STEPS Students Report

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It has been a hot topic on how to obtain the precise potential energy curves of electronic states for alkali dimers at not only bound region, but also repulsion region and dissociation limit. Among alkali dimers, it is difficult to find precisely analytical potential energy curve for electronically excited A singlet sigma state and b triplet pi state, because of the strong mixing between the vibronic states with the same rotational quantum number. However, professor Stolyarov's group has developed coupled channel deperturbation analysis within a homemade program, which is expected to be efficient in deperturbing the strong spin-orbital coupling between A state and b state in K2, so that potential curves at wide nuclear distance range can be obtained.

The method starts from ab initio calculation of the electronic structure, from which ab initio data of potential curves, spin-orbital coupling elements and transition dipole moments between the two electronic states are obtained. Ab initio potential curves and spin-orbital coupling elements are used to calculate the eigen energies and eigen functions on each quantum states. The eigen functions and transition dipole moments can be used in calculation of radiative properties, such as lifetimes, branching ratios, and Einstein coefficients for spectrum simulation. However, usually the ab initio data are not accurate enough to reproduce the experimental data. Thus, non-linear least-squares fitting procedure is needed and analytic form of potential curve such as extended morse oscillator (EMO), morse-long-range (MLR) and double exponential long-range (DELR) are implemented. By comparing the eigen energies with experimental data, parameters of the analytic function are refined until the eigen energies achieve good agreement with the experimental data.

The project on obtaining potential energy curves of A and b states in K2 has been carried on in professor Stolyarov's group. Ab initio data of potential curve and spin-orbital coupling elements have been obtained. They managed to fit the potential energy curves except the dissociation range by EMO function with 18 function parameters. However, at dissociation limit, the EMO potential dies off exponentially so that it provides a poor representation of electronic states at large nuclear distance. Therefore, another analytical form should be applied.

We decided to try DELR function because of its simplicity and flexibility. During my staying in their group, I read through and tried to understand the homemade program, which is written in Fortran, for the potential curve fitting. After that, I replaced the section implementing EMO function with that of DELR function. Besides, I integrated all the experimental data into one pool and rearranged with increasing energy, so that the fitting procedure can be separated into several steps from a group of levels at the bottom of the potential energy curve up to a group of levels at near dissociation region.

At the end of my staying, I was able to fit more than half of the experimental data with the analytical potential curve to a very good agreement. However, the further fitting procedure is not easy, more complicated analytical function should be taken into consideration.