The Electron-pair Density Distribution of the $^{1,3}\Pi_u$ Excited States of H_2

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Abstract

The non-monotonic bahavior of the electron repulsion energy and the interelectronic distance, as a function of the internuclear separation, in the $^3\Pi_u$ excited state of the hydrogen molecule has been assessed by explicitly calculation and analysis of the electron-pair density distribution functions from high level ab initio Full Configuration Interaction wave functions, for both the $^3\Pi_u$ and the $^1\Pi_u$ states. Additionally, the Hund's rule as applied to these two states has been accounted for in terms of simple electronic shielding effects induced by wave function antisymmetrization.

1 Introduction

Electron-pair densities describe the relative motion of any two electrons of the system and were first introduced by Coulson et al. to gain insight into the physical consequences of electron correlation [1, 2, 3]. Nowadays, however, interest on electron-pair densities stems from their usage to develop faster and more accurate computational methods within both, the molecular orbitals theory [4] and the density functional theory frameworks [5]. Additionally, electron-pair densities have recently been used to unveil the distinctive features of the two-electron density in different types of chemical bonds [6, 7, 8, 9, 10].

Electron-pair densities do also reveal, even for electronic ground states [11, 12, 13], a number of features of the quantum correlations between electrons that are challenging to predict at a first sight for, in many cases, they are counterintuitive. Excited states, as expected, exhibit such counterintuitive effects

more commonly. Thus, the double-well first and second excited states of $^1\Sigma_g^+$ symmetry, known respectively as the EF and GK excited states, of the hydrogen molecule show an intriguing non-monotonic behavior of the mean electron-electron distance with respect to increasing the internuclear distance. Indeed, at sharp variance with the ground state [14], the mean electron-electron distance decreases as the internuclear distance increases in the transition from the E to the F minima [15], and in the transition from the G to the K minima [16], respectively.

In this vein, Tal and Katriel [17] and Colbourn [18] reported the (counterintuitive) non-monotonic behavior of the electron repulsion energy in the $^3\Pi_u$ excited state of H_2. Indeed, based on their (crude) Hartree-Fock (HF) calculations, with a small basis set consisting of four uncontracted sp primitives, they found that an increase of the internuclear distance carries an increase of the electron repulsion energy and a concomitant decrease of the mean interelectronic distance, in the domain of the short internuclear distances. This remarkable counterintuitive feature is not seen in the parent, as arising from the same $1\sigma^1 1\pi_u^1$ configuration, $^1\Pi_u$ excited state. For this state, the electron repulsion energy decreases monotonically as the internuclear separation increases, in the whole range of internuclear separations, in accordance with common (classical) intuition. One is naturally prone to attribute this unexpected counterintuitive behavior of the triplet state to the expected failure of HF method for states like these ones which bear substantial multiconfigurational character, in spite of Tal and Katriel hypothesis:"...*the non-monotonic trend is real rather than a Hartree-Fock artifact*".

In this paper, electron-pair densities obtained from high-level ab initio Full Configuration Interaction calculations will be used to examine these issues and to put into proper perspective earlier preliminary calculations [19], demonstrating that the Tal and Katriel hypothesis is true.

2   Calculations

The radial electron-pair density distribution, $h(u)$, of an electronic state $\mid \Psi \rangle$, is:

$$h(u) = u^2 \int I(\mathbf{u}) \, d\Omega_{\mathbf{u}} \tag{1}$$

where, $I(\mathbf{u})$, the so–called [20] intracule density,

$$I(\mathbf{u}) = \langle \Psi \mid \sum_{i>j} \delta(\mathbf{u} - \mathbf{r}_i + \mathbf{r}_j) \mid \Psi \rangle \tag{2}$$

stands for the probability density of the coordinates $\mathbf{u} - \mathbf{r}_i$, $\mathbf{r}_j$ of any two electrons to be separated by the vector $\mathbf{u}$. $\Omega_{\mathbf{u}}$, in Eq. (1), stands for the solid angle subtended the interelectronic vector $\mathbf{u}$.

