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Theoretical investigation of Rydberg and doubly-excited states of molecular hydrogen: The halfium model

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Abstract. The halfium model is presented and its application to \(1^1\Sigma_g^+\) ionization channels of \(\text{H}_2\) is described. \textit{Ab initio} calculations of the \((2p\sigma)^2\) doubly excited state of \(\text{H}_2\) are presented and compared with previous calculations. The connection with a fully \textit{ab initio} study of the \(\text{H}_2\) dissociative recombination process is outlined.

1. Introduction
The important role of the doubly-excited states of molecular hydrogen in the dissociative recombination process (DR) of the \(\text{H}_2^+\) ion has been recognized many years ago, and a key role has been attributed to the \((2p\sigma)^2\) \(1^1\Sigma_g^+\) doubly-excited state which mediates the DR process with slow electrons [1]. Despite the apparent simplicity of the hydrogen molecule, a fully \textit{ab initio} description of this process as well as of photoionization and photodissociation including the rotational degree of freedom has not yet been yet achieved in a global way. Multichannel quantum defect theory (MQDT) [2] is the only presently known theoretical framework able to describe these processes accurately.

A complete \textit{ab initio} treatment of the DR process requires an accurate description of the \(\text{H}_2\) dynamics both above and below the ionization threshold. We have recently developed the halfium model which is intended to constitute a step towards this goal [3]. In a series of preliminary applications to ungerade [3] and gerade symmetries [4] of \(\text{H}_2\) including doubly-excited channels, we obtained sets of \textit{ab initio} quantum defects that exhibit smooth variations with energy and internuclear distance. This property is essential for a fully \textit{ab initio} MQDT study of \(\text{H}_2\) dynamics including the dissociative recombination process. In this contribution we focus on some aspects related to the role of the \((2p\sigma)^2\) \(1^1\Sigma_g^+\) doubly-excited state.

2. The halfium model
The halfium model combines the eigenchannel variational R-matrix method [5] with the generalized multichannel quantum defect theory (GMQDT) in prolate spheroidal coordinates [3]. A reaction zone is defined which encloses the \(\text{H}_2^+\) ion core left behind when one of the electrons is far away, e.g. before a DR process occurs. The outer electron then experiences only the net Coulomb field created by the ion core. Specifically, one may assume that the core electron screens each proton equally, thus producing an effective positive half-charge on each center. The neutral system consisting of two...
positive point half-charges plus one electron is called the halfium particle which is intermediate between atomic hydrogen (zero bond length) and molecular hydrogen (whose core differs from two point half-charges). The halfium model applies to real molecular hydrogen when one of the electrons is outside the reaction volume. The electronic wavefunction is then expressed as a scattering wavefunction in the form of a linear combination of regular and irregular two-center (halfium) radial functions, multiplied by the appropriate elliptical harmonics (which are two-center generalizations of the familiar spherical harmonics [3]) and the electronic wavefunction of the core. The regular and irregular radial functions become equivalent to radial Coulomb functions at very large distances, but are distinct from these at shorter distances. They are calculated for positive and negative energy using the phase-amplitude formalism based on the Milne equation (see e.g. [6]).

When both electrons are present inside the reaction zone the full (non-relativistic) electronic Hamiltonian including electron-electron repulsion must be taken into account. A variational eigen-channel R-matrix calculation is set up in this region in terms of a basis set of two-electron functions that are antisymmetrized products of one-electron functions. Two types of basis functions are used. The ‘closed-type’ part of the basis, consisting of functions that vanish at the boundary of the reaction zone, describes the short-range part of the two-electron wavefunction. The diagonalization of the Hamiltonian restricted to this part of the basis gives a set of eigenstates associated with the poles of the R-matrix in analogy with the original Wigner-Eisenbud theory [7]. In the variational R-matrix method so-called ‘open-type’ functions that have non-zero values on the boundary are added to the basis in small number in order to ensure the smooth connection with the outer zone where the wavefunction takes the scattering form discussed above. These functions must be chosen carefully in order to avoid linear dependencies. The choice of these ‘open-type’ functions must in addition obey specific criteria in order to ensure that the number of solutions obtained in the variational procedure equals the number of solutions required physically by the problem [3].

