

Potential Energy Curves and Generalized Oscillator Strength for Doubly Excited States of the Hydrogen Molecule

L. O. Santos^{†1}, R. F. Nascimento*, A. B. Rocha[‡], N. V. de Castro Faria[†], Ginette Jalbert[†]

[†]Instituto de Física, Universidade Federal do Rio de Janeiro, Cx. Postal 68528, Rio de Janeiro, 21941-972, RJ, Brazil

*Centro Federal de Educação Tecnológica Celso Suckow da Fonseca - 25620-003, Petrópolis, Brazil

[‡]Instituto de Química, Universidade Federal do Rio de Janeiro, Cx. Postal 68528, Rio de Janeiro, 21941-972, RJ, Brazil

Synopsis In this work we report calculations of potential energy curves in the $1.2a.u. \leq R \leq 100a.u.$ range at the Multireference Configuration Interaction (MRCI) level for doubly excited states of the H_2 molecule. The molecular state which dissociates into two $H(2s)$ atoms is clearly identified. The Generalized Oscillator Strength as a function of transferred momentum for three doubly excited states is also presented.

Recently, our experimental group [1] observed the pair $H(2s) + H(2s)$, measuring the neutral fragments in coincidence after the dissociation of H_2 induced by electron impact, confirming thus the existence of such dissociation channel. The purpose of the present work is to shed light on the description of the doubly excited states that may dissociate onto a pair $H(2s) + H(2s)$. In order to do that, we have used an approach that mixes the standard CI method with MCSCF, known as MRCI [2] and implemented a Huzinaga basis-set (which consists of cartesian gaussian-type [12s, 6p, 3d, 1f]/[9s, 6p, 3d, 1f] and provides a total of 110 molecular orbitals: $29\sigma_g$, $29\sigma_u$, $22\pi_g$, $22\pi_u$, 4δ and 4ϕ) in the treatment of two-electron diatomic molecules allowing us to rise accurate potential curves at every internuclear distance. We have used an active space composed of 12 molecular orbitals, $n\sigma_g$ ($n = 1-3$), $n\sigma_u$ ($n = 1-3$), $n\pi_g$ ($n = 1-2$), $n\pi_u$ ($n = 1-2$) which comprise the main configurations of the electronic states from the Franck-Condon to the dissociative region. The main feature of our calculations is to provide for the first time an unambiguous characterization of the electronic state that goes, in the dissociation limit, to $H(2s) + H(2s)$ fragments.

The Generalized Oscillator Strength (GOS) for some doubly excited states, in the vertical approximation, has been calculated as a function of the momentum transfer within Gauss-Hermite quadrature to the electronic coordinates integrals. The electronic states have been obtained as previously mentioned, i.e., with the MRCI approach. One should note that our tech-

nique takes into account highly correlated wavefunctions, allowing us to calculate transition matrices between ground and doubly excited states even in the first Born approximation approach.

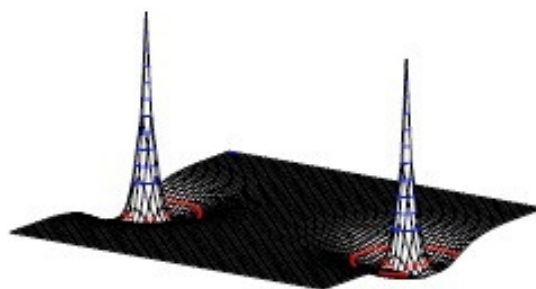


Figure 1. Electronic amplitude calculated at $R=80$ a.u. for the $1\Sigma_g^+$ doubly excited state.

In Fig. 1, the electronic amplitude calculated for the doubly excited state $1\Sigma_g^+$ at a internuclear distance $R=80$ a.u.. It is clear from this picture that, on the separated atoms regime, both atomic orbitals present one node which is characteristic of a 2s atomic orbital.

References

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¹E-mail: leonardosantos@if.ufrj.br

