WP6: Supercomputer quantum simulations

1. Main activities and results

Task 6.1: Correlated quantum dynamics of many-body systems. During the current period we conducted research on correlated quantum dynamics in atoms and molecules. Within the frames of the developed one-dimensional Monte Carlo model it was shown that the exponential scaling inherent to the many-body Schrodinger equation can be reduced to polynomial time scaling while preserving most of the essential features of the correlated quantum dynamics. To this end we employ in an unified manner the standard Copenhagen interpretation of quantum mechanics together with that introduced by de Broglie and Bohm, where sets of coupled equations for particles and waves are used. That system of equations is next interpreted as quantum Monte Carlo model with time dependence where an advanced parallel computer code was developed which uses the natural parallelism of that type of models. It has been described in [C_09] that there is a very good correspondence between the results from the Monte Carlo model and the direct numerical solution of the Schrodinger equation for helium atom. Our results also predict the distribution of Monte Carlo walkers in configuration space for para- and ortho-helium where the quantum spin effects have been introduced as a direct "exchange hole" that surrounds each walker. In practice this is done by additional screening of the electron-electron interaction.

Since the testing of the processes that occur in a rapidly ionizing atoms and molecules is critical with respect to the accuracy of the numerical methods used we can say that the results obtained so far are encouraging. The TDQMC method was next extended to two spatial dimensions and time, where we are currently working on the stability of the numerical schemes and to finding optimal regimes with respect to the joined wave-particle dynamics. The studies on this task have been done by I. Christov. During the last three months of the project a review article was prepared and submitted, and it will be published in the Proceedings of the American Institute of Physics.

Task 6.2: Hydrogen adsorption on gas-phase or supported transition metal clusters.

Since the interaction of gas-phase transition metal clusters with H_2 from the gas phase is of crucial importance for the characterization of the metal species and their application as catalysts, in the frames of the current investigation we have modeled the dissociative adsorption of up to 6 H_2 molecules on neutral and positively charged iridium tetramers in the gas phase as the charge of the metal cluster was varied from +1 to +3 e. The structures of the bare and hydrogenated species are optimized without any symmetry constrains at DFT level as the exchange-correlation functional of Becke and Perdew was applied.

With increasing the number of hydrogen ligands, coordinated to the metal cluster, the average interatomic distances in the metal moiety increases from 247±1 pm in the bare cluster (neutral or positively charged) to 268±2 pm in the species with 12 H ligands. Except for the structure of the obtained particles, other features of interest are their relative stability and electronic structure. The relative energy, ΔE, of each modeled $[Ir_4H_n]^k$ complex was estimated with respect to the energy of the corresponding bare $[Ir_4]^k$ particle and the required number of hydrogen molecules. It was found out that the relative stability of the hydrogenated species increases with increasing the hydrogen loading of the particle. The comparison between the four series of modeled clusters, $[Ir_4H_n]^k$ (k = 0-3), shows that the highly charged clusters $[Ir_4H_n]^{3+}$ are the most stable species followed by the neutral particles. The energy of dissociative adsorption of hydrogen, related to one H atom, is estimated to -76.7 and -72.6 kJ/mol for $[Ir_4H_n]^{3+}$ and the neutral Ir_4H_n particles, respectively. The adsorption energy in the case of $[Ir_4H_n]^+$ and $[Ir_4H_n]^{2+}$ clusters is by

10 kJ/mol lower (-63.4 and -65.8 kJ/mol, respectively), but still the process of hydrogen adsorption remains exothermal.

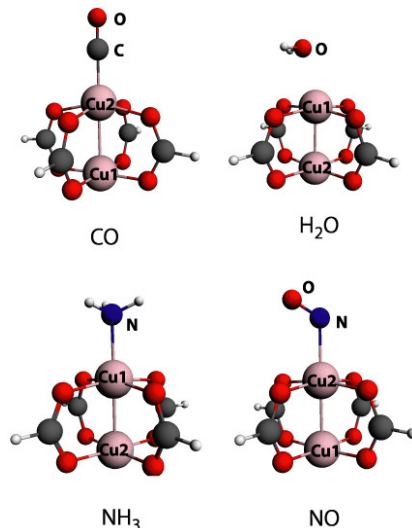The study was performed by G. Vayssilov and G. Petrova.

