

# Application of Computational Quantum Chemistry to Nanotechnological Problems

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## ABSTRACT

Computer modeling and simulation are crucial in understanding and controlling structure-property relations by explaining experimental data and by revealing critical conceptual issues about the underlying mechanisms whose resolution requires excessive experimentation. There is a great increasing demand in methodological development due to a high complexity of real-life nanotechnology systems of interest in industrial research. In such cases, multiscale modeling is a promising approach combining different levels of description addressing the coupled phenomena at specific length and time scales. Multiscale modeling is particularly important in integrated computational materials engineering since it allows one to predict material properties or system behaviour, based on the knowledge of atomistic structure and elementary processes. The most difficult part is modeling of the interaction between subsystems at different scales. We have developed several models of molecular electronics, heterogeneous nanocatalytic, and biological systems, which utilize coupled quantum-chemical, statistical-mechanical, and molecular-mechanical tools to efficiently predict their properties. In this presentation, we are giving our recent results for quantum transport in molecular electronics junctions, reactivity of zeolite nanocatalysts in heavy oil upgrading, and self-assembly and conformational stability of large biomolecular nanoarchitectures.

**Keywords:** computational chemistry, quantum chemistry

## 1 INTRODUCTION

The modern computational chemistry has wide area of application from studying of isolated molecular systems up to a solid state, electrochemistry and surface chemistry and has close contact to many areas of physics, biology and chemistry such as the quantum physics, physical chemistry, etc. Quantum chemistry (QC) plays the special role in computational chemistry and multiscale modeling in nanotechnology as it is unique level of description which provides the information about chemistry of system (or process) of interest from the first principles and does not required the external parameters. It has been developed as

separate area from part of quantum mechanics studying of properties and dynamics of electronic structure of molecular systems.

.QC provides complete information about the individual system and can be used to determine the variety of properties:

- Structure of the molecule
- Energetic (bond energies, enthalpies of formation,...)
- Spectra (electronic, vibrational, rotational, etc)
- Electrical properties (dipole moment, polarizability)
- Molecular orbitals and derived properties.
- Reaction barriers and other rate constants.
- Molecular wire transport properties.

Its combination with statistical physical methodology allows also to calculate the kinetic and environmental characteristics like reaction constants, thermodynamics. Usually more detailed level of description does not required to study process so in multiscale modeling QC is the \_nest possible level of description from few angstroms ( $\text{\AA}$ ) to several nanometers (nm). Typically due to computational difficulties the regular system treated by QC is approximately up to 150-200 atoms but modern approximation methods allow to treat the systems with thousands of atoms.

To be applied for larger systems QC description should be combined with less accurate but more applicable methodology. In such combination it describes the most interested part of the system and the rest is treated by less accurate method(s). In order to combine QC with other levels of description two problems should be solved: (i) to modify the energy expression for QM part, (ii) to connect the QM part to the rest of system to introduce the influence of the rest part of the system into QM equations. In order to understand better the ways how the QM part is interact with the rest part of the system lets briefly review the QC methods used in practical calculations.

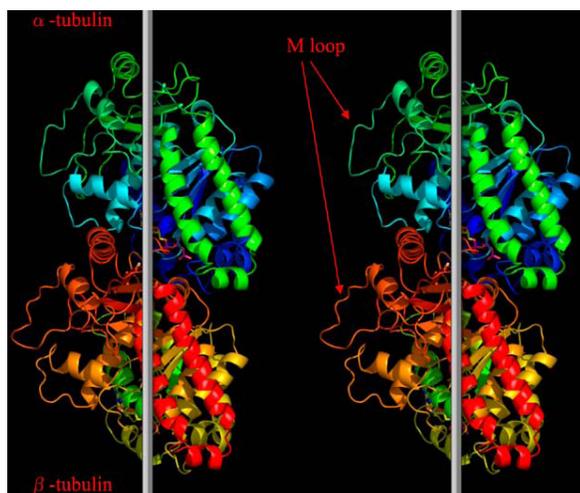
In this work we provide the several examples of combinations and application of QC to the practical problems.

## 2 MICROTUBULE BY THREE-DIMENSIONAL MOLECULAR THEORY OF SOLVATION

We study microtubular supramolecular architectures of tubulin dimers self-assembling into linear protofilaments, in turn forming a closed tube, which is an important component of the cytoskeleton.

