

学位論文の要約

題目 Open Quantum Dynamics Theory for Atomic and Molecular Electronic States
 (開放系量子動力学における電子状態理論)

氏名 ZHANG Yankai

Introduction

At the beginning of this chapter, we briefly introduce the open quantum dynamic (OQD) framework and its physical meaning. After that, we introduce the progress in recent years to emphasize the importance of the hierarchy equations of motion (HEOM) method in the OQD theory. Then several examples using HEOM method are simply mentioned to explain that the HEOM method can adapt to both spin and coordination space. We also introduce the failure example and the prescription in treating rotation system and angular coordinates by citing the RISB model article. With the inspiration of RISB model, we introduce the motivation of developing the HEOM method for atomic orbital (AO) and molecular orbital (MO) and the difficulties of this. Last, we state the structure of this paper to give a brief image.

Fundamental theory for open quantum dynamics

In this chapter, we introduce the fundamental theory in open quantum dynamics. We firstly introduce the total Hamiltonian structure and the typical dissipation model for open quantum dynamic: the Caldeira-Leggett model. Then we state the motivation of evaluating the reduced density operator rather than the total density operator. After that, we give the path integral result, which is non-perturbative and non-markovian. From the path integral result, we introduce the domination role of the reduced density operator in Caldeira-Leggett model: the spectral density function (SDF) and some typical examples. Lastly, we introduce the pade approximation and show the derivation of the original HEOM.

Theory: HEOM for atomic/molecular orbital

In this chapter, we firstly emphasize the importance of bath entanglement and the RISB model in rotational invariance system. After that, we introduce the 3D-RISB model Hamiltonian and then give the HEOM result for AO and MO system. We also mention some points to note, such as treating multi-electron wavefunction in AO-HEOM and the treatment of counter term in MO-HEOM, which will be used in later chapters.

Example application I: hydrogen atom

In this chapter, we apply the AO-HEOM theory into hydrogen atom system, which is the simplest example of coulomb potential and is also the fundament of quantum chemistry. In the beginning of the chapter, we review the Hamiltonian of hydrogen atom and give the result of eigenvectors. Then we use the eigenvectors to append Hamiltonian and coordinate operators into matrix form, which will be used in numerical computation. To ensure the computed result is correct, we also derive the Fermi golden rule by separate the bath in the absorption spectra equation. Beside above, because the Hamiltonian of hydrogen atom is in infinite dimensional Hilbert space, we can't take all eigenvectors into consideration, and it's necessary to prove that it's proper to truncate the basis due to some evidence such as convergency. So, in the numerical result part, we firstly give the comparison of the result using different truncated basis. Then, we vary the SDF parameters to clarify the influence of the heat bath to coulomb potential system. As the figure shows, although the partial function is divergent, the thermal effect will suppress the low frequency peak intensity, although the normalization coefficient will change, the shape of spectra is convergent when we take the larger basis. Due to this analytically accurate result, we can use the truncated basis of coulomb potential system to calculate the open quantum dynamics, which is the theoretical foundation of using AO/MO-HEOM to calculate the multiple electron system.

Example application II: helium atom

In this chapter, we give the trial demonstration using AO-HEOM framework to calculate helium atom. Different from hydrogen atom, helium has no analytical solutions due to the two-electron interaction. Although we can use quantum chemistry software to calculate the approximate energy and eigenvector, the result fits well with observed frequency gap only in low energy but already needs large basis functions set. However, with the conclusion of hydrogen's research, we can neglect the high energy state because the heat bath will suppress the peak in low frequency. We give a detailed description of the procedure using free and python-based quantum chemistry software "Psi4" to obtain the "numerical" exact eigenvalues and eigen vectors solution with CCSD and EOM-CCSD method, because helium atom just has two electrons. Also, the theory of quantum chemistry is briefly summarized in this chapter.

Example application III: hydrogen molecule and hydrogen molecule ion

In this chapter, we try to calculate the electron states of molecule in open quantum dynamics framework. Different from atom system, multiple atom molecules have additional degree of freedom because of the nuclear vibration. For past research, one treatment of nuclear vibration is to assume the model with the feature of Franck-Condon principle. Because the ground and excited state have

different coordinate at the minimum potential point, with the harmonical potential approximation, we can write the Hamiltonian with Pauli matrix in z axis to describe this property. Also in past research, attempting to add the nuclear vibration into bath vibration gave the nuclear-electron coupling band in calculated spectra. However, directly using the result of quantum chemistry result as the input of HEOM hasn't been tried before, thus we give the detailed description of the procedure using quantum chemistry software to obtain the data we need, and then calculate the effective BO SDF with the data. We calculate the absorption spectra of hydrogen molecule ion and hydrogen molecule, the form is used for giving the accurate one-electron wavefunction to check the method, and the later represent the universal molecule with multiple electrons and atoms. We check the vibration-electron coupling in the spectra, while the other direction we also apply the AO-HEOM SDF to include the thermal effect.

Conclusion

We developed the open quantum dynamics theory for atomic and molecular orbital within HEOM method. This method can include non-markovian effect and can be applied to both analytical and numerical basis. From the hydrogen atom system demonstration, we confirm the thermal effect to coulomb potential system and obtain evidence of the rationality in truncating the basis set. Then we adapt the HEOM to multiple electron atom to give a further application example with the calculation of emission spectra. Lastly, we include nuclear vibration by introducing the effective BO SDF, whose parameter is strictly calculated by quantum chemistry result and the exact SDF parameter. We also give the demonstration of absorption spectra to check the result.