Observe that the moments of radial electron-pair density,

$$\langle u^n \rangle = \int_0^\infty u^n h(u) \, du \tag{3}$$

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yield various interesting two–electron properties, like the electron repulsion for $n=-1$, the number of electron pairs, $n=0$, and the mean interelectronic distance for $n=1$. Additionally, it is worth noting that the intracule density can be inferred from accurate total X-ray intensities [21].
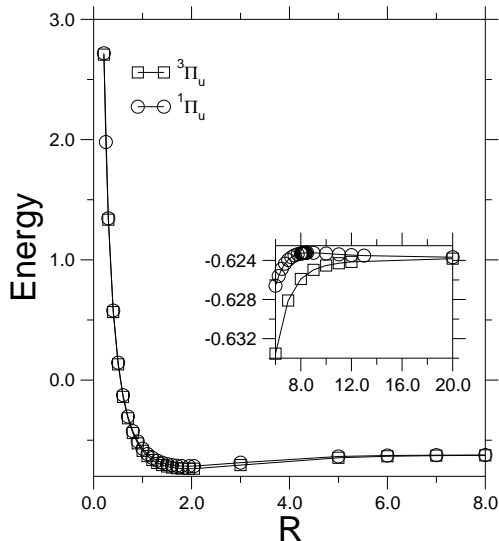

Figure 1: Calculated potential energy curves for the $^{1,3}\Pi_u$ excited states of H_2. Energy and internuclear distance, R, in a.u.

3 Results

We have calculated the intracule density, $I(\mathbf{u})$, and its spherically averaged electron-pair density distribution function, $h(u)$, for both the $^3\Pi_u$ and the $^1\Pi_u$ states of H_2 from an accurate *Full Configuration Interaction* (FCI) wave function constructed from a large Gaussian basis set which is described in detail in Ref. [22].

The calculated potential energy curves resulting from the calculations are shown in Figure 1, and Table 1 gives the spectroscopic constants calculated at the equilibrium geometries, along with the available experimetal data. Observe that the equilibrium distance of both states and the harmonic vibrational frequencies, ω_e, are given rather accurately with repect to their experimental marks.

The inset graph of Figure 1 shows that the $^1\Pi_u$ state rises above the dissociation limit asymptote at $R = 7.17$ a.u., and reaches a tiny maximum at

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the large internuclear distance of $R = 9.0$ a.u. Its height with respect to the dissociation asymptote is 0.014 eV. These results are consistent with respect to earlier calculations of the potential energy curve of this state [23] and lend support to the accuracy of our calculated wave functions.

Table 1: Equilibrium distances, in a.u, Energies, in a.u., vibrational frequencies, in cm^{-1}, electron repulsion energies, in a.u., and electron-electron coalescence densities, in a.u, for the $^{1,3}\Pi_u$ excited states of H_2. Experimenatal values, in parenthesis, from Ref. [24].

	$^1\Pi_u$	$^3\Pi_u$
R_e	1.95	1.96
	(1.952)	(1.961)
E	-0.716055	-0.736850
ω_e	2446.2	2460.9
	(2442.7)	(2465.0)
$\langle u^{-1} \rangle$	0.229863	0.246438
$I(0)$	0.81×10^{-2}	0.26×10^{-6}

The calculated mean values ($n = \pm 1$) of the intracular coordinate u, evaluated as in Eq. (3), are shown in Figure 2 as a function of the internuclear separation, R. The counterintuitive bahavior of both the electron repulsion energy and the interelectronic distance, within the domain of short internuclear separations, i. e.: $R \in [0.2 - 0.5]$ a.u., for the $^3\Pi_u$ state is readily seen upon inspection of Figure 2, which is in sharp contrast with the smoothly monotonic behavior observed for its parent $^1\Pi_u$ state.

This puts in place that the non-monotonic behavior of the electron repulsion and its associated interelectronic distance in the $^3\Pi_u$ state, in the domain of short internuclear distances, is not an artifact arising from the crudeness of its HF description.