The dynamic nature of microtubules makes them susceptible to pharmacological agents. Compounds that perturb microtubule dynamics are currently some of the most effective drugs to treat medical conditions. Tubulin-assembly modulators represent an important class of antitumor drugs, as they have been proven to be an effective tool for cancer chemotherapy. Apart from pharmacology, microtubules can be used in bionanotechnology to form nanowires (when plated with metals) and scaffolds for nanofabrication. Another potential nanotechnology application involves the molecular transport machinery of microtubules and kinesin proteins that can be integrated in kinesin-powered microdevices. This opens up new possibilities for the development of guided nanotransport mechanisms in nanodevices.

Microtubules are composed of dimers of protein tubulin. The heterodimer consists of one  $\alpha$ -tubulin and one  $\beta$ -tubulin subunit (each  $\approx 40 \text{ \AA}$  in diameter). The dimers are aligned head-to-tail in rows called protofilaments. A variable number of protofilaments form a hollow tube, that is, a microtubule. The external and internal diameters of the microtubule are  $\approx 240$  and  $150 \text{ \AA}$ ; in vitro, the length can reach up to 10–50  $\mu\text{m}$ . Polymerization is a polar process that reflects the polarity of the microtubule. Tubulin polymerizes more quickly from the plus end, which is terminated by the  $\beta$ -subunit. The other end, growing more slowly, is known as the minus end, and is terminated by the  $\alpha$ -subunit. In vivo, microtubule cylinders usually have 13 protofilaments, though the number may be different in particular situations.



**Fig. 1** Tubulin dimer and the schematic orientation of tubulin dimers in two adjacent protofilaments.

Microtubules constitute one of the most intriguing questions of modern biophysics. Although much progress has been made, there are still many unresolved issues concerning their molecular structure, architecture, and

dynamic behavior. Various aspects of the structure, dynamics, self-assembly, and stability of microtubules have been studied using theoretical and computational approaches. However, most of these studies included no atomic representation of microtubules.

In this study, we treat sets of protofilaments in the all-atom representation using a method of integral equation theory of molecular liquids and solutions, namely, the three-dimensional reference interaction site model (3D-RISM).

First, we identify the protofilament arrangements with the lowest free energy using MD to optimize tubulin conformations. We then use the three-dimensional molecular theory of solvation to obtain the hydration structure of protofilaments built of optimized tubulins and the solvent-mediated effective potential between them. The latter theoretical method, based on first principles of statistical mechanics, is capable of predicting the structure and thermodynamics of solvation of supramolecular architectures. The theory yields the solvation structure in the form of a three-dimensional distribution of normalized probability density, the three-dimensional distribution function  $g_\alpha(r)$  of solvent site  $\alpha$ , showing site density enhancement around the solute macromolecule relative to the average site number density  $\rho_\alpha$  in the solution bulk. The 3D-RISM integral equations [2] is written as

$$h_\gamma(\vec{r}) = \sum_\alpha \int d\vec{r}' c_\alpha(\vec{r} - \vec{r}') \chi_{\alpha\beta}(r')$$

where  $h_\gamma$  is the three-dimensional total correlation function of site  $\gamma$  (related to the three-dimensional distribution function  $g_\gamma = h_\gamma - I$ ),  $c_\alpha$  is the three-dimensional direct correlation function,  $\chi_{\alpha\gamma}$  is the site-site susceptibility of pure solvent. The convolution is calculated by using the three-dimensional Fast Fourier Transform technique, with special analytical treatment of the electrostatic asymptotics of all the correlation functions. The other relation between the three-dimensional total and direct correlation functions, complementing the 3D-RISM integral equation is the 3D-Kovalenko-Hirata closure approximation. For a given arrangement of the solute supramolecule immersed in multicomponent solvent, the solvation free energy is obtained from the 3D-RISM-KH integral equations (Eqs. 1 and 2) in a closed analytical form in terms of the three-dimensional correlation functions  $h$  and  $c$ . The potential of mean force (PMF) between protofilaments can then be obtained as

$$W(r_{12}, \Omega_2) = -k_B T \ln g(r_{12}, \Omega_2)$$

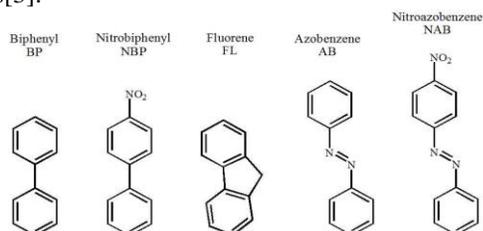
where  $r_{12}$  and  $\Omega_2$  are the position and orientation of solute molecule 2 with respect to the coordinate system fixed at solute molecule 1.