3. The \((2p\sigma)^2 \Sigma_g^+\) doubly-excited state of \(H_2\)

An adequate DR calculation requires inclusion of both electronic (ionization) channels and nuclear (dissociation) channels. Here we discuss a preliminary step which involves the calculation of fixed-nuclei reaction or scattering matrices which constitute the input for the treatment of the DR dynamics itself. The calculations cover the bound and resonance energy ranges over about half an atomic unit and the range of internuclear distances \(R\) between 1 and 5 Bohr. Details can be found in [4].

In the calculations described here, we have explicitly taken into account four channels in the outer region: two Rydberg channels built on the \(1s\sigma H_2^+\) ground state, namely the \(1s\sigma 1s\sigma\) and \(1s\sigma 1d\sigma\) channels, and two doubly-excited channels built on the \(2p\sigma H_2^+\) excited state, namely the \(2p\sigma 2p\sigma\) and \(2p\sigma 2e\sigma\) channels. Inside the reaction volume these four channels and their interaction are represented by correlated wavefunctions set up in terms of a variational basis of about 200 two-electron functions. The connection between the inner multiconfiguration wavefunction and the outer scattering wavefunction yields a \(4 \times 4\) short-range reaction or scattering matrix whose elements behave smoothly as functions of the energy and the internuclear distance (see e.g. figure 1 of [4]).

We shall now discuss the \((2p\sigma)^2 \Sigma_g^+\) doubly-excited state in some detail. This state appears above the \(1s\sigma H_2^+\) ionization threshold as a resonance produced by electronic preionization, while in the bound spectrum below threshold it interacts with the manifold of Rydberg states of the same symmetry, thus perturbing the Born-Oppenheimer potential energy curves of the Rydberg states and producing peculiar potential curve shapes such as shelf-states and double-well states.

The \((2p\sigma)^2\) state emerges in the calculations once physical boundary conditions are applied to the four-channel electronic wavefunction in the outer zone: When the total energy is less than the \(1s\sigma\) threshold, the wavefunction must go to zero at infinity. The GMQDT procedure yields the energies of the bound states, i.e., the Born-Oppenheimer potential energies for each \(R\) value. For positive energies (i.e. above the \(1s\sigma\) threshold), the channels associated with the lowest threshold are electronic continua. These are coupled to the core excited Rydberg states associated with the higher \(2p\sigma\) threshold which
hence become ‘quasi-bound’. The GMQDT procedure in this situation yields the phase shift of the electron wavefunction for each channel (the so-called eigen-phase shift [3]). The energy-derivative of the sum of these is known to be proportional to the time-delay or state density of the ionizing electron, and exhibits a Lorentzian Breit-Wigner type profile near each resonance. The resonance position and half-width is easily extracted from this profile.

Figure 1 presents the state density as a function of energy above threshold for several values of the internuclear distance \( R \). The arrows indicate the evolution of the resonance as \( R \) increases. It can be seen that the resonance moves towards the threshold, indicated by a vertical dashed line, which is reached at \( R \approx 2.6 \text{ a.u.} \). At the same time the width is seen to increase, indicating that the lifetime shortens as the threshold is approached.

Table 1 gives the positions of the \((2p\sigma)^2\) resonance for a number of \( R \) values and compares the present results with previous theoretical studies. The quantity given is not the energy but the effective principal quantum number \( \nu(R) \) evaluated with respect to the \( 2p\sigma \) \( H_2^+ \) second ionization threshold. \( \nu(R) \) is defined by the Rydberg equation, viz. \( \nu(R) = (U^+(R) - U(R))^{-1/2} \), where \( U^+(R) \) is the energy of the threshold (here \( 2p\sigma \) of \( H_2^+ \)) and \( U(R) \) is the resonance energy (all in Ry). It can be seen that the various results agree to within 0.05 or less, showing that the present calculations correspond to the state of the art. Note that unlike in bound state calculations for \( H_2 \), where quantum chemical potential energy curves

