

Rotational symmetry adapted semi-classical theory and it's application to molecules

Hiroshi Teramoto and Kazuo Takatsuka

Department of Basic Science,

Graduate School of Arts and Sciences, The University of Tokyo,

Komaba 3-8-1, Meguro-ku, Tokyo 153-8902, Japan

teramoto@mns2.c.u-tokyo.ac.jp

日本語要約

回転対称性を持つ分子に関して、各々の回転固有状態ごとに自己相関関数を計算する方法論を半古典理論の枠組みの中で構築した。エネルギー固有値は半古典自己相関関数を Fourier 変換することにより得られる。この方法論は既存の周期軌道が必要なトレース公式によるものとは比べ、多自由度系にも適用可能である。回転対称性を考慮することは必要な半古典自己相関関数の長さが短くてすむという点と、回転定数などを通して分子の形の情報を抽出できる点という二つの点で重要である。

Abstract

We construct a methodology to calculate auto-correlation function in each rotational symmetry eigenstate, semi-classically. Eigenvalues of Hamiltonian are given by Fourier transform of this auto-correlation function. This methodology, compared to trace formula presented by Creagh and Littlejohn[1-2], can be applied to systems that have many degrees of freedom. Symmetry-adaptation is important for the following two reasons. The one is that the shorter length of the auto-correlation function is needed in order to get same resolution of energy spectrum. The other is we can get some information of molecular morphology such as rotational constants.

Introduction

Various interesting phenomena are known in cluster chemistry. The one of them is the phenomena known as the glassy dynamics, the structural transitions intermittently occur. These phenomena can be seen numerically in classical mechanical system such as Van-der-Waals clusters.

Our question is “What is the molecular shape in the corresponding quantum states of the glassy dynamics? Is the corresponding eigenstates are superposition of several molecular shape?” To answer this question, we construct a rotational symmetry adapted semi-classical theory, because some information of molecular morphology is reflected by the energy spectrum of each rotational symmetries such as rotational constant B .

We use semi-classical theory because full-quantum calculation is not possible in such multi-dimensional systems and semi-classical calculation dose not require global information of wave packet so the global topology of inner-coordinate space dose not cause problem in semi-classical calculation.

Such symmetry adaptation is also important in practical sense, as the energy spectrum of each rotational states get lined up alternately and the resolution of energy spectrum ΔE inversely relate the length of auto-correlation function T such as $T \sim 1/\Delta E$, so the shorter length of auto-correlation function is needed. This aspect is especially important in semi-classical theory that the long time calculation of auto-correlation function are in many cases difficult due to underlying chaos of classical mechanics.

In present case, the interval of energy of each rotational symmetries is an order of rotational constant $B = \hbar^2/2I$ (I is the magnitude of inertia), so this constant is smaller and smaller as the molecular size is larger and larger. On the contrary, the interval of energy of each vibrational state is an order of \hbar . So, in this case, the rotational symmetry adaptation result in the shorter length $T_{\text{symmetry adapted}} = \hbar/2I \times T_{\text{full}}$ is needed to get the same resolution of energy spectrum in case not symmetry adapted(T_{full}).

Methodology

First, using principal-axis hyperspherical coordinate, we separate each eigenstate which has different rotational symmetry. Then We assume that the solution of Schrodinger equation can be written as , and insert this into Schrodinger equation. By comparing each order of , we got equations of motion of each eigenstate which has different rotational symmetry. We calculate the auto-correlation function of and states using AFC.

Result

Using this methodology, we calculate energy spectrum of and states of three-body Ar cluster system. Figure shows we can separate energy spectrum of different rotational symmetry, or else such separation is difficult.

[1] Creagh and Littlejohn, Semiclassical trace formula in the presence of continuous symmetries, Phys. Rev. A. 44, 836(1991).

[2] Creagh and Littlejohn, Semiclassical trace formulae for systems with non-Abelian symmetries, J. Phys. A. 25, 1643(1992).

[3] Hotta and Takatsuka, Semiclassical quantization of chaos in terms of an amplitude-free quasi-correlation function, J. Phys. A, 36, 4785(2003)

Fig.1 The energy spectrum of three body atomic cluster

