Calculation of potential energy curves and quantum defects of the diatomic hydrides of first-row elements

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Synopsis Potential energy curves (PECs) of the hydrides of first-row elements are calculated by multi-reference configuration interaction method (MRCI).

To calculate the photoabsorption and photoionization spectra of molecules, one needs to know the potential energy surfaces of the dipole-allowed states. In particular, the potential energy surfaces of the Rydberg states are the basic input for calculating the photoionization by multichannel quantum defect theory (MQDT) [1,2]. Modern electronic structure theory is believed to be able to calculate the potential energy surfaces for the excited states, including Rydberg states, with chemical accuracy. The multi-reference configuration-interaction (MRCI) method, complete active space second-order perturbation (CASPT2) method, equation of motion coupled-cluster singles and doubles (EOM-CCSD) method, and time-dependent density functional theory can be used to obtain the potential energy surfaces for excited states. Among these methods, MRCI is known to always yield reliable potentials and thus was chosen for this study. Comparison of MRCI PECs of H_2 with the highly accurate potentials of Kolos, Wolniewicz, and their collaborators reveals that the use of appropriate basis functions for the Rydberg states is essential. With Kaufmann's Rydberg basis functions [3], accuracy within an accuracy of 1×10^{-4} hartree is obtained.

We are now applying this method to the calculations of PECs of the hydrides of first-row elements. Some of the preliminary calculational results are shown in Figs. 2 and 3 for the PECS of BH and CH radicals which are already obtained in Refs. [4] and [5]. We hope to finish this project until the meeting.

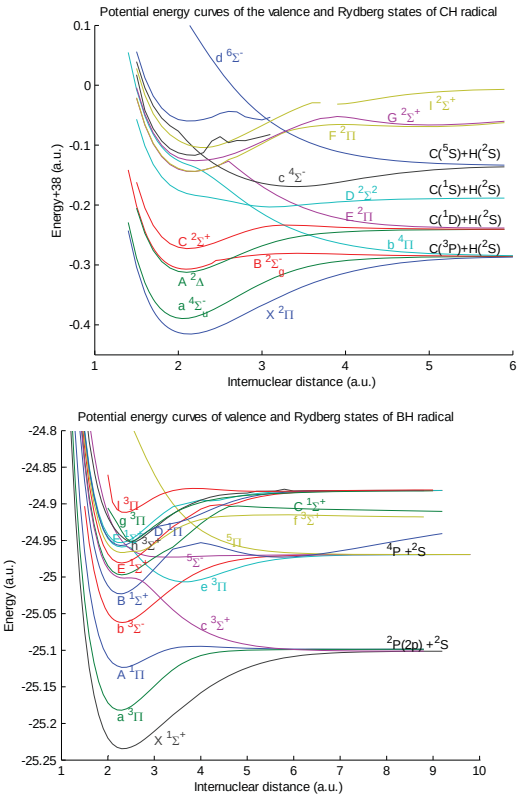

Figure 1. Potential energy curves of valence and Rydberg states of CH and BH radicals.

References

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