

Report for the first year for the project NSC96-2113-M-009-022-MY3 (Theoretical Modeling of Carbon Nanostructures)

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附錄一. 請求追加人事工作費

參與計畫之人員的增長會增加研究的深度及多樣性。目前有四位博士班全薪學生以及兩位碩士班學生參與此研究計畫，並且從八月開始將會有另一名碩士班學生參與。由於原先計畫（NSC96-2113-M-009-022-MY3）中預估只會有兩位博士班學生領全薪，兩位博士班領部份薪，以及兩位碩士班學生，所以我們不得不請求國科會增加此計畫之人事費，我們希望能夠追加50萬新台幣的業務費作為學生之工作費，確保此計畫能有好的執行成效。

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The main idea of the current research project is to investigate various physical and chemical properties of carbon nanostructures. In recent years a large number of new interesting and fascinating forms of carbon-containing molecules and structures have been found. The reported structures have been mostly observed in experiment, leaving vast space for speculations regarding the mechanism of their emerging and decomposition, and also raising numerous issues about their stability and their various molecular properties. A theoretical assistance in computer-aided simulations of these carbon nanostructures is not easy since in most cases they contain a large number of atoms and at the same time require quantum treatment. Our technique, the self-consistent-charge density-functional tight-binding (SCC-DFTB) method, which has been developed for a number of years in our and our collaborators laboratories, is a perfect theoretical tool that can provide answers to multiple questions posed by experimentalists. We believe that our studies can closely assist the experimental investigation of carbon nanostructures and help to uncover the theoretical mechanisms and principles underlying their chemistry and physics.

For the first year of this project, we have been mainly working on studying the structural, spectroscopic, and physicochemical properties of various simple organic molecules upon their transition into bulk materials. This study has a number of practical purposes. First, we want to show that our technique can be successfully used for modeling both: finite molecular and solid-state extended systems. It is very important to show that both types of structures can be adequately described using the same set of Slater-Koster parameters, since in many cases it is difficult to differentiate if a given system is already a molecule or it is still a part of the surface or a bulk. Second, it is important to understand how big must be the studied system to display properties particular (or at least very similar) to those of the infinite extended crystals or amorphous

materials. Clearly, modeling infinite systems undergo many serious limitations. Therefore, it is advantageous to replace infinite or very large systems with smaller atomic ensembles that still evince the behavior characteristic for the infinite models. A number of molecular systems are studied to understand where the border between finite and infinite is located. In particular, we have been involved in simulating the following model systems: 1) transition from acetylene to infinite polyynes and cumulene chains, 2) transition from ethylene to all-*cis*- and all-*trans*-polyacetylene chains, 3) transition from ethane to all-*anti*-polyethylene chains, 4) transition from biphenyl to polyphenyl chains, 5) transition from pyrrole to polypyrrole chains, 6) transition from aniline to polyaniline chains, 7) transition from benzene through coronenes to graphene, 8) transition from cyclic alkanes to carbon nanotubes, 9) transition from methane to diamond. Our results show that the size of the studied systems can be surprisingly small in order to reveal the properties characteristic for the infinite chains, surfaces, or bulk. This is a very important finding with far-reaching implications. IR and Raman spectra of medium-size oligomers are almost identical to those obtained for infinite systems. A method of constructing density-of-states (DOS) and density-of-phonons (VDOS) plots is tested that uses the data obtained from calculations for finite oligomers. The density plots, derived from standard Brillouin zone calculations and from our extrapolations, look almost indistinguishable. This fact allows for plotting the evolution of the DOS and VDOS plots *in statu nascendi*, which can be used for various interpretations of the observed DOS and VDOS diagrams in terms of molecular orbital theory.

Another important direction of our recent investigations is the study of interactions of various nanostructures while they combine into larger, mesoscopic structures. The main purpose of such studies is to understand the energetic, dynamical, and structural changes occurring upon interaction of two stable fragments during the self-assembly process. We have studied the energy path for a C₆₀ fullerene that enters a carbon nanotube. The stabilization energy is approximately 100 kcal/mol. The largest energy change is observed when the fullerene crosses the nanotube entrance. The energy profile for the fullerene already inside the nanotube is almost flat showing that the fullerene can travel almost freely inside CNT.

