

Contour of full potential energy curves of molecular hydrogen ($N \leq 3$)

Xian-Fang Yue^{‡*1}, Xiang Gao^{*2}, and Jia-Ming Li^{†§†3}

[‡] Department of Physics and Information Engineering, Jining University, Qufu 273155, China

^{*} Beijing Computational Science Research Center, Beijing 100193, China

[†] Key Laboratory for Laser Plasmas (Ministry of Education) and Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China

[§] Department of Physics and Center for Atomic and Molecular Nanosciences, Tsinghua University, Beijing 100084, China

[†] Collaborative Innovation Center of Quantum Matter, Beijing 100084, China

Synopsis We present the full potential energy curves of molecular hydrogen ($N \leq 3$). A new basis set of hydrogen atom is constructed, which can successfully describe the characters of the molecular hydrogen (H_2) in large scale of $0 \leq R_{H-H} \leq 120$ Bohr. The spectroscopy orbitals determined by the key physical states for the H_2 are used in calculations of the full potential energy curves. These results are very useful for studies on spectroscopy, photoionization and photodissociation of the H_2 .

Molecular hydrogen of H_2 is the simplest diatomic molecule and also a benchmark molecule to study the spectroscopy, photoionization, photodissociation, and so on. Many astronomical, physical and chemical researchers had paid much attention to this molecule system and carried out both the experimental and theoretical studies. In theoretical aspects, the potential energy curves (PECs) of molecules are the basis of studies in the collisions, spectroscopy, photoionization, photodissociation, etc [1-4]. Sharp [1] had summarized some early PECs of the H_2 . However, most of previous calculations on PECs of the H_2 are focused on the ground and singly excited states. As for the highly or doubly excited state PECs, there are few studies had been reported, which may be because it is a rather difficult and challenge work for the calculations.

By optimizing the lower energy of the hydrogen atom (H), we construct a new basis set of the H. This basis set can successfully describe the characters of the H_2 in large scale of $0 \leq R_{H-H} \leq 120$ Bohr for $N \leq 3$. In our calculations, there are roughly divided into three districts. In large scale ($R_{H-H} \geq 7$ Bohr), the wave function of the hydrogen molecular orbital can only be constituted of the basis set of the hydrogen atom. With decrease of the H_2 distance (in the medium distance), the problem of redundant appears.

This problem can be solved by reduce some basis set of the hydrogen atom, and put a dummy atom in the center of the H_2 . The basis set of the dummy atom is the same with that of the helium atom. It can be understand because the two hydrogen atoms become one helium atom when the distance of the H_2 is approach zero. Adding some basis set of the dummy atom instead of that of the hydrogen atom, the redundant problem disappears. In the small scale ($R_{H-H} \leq 0.1$ Bohr), the wave function of the H_2 is only constructed by the basis set of the dummy atom.

Based on the above method, we obtained the spectroscopy orbitals by optimizing the main physical states. Then, we carried out the Configuration Interaction (CI) calculations on the full PECs of H_2 .

The quantum defects of the spectroscopic orbitals should have channel properties according to the quantum defect theory. To achieve this, the quantum defects of these orbitals are extracted from the calculations and are used as an important criterion for the convergence.

References

- [1] T. E. Sharp 1971 *Atomic Data* **2** 119
- [2] J. M. Ajello et al 1995 *Phys. Rev. Lett.* **75** 3261
- [3] M. Glass-Maujean, 1986 *J. Chem. Phys.* **85** 4830
- [4] G. Staszewska et al 2002 *J. Mol. Spectr.* **212** 208

E-mail: xfyuejnu@163.com

² E-mail: xgao@csrc.ac.cn

³ E-mail: jmli@tsinghua.edu.cn