Correlations of Rydberg orbitals of diatomic molecules

Journal of Physics: Conference Series **635** (2015) 112097 doi:10.1088/1742-6596/635/11/112097

CORRELATIONS OF RYDBERG ORBITALS OF DIATOMIC MOLECULES

Hyun-Jin Kim[1] and Chun-Woo Lee[2,*]

[1]Department of Energy Systems Research, Ajou University, Suwon, 443-749, Korea

[2]Department of Chemistry, Ajou University, 206 Worldcup-ro, Yeongtong-Gu, Suwon, 443-749, Korea

Synopsis Calculations of the potential energy curves of diatomic molecules are performed for the entire range of internuclear separation in order to correlate Rydberg orbitals at the united atom and separated atoms which are needed to properly assign highly excited Rydberg states.

The assignment of highly excited Rydberg states is difficult because of the absence of the knowledge on the behaviors of potential energy curves (PECs) at small internuclear separation R for most of cases whereby the correlation between the united atom (UA) limit and separated atoms (SA) limit cannot be given. We performed all electron multi-reference configuration interaction calculations of PECs for H_2, He_2, Li_2 [1], HeH, LiH [2], BeH and BH to obtain the correlation diagrams between Rydberg orbitals at both limits.

Calculations show that the behaviors of quantum defect curves (QDCs) are dominated by electrons in Rydberg orbitals in contrast to those of PECs which are dominated by core electrons (see Fig. 1), indicating that QDCs are suitable for the study of correlations between Rydberg orbitals at the UA and SA limits. Note that usual UA and SA designations of Rydberg orbitals are derived from the studies of one-electron molecular systems and cannot be used for many-electron molecular systems. There may be several reasons for this failure. One of the reasons comes from the strong influence of core electrons in the neighborhood of united atoms. Their influence can be ignored in the Franck-Condon region so that groupings of Rydberg states into series akin to that of the molecular ion are attained. There is another reason coming from the incompatibility between Rydberg orbitals at both limits which causes distortion to the behaviors of Rydberg series. Diversities in the correlation patterns are observed for different molecules.

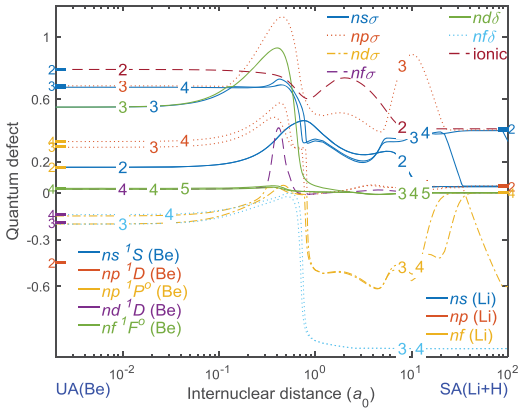

Figure 1. Correlations of Rydberg orbitals of a LiH molecule at the united atoms and separated atoms.

References

[1] H-J Kim and C-W Lee 2015 *J. Phys. B* **48** 015101

[2] Y Gim and C-W Lee 2014 *J. Chem. Phys.* **141** 144313

* E-mail: clee@ajou.ac.kr