The intensity of our investigations and the relative diversity of research topics stimulated dynamic growth of our research group. At present, the group consists of 4

fully-paid PhD students and 2 MS students. A new MS student will join our group starting from August. Since in our plans for the NSC96-2113-M-009-022-MY3 proposal we have estimated that the growth of the research group will be not so dynamic (only 2 full-paid PhD, 2 partially paid PhD and 1 MS students in 2008), we are presently obliged to request from NSC additional funding to cover the scholarship of the new students. We would like to request additional 500,000 NT per year to assure the salaries of the new students.

Another achievement of the first year of this project is purchasing additional nodes to our computational cluster. The additional nodes have been equipped with large working memory that can permit CASSCF calculations with large active spaces. The new nodes have been assembled and tested; information about the cluster can be accessed on-line <http://140.113.224.43>. Presently, we use the cluster for many calculations on SCC-DFTB related projects. In the future, we are planning to expand this cluster further to be able to cover all necessary computing needs of our group.

The described above research directions constitute the main stream of the research work in our group at the moment. In addition to these projects a number of other related investigations is taking place that are closer or looser connected to the main investigation topic. In particular, we try to develop a few-body carbon-carbon interaction potential that would possibly be capable of describing the many-body-like interactions in quantum systems. We are testing if the new potential can be reduced to interactions of three bodies, if the short-range interactions contribute significantly to the shape of the potential, and if the resultant potential can properly describe conjugated systems. Another very important track in our investigations is the development of the Slater-Koster files for the interactions between carbon nanostructures and various transition metals. Such types of interactions are very important to model the nucleation and growth of the nanostructures on various metal-based supports. To this end, we have performed accurate determination of potential energy surface for the ground state of manganese dimer, which will be subsequently used to determine appropriate manganese-manganese electronic and atomic SCC-DFTB parameters to be used in our carbon nanotubes growth simulations. Some of these additional calculations using various quantum chemical techniques to study interesting topics for the chemical community are described in detail below.

A. Theoretical Investigation of Molecular Properties of the First Excited State of the Phenoxy Radical

A theoretical study of molecular, electronic, and vibrational properties of the first excited state of the phenoxy radical, A^2B_2 , is presented. The calculated molecular geometries, vertical and adiabatic excitation energies, and harmonic vibrational frequencies are compared with analogous results obtained for the ground state. The calculated excitation energies correspond well to experimental data. The harmonic vibrational frequencies of the A^2B_2 and the ground state are similar except for modes involving the vibrations of the CO bond.

B. Theoretical Investigation of Molecular Properties of the First Excited State of the Thiophenoxy Radical

Accurate *ab initio* study of the lowest excited state (A^2B_2) of thiophenoxy radical is presented. The calculated equilibrium geometries, excitation energies, and harmonic vibrational frequencies show that the $A^2B_2 \leftarrow X^2B_1$ excitation in C_6H_5S has different characteristic than the analogous transition in phenoxy radical. Vertical excitation energies for other low-lying (<4.5 eV) excited states of thiophenoxy radical are also presented and compared with available experimental data.

C. Barrierless reactions between two closed-shell molecules. I. Dynamics of $F_2+CH_3SCH_3$ reaction

A detailed experimental and theoretical investigation of the first-reported barrierless reaction between two closed-shell molecules [*J. Chem. Phys.* **127**, 101101 (2007)] is presented. The translational energy and angular distributions of two product channels, $HF+CH_2SFCH_3$ and $F+CH_3SFCH_3$, determined at several collision energies, have been analyzed to reveal the dynamics of the studied reaction. Detailed analysis of the experimental and computational results supports the proposed reaction mechanism involving a short-lived $F-F-S(CH_3)_2$ intermediate, which can be formed without any activation energy. Other possible reaction mechanisms have been discriminated. The decay of the intermediate and competition between the two product channels have been discussed.