We obtained a set of profiles of the potential of mean force between protofilaments in a periodic two-dimensional sheet in aqueous solution. The profiles were calculated for a number of amino acid sequences, tubulin conformations, and spatial arrangements of protofilaments. The results

indicate that the effective interaction between protofilaments in aqueous solution depends little on the isotypes studied; however, it strongly depends on the M loop conformation of  $\beta$ -tubulin. Based on the analysis of the potential of mean force between adjacent protofilaments, we found the optimal arrangement of protofilaments, which is in good agreement with other studies. We also decomposed the potential of mean force into its energetic and entropic components, and found that both are considerable in the free-energy balance for the stabilized protofilament arrangements.

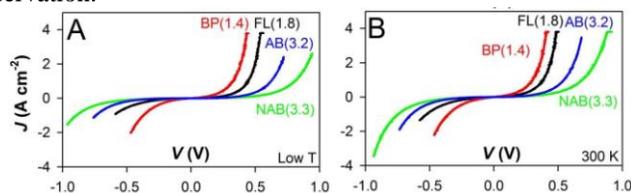
### 3 BROADENING OF MOLECULAR ENERGY LEVELS IN ENSEMBLE MOLECULAR

Here we report the electron transport characteristics of carbon/molecule/Cu molecular junctions. The experimental results shows the current/voltage behavior is independent of temperature from 5 K to  $\sim 250$  K for four different molecular structures and a wide range of molecular layer thickness[3].



**Fig. 2.** Structures and abbreviations for molecules

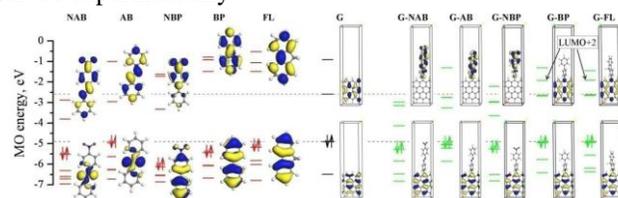
This suggests a common electron transport mechanism for all of the junctions. Perhaps most importantly, junctions with molecular layer thicknesses greater than 2 nm show similar temperature dependences to thinner junctions. Normally, efficient non-resonant tunneling cannot be maintained across such large distances. Junctions containing thicker molecular layers were tested at low temperature in order to determine the generality of this observation.



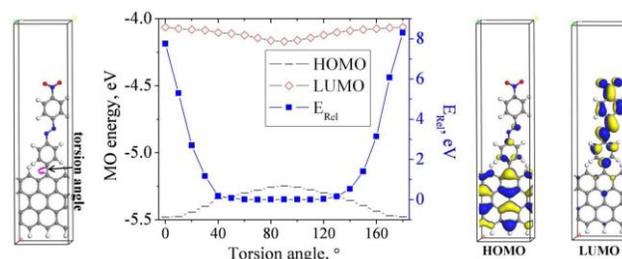
**Fig. 3**  $J$ - $V$  curves for PPF/molecule/Cu junctions (A) 9K, (B) 300K

In order to account for the observed trends, a model for charge transport is constructed based on the broadening of molecular energy levels induced from a variety of possible sources, including bonding of the molecular layer in a variety of geometric configurations and electronic coupling between the contacts and the molecular layer. Results show that if the distribution of energy levels is sufficiently broad, semi-classical resonant transport can take place. Computational models constructed using DMol3 show that

changes in the molecular energy levels occur when the aromatic molecules used to construct junctions are covalently bonded to a model carbon surface and also that the molecular orbital energy is sensitive to the particular surface bonding geometry. These theoretical predictions and experimental observations are consistent with significant broadening of molecular energy levels, and are used as a physical basis for derivation of a “resonant” charge transport model. Fitting of the experimental data to non-resonant tunneling models (i.e., the Simmons model for single-step tunneling and a tight binding model sequential tunneling) and the resonant model described in this work shows that while all must be considered, only the resonant model is consistent with the current/voltage behavior observed experimentally.



**Fig. 4** Molecular orbital (MO) energies, HOMO, and LUMO spatial distribution diagrams, molecules as well as molecules bonded covalently to the graphene surface



**Fig. 5** Dependence of the relative HOMO and LUMO energies on the torsion angle for NAB covalently bonded to the graphene surface