Inspection of the difference between the electron-pair density distribution functions calculated at two internuclear distances, namely,

$$\Delta h(u; R, \Delta R) = h(u; R) - h(u; R + \Delta R), \ \Delta R > 0 \qquad (4)$$

provides an alternative view of these unusual correlation effects, relative to the more familar $h(u) - h_{HF}(u)$ difference. Indeed, as seen in Figure 3, we observed that for the $^1\Pi_u$ state, increasing the internuclear distance from $R = 0.2$ a.u. to $R = 0.5$ a.u., from $R = 0.5$ a.u. to $R = 0.75$ a.u. and from $R = 1.5$ a.u to $R = 1.95$ a.u. results in a decreased probability of finding the electrons at short distances and a concomitant increased probability of finding the electrons at larger distances. Notice that the three curves of the right panel of Figure 3 are positive for small interelectronic distances, hence the probability of finding two electrons within these short interelectronic distances is larger for the small internuclear distance, and vice-versa for large interelectronic distances.
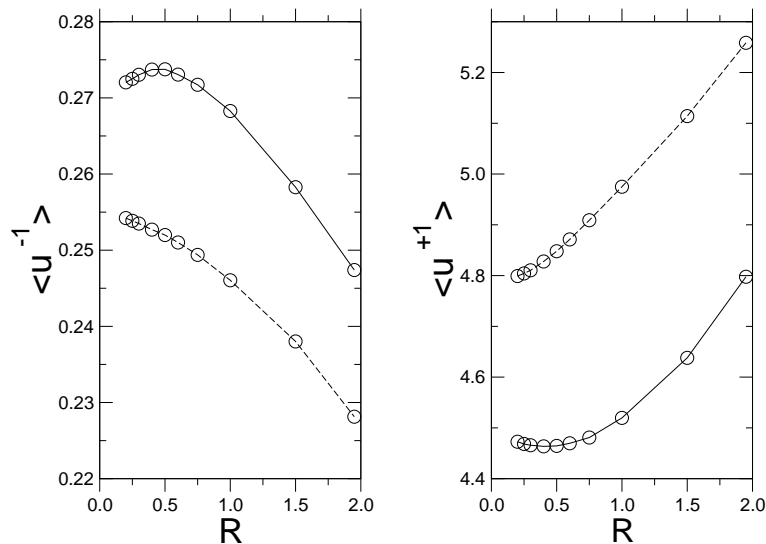
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Figure 2: Dependence of the mean interelectronic repulsion energy, $\left\langle u^{-1} \right\rangle$, (left panel) and the mean interelectronic separation, $\left\langle u^{+1} \right\rangle$, (right panel) in the $^3\Pi_u$ state (solid curve) and in the $^1\Pi_u$ state (dashed curve).

However, for the $^3\Pi_u$ state, the probability of finding the electrons at short relative distances is larger for $R = 0.2$ a.u. than for $R = 0.5$ a.u, in spite of the tiny positive peak at $u \sim 1.25$ a.u., and clearly much larger for $R = 0.75$ a.u. than for $R = 0.5$ a.u. (see dotted curve of the left panel of Figure 3), opposite to what is found for larger internuclear distances. For instance, the probability of finding the two electrons close to each other is larger at $R = 1.5$ a.u. than at $R = 1.95$ a.u., in accordance with intuition.

But, as mentioned above, at smaller internuclear distances, increasing the internuclear distance, increases the probability of finding the electrons at short interelectronic distances. This behavior is *counterintuitive*, and should be seen as one more (*unexpected*) effect of the symmetry constraints imposed by the Pauli principle.

