Quantum Force in Wigner Space

Thesis for the degree of PhD of Philosophy in Natural Science.
The thesis will be defended in English on the 28th of 2014 at
13:30 in KS101 of the chemistry building Chalmers, Göteborg

by **Li Huaqing**

Opponent: Dr. Dmitry Shalashilin
University of Leeds

This thesis is a summary of the following four papers.

I *Jens Poulsen , Huaqing Li , Gunnar Nyman* "***Classical Wigner method with an effective quantum force: Application to reaction rates***," *J. Chem. Phys. 131, 024117 (2009)*

II *Huaqing Li , Jens Poulsen , Gunnar Nyman* "***Application of the Classical Wigner Method With An Effective Quantum Force- Application to the collinear H + H2 reaction***," *J. Phys. Chem. 115, 7338 (2011)*

III *Huaqing Li , Jens Poulsen , Gunnar Nyman* "***Tunneling Dynamics Using Classical-like Trajectories with an Effective Quantum Force***," *J. Phys. Chem. Lett. 4, 3013 (2013)*

IV *Huaqing Li* "***Phase space trajectories with an effective quantum force: Application to two dimensional models***," *Manuscript*

UNIVERSITY OF GOTHENBURG

Quantum Force in Wigner Space

Li Huaqing
Department of Chemistry and molecular Biology
Göteborg University, Sweden

Abstract
In this thesis, I will present effective methods to study quantum dynamics using trajec-tories. Our methods are based on a method named the Classical Wigner model which starts with a quantum initial condition and generates trajectories which are propagated in time using a classical force. However, the Classical Wigner model can not describe the dynamical quantum effects, such as interference and dynamical tunneling, which are prominent in both gas-phase reactions and condensed matter systems. Another method under the name of 'Entangled tra- jectory molecular dynamics' (ETMD) describes the trajectories as dynamically entangled with each other and thus captures the essential quantum effects. However, the trajectories are no longer independent of each other and the expression of the force may encounter numerical problems for general applications. Thus it is challenging how one can improve the ETMD and CW to achieve independent trajectories with dynamical quantum effects, especially the tunnel- ing effects. In this thesis, I am going to unveil two such approaches.

First, we find a new parameter which can be used to symbolize the dynamical quantum effects in the CW model. An effective force is constructed from this parameter to substitute for the classical force. The new method is named Classical Wigner model with an effective quan- tum force (CWEQF) and tunneling effects are captured.

Then we also construct an effective force to present the entanglements in the ETMD method. The tunneling effects are explained for a quasi-bound potential. Then we implement the CWEQF on the collinear H + H2 reac- tion to obtain the rate constant which achieves consistently improved results as compared to the ordinary CW model. We also carried out two-dimensional reaction probability applications compared with ETMD. Although there is still room left for us to improve these methods, our methods are able to contain quantum effects in molecular dynamics and to be applied to higher dimensional applications.

Keywords: Wigner function, effective force, delocalization.

ISBN: 978-91-628-8770-4 Göteborg 2014