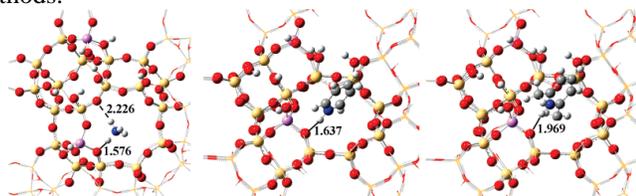
Finally, molecular junctions fabricated by covalent bonding of aromatic molecular layers to carbon electrodes show evidence of broadened molecular energy levels from experimental and computational results. This broadening could be responsible for an electron transfer mechanism that is fundamentally different from non-resonant tunneling, but can exhibit similar temperature independence and  $J$ - $V$  curve shape. The fundamental distinction between off-resonance theory and the proposed resonant model is the availability of molecular orbitals with energies equal to the Fermi energy of the contacts. The result is the apparent absence of injection barriers at  $< 10$  K, and much weaker thickness dependence than predicted by either Simmons or tight-binding models. The non-resonant models failed to predict the observed variation in  $J$ - $V$  curve shape with increasing thickness, by at least two orders of magnitude. However, a resonant model that treats the molecular energy levels as a distribution of states with a lack of any barrier for carrier injection can account for the experimental data

for two molecular layer thicknesses with reasonable accuracy. A consequence of the “broadened into resonance” mechanism is that if the amount of broadening is large enough to “wash-out” any variation in molecular energy levels (e.g., HOMO or LUMO) between two different molecules, it will be difficult to derive molecular signatures in the J-V curves directly.

#### 4 THEORETICAL MODELING OF ZEOLITE NANOPARTICLE SURFACE ACIDITY FOR HEAVY OIL UPGRADING

We performed periodic density functional theory (DFT) and quantum-mechanics/molecular mechanics (QM/MM) investigations of the surface acidity of zeolite nanoparticles derived from natural minerals that can be used for bitumen upgrading; in particular, in the process combining bitumen precracking with impurities removal that we recently reported. Bitumen molecules are large and cannot enter zeolite pores. These mainly adsorb on the outer surface of zeolite nanoparticles, which can be optimized for efficient bitumen upgrading and impurities removal. Two chabazite slab models obtained by (003) and (003h) cuts that have four and two surface OH groups per unit cell, respectively, are used for the periodic DFT modeling of nanoparticle surfaces. The first model is also treated by using the QM/MM method. Bitumen molecules are represented by probing bases such as ammonia, pyridine, and 2,6-dimethylpyridine that are commonly used for experimental acidity characterization. Analysis of the model acidity characteristics, such as deprotonation energies, aluminum substitution energies, OH stretching frequencies, and Fukui functions produces very good correlations. For the deprotonated chabazite, the electrophilic Fukui functions predict the most stable Brønsted site [6].

The three bases investigated become fully protonated upon adsorption to the chabazite Brønsted sites. The molecular orbital spatial distributions obtained by using the periodic and QM/MM methods are very similar, which indicates good correlations between the two modeling methods.



**Fig. 6.** Ammonia, pyridine, and 2,6-dimethylpyridine adsorption on the T2O1 site of a chabazite.

The values of our zeolite acidity calculations are in good agreement with experimental data and other computational studies available.

Summarize, our results suggest that: (1) The Al substitution near open zeolite surfaces does not destabilize the structure, despite the fact that Brønsted sites have not been found experimentally near open zeolite surfaces. (2) For Al substitution near open zeolite surfaces, Fukui functions predict

that surface hydroxyl groups and particularly hydroxyl nests are highly reactive regions. This suggests surface defect formation and surface reconstruction reactions. (3) Aluminum substitution near chabazite open surfaces creates stable acid sites that are accessible to bitumen fragments. (4) The most stable bulk and slab chabazite models contain Brønsted protons, in agreement with the experiment. (5) The electrophilic Fukui functions calculated for deprotonated chabazite accurately predict the most stable Brønsted proton location. This approach could be useful for prediction of metal ion locations. (6) The nucleophilic Fukui functions predict the preferred sites for an attack by a base in protonated Al-substituted chabazite. (7) Predictions from deprotonation energies, Al substitution energies, and Fukui functions correlate very well. (8) The periodic and QM/MM calculations show that base adsorption occurs through the ion-pair model. (9) The base adsorption geometries from the two methods are in good agreement.

#### 5 CONCLUSION

In this study we apply several computational chemistry methods to practical problems. In all cases the results shows good agreements with experimental data and can be used for better understanding of studying system and further to its rational design.

Innovative multiscale modeling and simulation combines methods that cover a of size scales (from the sub-atomic scales of quantum mechanics, to the atomistic level of molecular mechanics methods, to the micrometer focus of mesoscale modeling) in order to study and rationalize the design of material systems. Multiscale approach is essential, because it replaces extremely expensive and sometimes not feasible applications of the more fundamental methods in complex scientific problem solutions. The addition of complexity and functionality to the system requires application of different levels of description and, hence, bridging models between scales, from atoms to self-assembly to devices (multiple scale approach) is very essential.

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