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Electron pair density in the lowest $^1\Sigma_u^+$ and $^1\Sigma_g^+$ states of H_2

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We demonstrate and advocate the use of observable quantities derived from the two-electron reduced density matrix – pair densities, conditional densities, and exchange-correlation holes – as signatures of the type of electron correlation in a chemical bond. The prototype cases of the lowest $^1\Sigma_u^+$ and $^1\Sigma_g^+$ states of H_2 , which exhibit large variation in types of bonding, ranging from strongly ionic to covalent, are discussed. Both the excited $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states have been interpreted as essentially consisting of (natural) orbital configurations with an inner electron in a contracted $1s\sigma_g$ orbital and an outer electron in a diffuse (united atom type, Rydberg) orbital. We show that nevertheless totally different correlation behavior is encountered in various states when comparing them at a common internuclear distance. Also when following one state along the internuclear distance coordinate, strong variation in correlation behavior is observed, as expected. Switches between ionic to covalent character of a state occur till very large distances (40 bohrs for states approaching the $1s3\ell$ asymptotic limit, and 282 bohrs for states approaching the $1s4\ell$ limit). © 2011 American Institute of Physics. [doi:10.1063/1.3624571]

I. INTRODUCTION

The H_2 molecule is a prototype system for the study of electron correlation effects on chemical bonding.^{1–5} This holds true for both the ground state and the excited states. Attempts to develop wave functions for the ground state and the first excited $^1\Sigma_u^+$ state of the H_2 molecule were made in the early days of quantum mechanics.^{6–8} Nowadays, accurate wave functions for various states of H_2 are known.^{9–31} The energy levels from such calculations are invaluable for the analysis of spectral data.^{32,33} At long distances, the excited states may dissociate to ionic fragments, H^+H^- , and recently experimental observations have been reported on the Rydberg states of the heavy “Bohr atom,”^{34,35} where the composite particle H^- is considered as a heavy “electron” in the proton field of H^+ .

The correlation effects in the ground state ($X^1\Sigma_g^+$) are well known and serve as the paradigm of left-right correlation, in particular at stretched bond lengths. Experiments exploring the correlation between the two electrons in the ground state of H_2 , as a function of the instantaneous internuclear distance (in the Born-Oppenheimer approximation), have been realized.² They demonstrate the strong dependence of the correlation on the internuclear distance even in this simple state. The excited states show much more intricate electron correlation phenomena. Considerable analysis of the electronic correlation of several excited states has been performed.^{13,29,30,36–39} A problem with most analyses based on some expansion of the wave function (e.g., in “ionic” and

“covalent” states) is the nonuniqueness of such expansions, a problem that is often aggravated by nonorthogonality of the chosen basis states. It is clearly advantageous to use quantities which are observables, that can in principle be measured and are at least uniquely defined. This is of course the case for the pair density and for related quantities such as the intracule and extracule densities or the relaxation holes, which are averages over pair-density related quantities and offer already considerable insight.^{40,41} Ideally of course the different analyses should lead to the same conclusion. It is a recurring problem that the concepts in chemistry (and “ionic” and “covalent” characters are no exception) appear evident at first sight, but prove to be very hard to define in terms of measurable quantities. Disagreements then run the risk of being just a question of semantics. No such risk exists with observables. The only issue is then whether the wave functions used to evaluate them are accurate enough.

The expectation value of the interelectronic distance as a function of internuclear distance is a useful observable, and counterintuitive effects on this quantity have been noted and interpreted in terms of the varying balance between ionic and covalent configurations for some of the excited states of H_2 .^{38–40} The expectation value of the interelectronic distance has the disadvantage that it is a global property. It shows no position dependence. In the present paper, we will focus on the pair density, the probability of finding two electrons simultaneously at positions \mathbf{r}_1 and \mathbf{r}_2 , and derived quantities. This introduces explicit dependence on the positions. The simple H_2 system is ideal for our purpose. The system is simple enough that very accurate calculations on the excited states can be done.^{9–31} There is a large variety of bonding situations in the excited states. We

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