Fig. 1. Structures of the investigated complexes of Cu-BTC with one CO, H_2O, NO, NH_3 molecule.

Task 6.3: Interaction between metal particle and support – hydrogen transfer from and towards the support. Metal–organic frameworks (MOFs) posses large surface area and porosity, in addition their possibility chemical compound can varied, hence they are appropriate host for storage of hydrogen and other small gas molecules. Cu-BTC is porous material, which consists from binuclear complexes of Cu^{2+} and 1,3,5-benzene tricarbonyl acid, synthesized for first time by Williams.

One of the most interesting properties of this material is presence of metal centers close to the walls of the material, which are available for coordination of gas phase molecules after dehydration. We estimated the relative binding energies of one and two: H_2O, CO, NO, NH_3 molecules adsorbed on model cluster from the Cu-BTC structure. We calculated vibrational spectra of the complexes with CO. They were compared with available experimental data in order to clarify the behavior of some questionable peaks. Based on our theoretical results, one can conclude that both Cu^{2+} ions in the Cu-BTC structure are equivalent when they interact with ligands. The values of the adsorption energies of a H_2O, CO, or NO ligand (Fig. 1) are very close -0.35 – -0.40 eV, while this for the NH_3 molecule is significantly higher, -0.76 eV.

The study was performed by P. Petkov and H. Aleksandrov.

Task 6.4: Hydrogen release from hydrogen-storage materials, catalyzed by transition metals.
To be accomplished during the next stage of the project.

2. Publications on the topic of the project where project ДО 02-115/08 is acknowledged

a) published:

I. P. Christov, Polynomial-Time-Scaling Quantum Dynamics with Time-Dependent Quantum Monte Carlo, J. Phys. Chem. A 2009, 113, 6016–6021

б) accepted:

I. P. Christov, Time-Dependent Quantum Monte Carlo-principles and perspectives, American Institute of Physics Conference Proceedings.

в) submitted:

г) in preparation:

G. P. Petrova, G. N. Vayssilov, and N. Rösch, Oxidation or Reduction of Tetrahedral Iridium Clusters by Hydrogen Depending on the Cluster Charge

P. St. Petkov, G. P. Petrova, G. N. Vayssilov, and N. Rösch, Computational Model Study of Hydrogen Adsorption on Rhodium and Platinum Clusters in Gas Phase or Supported on Zeolite

3. Presentations

[1] I. P. Christov, Time-Dependent Quantum Monte Carlo-principles and perspectives, Invited talk at the CAMEL Conference in Nesebar, 24-28 June, 2009

[2] I. P. Christov, The same title, as invited plenary talk at the Light at extreme intensities Conference in Brasov, Romania, Oct.16-21, 2009

[3] G. P. Petrova, G. N. Vayssilov, N. Rösch, Density Functional Study of the Interaction of Ethene and Ethyne with Bare and Hydrogenated Ir_4 clusters, oral presentation at the 1st Workshop of the Catalysis Research Center of the TU Munich, Germany, January 2009

[4] G. N. Vayssilov, Computational Studies of Transition Metal Clusters in Zeolites and their Interaction with Hydrogen, invited talk at the 1st Workshop of the Catalysis Research Center of the TU Munich, Germany, January 2009

[5] G. Vayssilov, Computational Studies of Transition Metal Clusters in Zeolites, Invited lecture at the Jacobs University Bremen, Germany, March 2009

[6] G Vayssilov, Modeling the Interaction of Transition Metal Clusters with Hydrogen, Invited lecture at the University of Barcelona, Spain, July 2009