4   Hund's Rule in the $^{1,3}\Pi_u$ States of H$_2$.

The parent $^{1,3}\Pi_u$ states of the hydrogen molecule differ because of the different symmetry constraints which Pauli's principle imposes to the spatial part of their corresponding wave functions. Thus, while the singlet state transforms symmetrically with respect to exchanging the electronic coordinates, $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$,
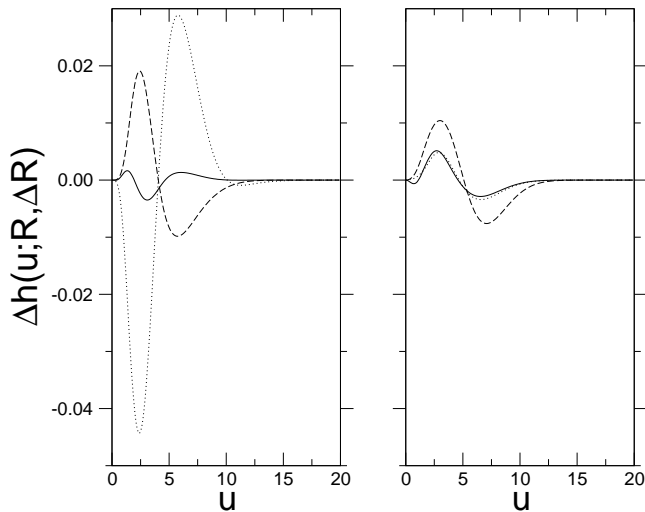
Figure 3: Difference of the electron-pair density probability function for the $^3\Pi_u$ state (left panel) and for the $^1\Pi_u$ state (right panel). Solid curve: $h(u; R = 0.2) - h(u; R = 0.5)$, dotted curved: $h(u; R = 0.5) - h(u; R = 0.75)$, and dashed curve: $h(u; R = 1.5) - h(u; R = 1.95)$

the triplet state's spatial part of the wave function must do it antisymmetrically, namely,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1), \quad \forall(\mathbf{r}_1, \mathbf{r}_2) \tag{5}$$

and, consequently,

$$\Psi(\mathbf{r}_1, \mathbf{r}_1) = 0, \quad \forall \mathbf{r}_1 \tag{6}$$

This allows for the straightforward evaluation of the electron-electron coalescence density [25], namely: $I(\mathbf{u} = 0)$, for the triplet state as:

$$
\begin{aligned}
I(0) &= \langle \Psi | \delta(\mathbf{r}_1 - \mathbf{r}_2) | \Psi \rangle \\
&= \int d\mathbf{r}_1 d\mathbf{r}_2 \Psi^*(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_2) \\
&= \int d\mathbf{r}_1 \Psi^*(\mathbf{r}_1, \mathbf{r}_1) \Psi(\mathbf{r}_1, \mathbf{r}_1) = 0
\end{aligned}
\tag{7}
$$

Our explicitly calculated values of $I(0)$ for the $^3\Pi_u$ state, shown in Table 1 agree with this prediction, and lend further support to our calculated intracule densities.

Furthermore, due to the continuity of the intracule density function, it is expected that the spherically averaged electron-pair density distribution function, $h(u)$, will start building up slower in the triplet state than in the singlet, because in the singlet state $I(0) > 0$ (see Table 1). Consequently one expects that the probability of finding two electrons at short interelectronic distances will be larger for the singlet than for the triplet.

The electron-pair density distribution function differences of the $^3\Pi_u$ state minus that of $^1\Pi_u$ state, at a number of selected internuclear distances, plotted in Figure 4, confirm this assumption. Namely, as stated above $h(u)$ is smaller at small interelectronic distances, u, for the triplet than for the singlet, hence the negative values shown in Figure 4 at short interelectronic distances u, irrespective of the internuclear distance.
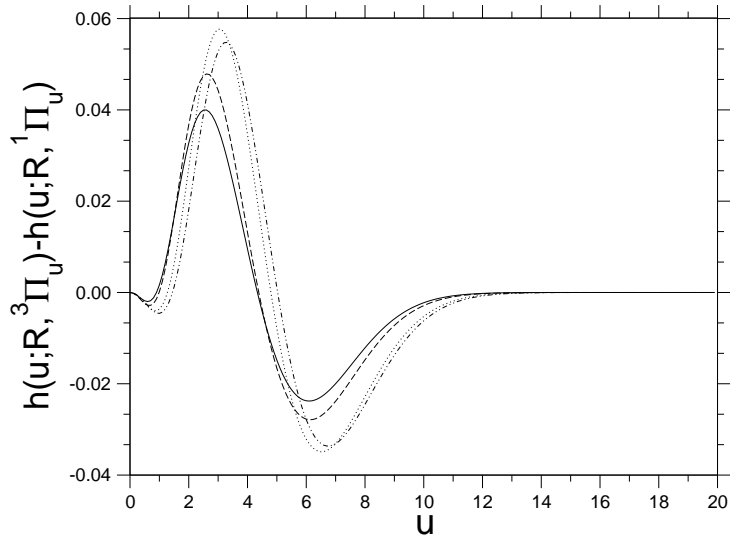