D. Theoretical study of noble-gas containing metal halides

Geometrical structures and energetic stability of noble-gas containing metal halides, $MNgX$ and $NgMX$, ($Ng = Ar, Kr, Xe$; $M = Cu, Ag, Kr$; $X = F, Cl, Br$) have been studied computationally using coupled cluster and perturbation theories. Two possible dissociation channels, (1) $M + Ng + X$, and (2) $MX + Ng$, and a reorganization reaction $MNgX \rightarrow NgMX$ have been explicitly considered. The results suggest that the argon-containing compounds are unstable or very weakly bound. For most of the krypton- and xenon-containing species, well-defined $M^{\delta+}NgX^{\delta-}$ and $NgM^{\delta+}X^{\delta-}$ equilibrium structures have been found. Large reorganization barriers for some of the $MNgX$ molecules, e.g. $AuXeF$ and $AuXeCl$, indicate their considerable thermodynamic stability. We believe that direct observation of the most stable of the $MNgX$ molecules might be possible in experiment.

E. Choosing a proper complete active space in calculations for transition metal dimers: Ground state of Mn_2 revisited

The potential energy curve of the ground state of Mn_2 has been studied using a systematic sequence of complete active spaces. Deficiencies of the routinely used active space, built from atomic $4s$ and $3d$ orbitals, has been identified and discussed. It is shown that an additional σ_g orbital, originating from the atomic virtual $4p_z$ orbitals, is essential for a proper description of static correlation in the ${}^1\Sigma_g^+$ state of Mn_2 . The calculated spectroscopic parameters of the ${}^1\Sigma_g^+$ state agree well with available experimental data. The calculated equilibrium bond lengths are located between 3.24 and 3.50 Å, the harmonic vibrational frequencies, between 44 and 72 cm^{-1} , and the dissociation energies, between 0.05 and 0.09 eV. An urgent need for an accurate gas-phase experimental study of spectroscopic constants of Mn_2 is highlighted.

F. Intruder states in multireference perturbation theory: ground state of manganese dimer

A detailed analysis of a severe intruder state problem in the multistate multireference perturbation theory (MS-MRPT) calculations on the ground state of manganese dimer is presented. An enormous number of detected intruder states (>5000) do not permit finding even an approximate shape of the $X^1\Sigma_g^+$ potential energy curve.

The intruder states are explicitly demonstrated to originate from quasidegeneracies in the zeroth-order Hamiltonian spectrum. The electronic configurations responsible for appearance of the quasidegeneracies are identified as single and double excitations from the active orbitals to the external orbitals. It is shown that the quasidegeneracy problem can be completely eliminated using shift techniques despite of its severity. The resultant curves are smooth and continuous. Unfortunately, strong dependence of the spectroscopic parameters of the $X^1\Sigma_g^+$ state on the shift parameter is observed. This finding rises serious controversies regarding validity of employing shift techniques for solving the intruder state problem in multistate multireference perturbation theory. Various alternative approaches of removing intruder states (e.g., modification of the basis set or changing the active space) are tested. None of these conventional techniques is able to fully avoid the quasidegeneracies. We believe that the MS-MRPT calculations on the three lowest A_g states of manganese dimer constitute a perfect benchmark case for studying the behavior of MRPT in extreme situations.

Publications:

1. C.W. Cheng, Y.P. Lee, and H. A. Witek, "Theoretical investigation of molecular properties of the first excited state of phenoxy radical", *J. Phys. Chem. A*, **112**, 2648 (2008)
2. Y.-J. Lu, L. Lee, J.-W. Pan, H. A. Witek, and J. J. Lin, "Barrierless reactions between two closed-shell molecules. I. Dynamics of $F_2+CH_3SCH_3$ reaction", *J. Chem. Phys.* **128**, 104317 (2008)
3. C. Camacho, S. Yamamoto, and H. A. Witek, "Choosing a proper complete active space in calculations for transition metal dimers: Ground state of Mn_2 revisited", *Phys. Chem. Chem. Phys.*, in press, DOI: 10.1039/B805125A (2008)
4. C. Camacho, S. Yamamoto, and H. A. Witek, "Intruder states in multireference perturbation theory: ground state of manganese dimer", *J. Comput. Chem.*, submitted (2008)
5. C.W. Cheng, Y.P. Lee, and H. A. Witek, "Theoretical investigation of molecular properties of the first excited state of thiophenoxy radical", *Chem. Phys. Lett*, submitted (2008)
6. C.-H. Mou and H. A. Witek, "Theoretical study of noble-gas containing halides", *J. Chem. Phys.* in revision (2008)
7. C.-P. Chou, W. Li, and H. A. Witek, "Vibrational spectra of extended systems", to be submitted to *Phys. Rev. Lett.*