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Efficient semiclassical quantization methods
— Combination of the AFC-II theory and cellularized dynamics —

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Abstract

We propose new efficient semiclassical quantization methods, which are combinations of the amplitude-free correlation function II (AFC-II) theory and cellularized dynamics. We analyze the semiclassical spectra obtained here by using the classical trajectory. In addition, we show that the AFC-II formulation can be derived by the celluarization procedure. Using this derivation, we can extend the AFC-II theory straightforwardly in order to quantize the non-zero initial momentum trajectories. We demonstrate that the extended AFC-II quantization is successful. We also discuss the effect of the interference between the different initial momentum trajectories.

本研究では、AFC-II 理論とセル化の手続きを組み合わせて効率的な半古典量子化の方法を導入する。こ
の方法で得られたスペクトルを古典トラジェクトリーに基づき解析する。さらに、AFC-II の公式はセル化
の手続きによっても導くことが可能であることを示す。この証明によって、AFC-II 理論を初期運動量を持
つトラジェクトリーにまで拡張することが可能である。また、異なる初期運動量を持つトラジェクトリー間
の干渉の効果を議論する。

§1. Introduction

It is widely recognized that calculation of highly excited vibrational states of molecules in the many degrees of freedom systems is difficult since the quantum calculation methods require very large number of basis set functions. Many semiclassical quantization methods have been proposed as efficient calculation methods. Hotta and Takatsuka [1] introduced the amplitude-free correlation function type-II (AFC-II) theory based on the concepts of the turn-back orbit and weak periodicity. They showed the successful quantization of the chaotic trajectories. Walton and Manolopolous [2] used the celullarized dynamics in order to overcome the oscillatory integrand problem in the Herman-Kluk method. This problem also emerges in the other semiclassical methods including the AFC-II. In this paper, we propose two semiclassical methods based on the AFC-II theory and cellularized dynamics. In Sec. 2, we present the cellularized AFC (CAFC) method in order to converge faster than the original AFC-II method. Section 3 gives the extended AFC (EAFC) method. We extend the AFC-II theory to the quantization of the trajectories which have non-zero initial momenta.

§2. Cellularized AFC theory

First, we cellularized the AFC-II formula. The resultant formulation can be given by

$$C^{\mathrm{CAFC}}(t) = \int dq f^{cell} |F(q_t, 0)F(q_0, 0)| \exp(\frac{i}{\hbar}S_1 + \frac{i\pi}{2}M). \tag{1}$$

This resembles the original formula except for the cellularization factor f^{cell}, which is given in more detail elsewhere.[3] We found the faster convergence compared with the AFC-II. In

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particular, the spectra of the CAFC has much smaller noise than those of the AFC-II. Note that the original AFC-II calculation converges faster than that of Walton and Manolopolous method, since the AFC-II formula includes only the configuration space integral. We performed the fast Lyapunov indicator (FLI) analysis[4] in order to characterize the trajectories used in the quantization. In the chaotic case, the semiclassical spectrum is wider than the quantum one, because the semiclassical autocorrelation function is damped faster. Figure 1(a) shows the relation of the FLI and the trajectory energy. We decompose the semiclassical spectrum to the three components which are calculated from different different trajectory energy regions, respectively. The results is given in Fig. 1(b). Although the chaotic trajectories in $0.14 \leq E \leq 0.18$, is dominant, the regular trajectories in $E \leq 0.14$, contribute to the spectrum constructively. This result is interesting from the viewpoint of quantum-classical correspondence.
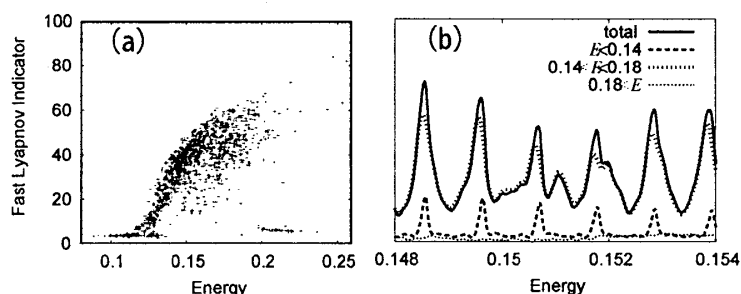
Figure 1: (a)Relation of FLI and trajectory energy. (b)Decomposition of spectrum.

§3. Extended AFC theory

While the original derivation is based on the concept of the turn-back orbit, we found that the AFC-II formulation can be derived from the cellarization procedure. Then we can extend the AFC-II theory straightforwardly in order to quantize the non-zero initial momentum trajectories. We demonstrate that the EAFC is successful in the box-type potential system and rotational motion system. We found the effect of the interference between the different initial momentum trajectories in these systems.

§4. Conclusion

In this paper, we proposed the CAFC and EAFC methods. Due to the efficiency of these methods, they can be applied to the highly excited state problems of molecules, which are related to the quantum chaos as well as chemical reactions. Thus we now attempt the semiclassical study of the NOCl molecule[5] from the viewpoint of quantum-classical correspondence.

References

[1] K. Hotta and K. Takatsuka, J. Phys. A; Math. Gen. **36** (2003), 4785.

[2] A. R. Walton and D. E. Manolopolous, Mol. Phys. **87** (1996), 961.

[3] T. Yamashita and K. Takatsuka, (in preparation).

[4] E. Shchekinova, C. Chandre, Y. Lan, and T. Uzer, J. Chem. Phys. **121** (2004), 3471.

[5] T. Yamashita and S. Kato, J. Chem. Phys. **119** (2003), 4251.