Figure 4: Difference between the electron-pair density probability functions of the $^3\Pi_u$ state and the $^1\Pi_u$ state. Solid curve: $R = 0.2$ a.u. Dashed curve $R = 0.5$ a.u. Dotted curve: $R = 1.5$ a.u. Dotted and dashed curve: $R = 1.95$ a.u.

The Pauli principle, therefore, prevents electrons to come into close proximity of each other, as is well known. A natural consequence of this is (hypothesized) that the electron repulsion in the triplet state should be smaller than in its parent same-configuration singlet state, where electrons are not impeded to approach each other, and consequently, due to associated decreased electron repulsion energy, the triplet (high) spin state results to be more stable that the singlet (low) spin state. This has been claimed to constitute the physical basis

of the Hund's rule [26, 27, 28], which the $^{1,3}\Pi_u$ excited states of H_2 strictly fulfill.

However, the data reported in Table 1 and in Figure 2, shows that this is not the case for the $^{1,3}\Pi_u$ excited states of H_2. Indeed, the electron repulsion energy for the triplet state is larger than for the singlet state, irrespective of the internuclear distance. Additionally, it is worth recalling that numerous explicit evaluations of the electron repulsion energy for the various spin states arising from the same configuration found, with no exception, that the electron repulsion energy is larger in the high-spin state (see Ref. [29], page 234). This invalidates the explanation outlined above for the Hund's rule as it was elegantly put forward by Boyd [30, 31] and subsequently elaborated by others [32, 33].

The physical basis of the lower energy of the $^3\Pi_u$, with respect to its parent $^1\Pi_u$ state, is drawn in Figure 4. Notice that although the probability of finding the electron in close proximity is smaller in the triplet than in the singlet, the triplet favors intermediate interelectronic distances, as compared to the singlet state. Additionally, notice also that the probability of finding the electrons at large separation, is larger in the singlet than in the triplet, alike the behavior found for short interelectronic distances. The triplet state, therefore, favors intermediate interelectronic distances which makes the electronic cloud more compact in the triplet than in the singlet and, consequently, makes the electron-nucleus attraction energy larger in the triplet than in the singlet, in such an amount that it outweighs the larger electron repulsion of the latter [34, 35, 36, 37, 38].

In other words, since the electrons of the triplet avoid each other in the vicinity of the nuclei they screen less the nuclear charge and, consequently the electron cloud gets more compact than in the singlet for which the nuclear charge is screened more efficiently [39]. This leads ultimately to an increased electron-nucleus attraction for the triplet, which overweights the larger electron repulsion of the triplet yielding, therefore, a more stable triplet state.

5   Summary

We have demonstrated, in accordance with Tal and Katriel [17], that the non-monotonic behavior with respect to the internuclear separation of the electron repulsion energy and its associated mean interelectronic distance in the $^3\Pi_u$ excited state of the hydrogen atoms are real, *counterintuitive*, effects of the symmetry constraints imposed by the Pauli principle on the wave function of triplet states. High-level Full Configuration Interaction calculations show that while in the $^1\Pi_u$ excited state the electron repulsion energy and its associated mean interelectronic distance behave monotonically, in the $^3\Pi_u$ excited state, the electron repulsion energy increases and the mean interelectronic distance decreases as the internuclear separation increases.

Finally, we have found that the Hund's rule, which holds also for these $^{1,3}\Pi_u$ same-configuration, $1\sigma_g^1\pi_u^1$, excited states, can be accounted for in terms of simple electronic shielding effects induced by wave function antisymmetrization,

in consonance with the accepted interpretation [31].

6   Acknowledgment

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