodology for optoelectronic materials from excited state theory. We stress that excited state theory is at the heart of theoretical chemistry and consists of the most prominent challenge issue. It is also essential for understanding the fascinating properties of the functional materials through excited state dynamics and response. In addition, by carrying out the project, our younger generation can be well trained to meet the future challenges in theoretical chemistry.

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