**Table 1.** Clamped nuclei effective Rydberg principal quantum numbers for the \((2p\sigma)^2 \Sigma_g^+\) resonance of \( H_2 \).

| \( R \) (a.u.) | \( \nu_{\text{present}} \) | \( \nu \) [9] | \( \nu \) [10] | \( \nu \) [11] | \( \nu \) [12] | \( \nu \) [13] |
|----------------|-----------------|-------------|-------------|-------------|-------------|-------------|
| 1.0            | 1.594           | 1.630       | 1.589       | 1.637       | 1.615       |
| 1.2            | 1.576           | 1.603       | 1.569       | 1.607       | 1.595       | 1.617       |
| 1.4            | 1.563           | 1.571       | 1.542       | 1.574       | 1.566       | 1.606       |
| 1.5            | 1.572           |             |             |             |             |             |
| 1.6            | 1.535           | 1.536       | 1.507       | 1.540       | 1.535       | 1.547       |
| 1.8            | 1.495           | 1.501       | 1.471       | 1.505       | 1.505       | 1.561       |
| 2.0            | 1.473           | 1.467       | 1.439       | 1.471       | 1.476       | 1.461       |
| 2.2            | 1.460           | 1.434       | 1.408       | 1.440       |             | 1.412       |
| 2.4            | 1.407           | 1.403       |             | 1.410       |             | 1.373       |
| 2.5            | 1.396           | 1.381       | 1.396       | 1.419       |             |             |
| 2.6            | 1.387           | 1.377       | 1.383       |             |             |             |
Table 2. Widths (in Rydbergs) for the \((2p\sigma)^2\,^1\Sigma_g^+\) resonance of \(H_2\)

| \(R\) (a.u.) | \(\Gamma\) \(\text{present}\) | \(\Gamma\) [9] | \(\Gamma\) [10] | \(\Gamma\) [11] | \(\Gamma\) [13] |
|-------------|-----------------|-----------|-----------|-----------|-----------|
| 1.0         | 0.0225          | 0.0282    | 0.0458    | 0.0300    |           |
| 1.2         | 0.0375          | 0.0396    | 0.0482    | 0.0414    | 0.0190    |
| 1.4         | 0.0491          | 0.0534    | 0.0502    | 0.0552    | 0.0018    |
| 1.5         | 0.0362          |           |           |           |           |
| 1.6         | 0.0519          | 0.0689    | 0.0518    | 0.0704    | 0.0360    |
| 1.8         | 0.0674          | 0.0845    | 0.0530    | 0.0862    | 0.0004    |
| 2.0         | 0.0834          | 0.1006    | 0.0576    | 0.1018    | 0.0590    |
| 2.2         | 0.1110          | 0.1162    | 0.0607    | 0.1170    | 0.0670    |
| 2.4         | 0.1194          | 0.1403    |           | 0.1304    | 0.0740    |
| 2.5         | 0.1487          |           | 0.0918    | 0.1352    |           |
| 2.6         | 0.0905          | 0.1050    | 0.1396    |           |           |

up to \(\nu \approx 5\) accurate to about \(10^{-5}\) Ry exist [8], no equivalent benchmark calculations are available for the resonances. Nevertheless, a generally accepted rule states that improved convergence leads to lower positions and smaller widths. Table 2 gives the width of the \((2p\sigma)^2\) resonance as function of \(R\) and again compares the present data with previous evaluations. The overall agreement is reasonable, but some discrepancies stand out also. Note in this context that the value of the width for \(R \approx 2.6\) a.u. is not well defined because part of the resonance has moved into the discrete range (cf. figure 1).

We now turn to the discussion of the effect of the \((2p\sigma)^2\) doubly-excited state on the spectrum of bound Rydberg states. Figure 2 is a plot of the effective quantum defects \(\mu = n - \nu\) as functions of \(R\). Here \(n\) is the principal quantum number defined for \(R = 0\) (united atom), and \(\nu\) is the effective principal quantum number evaluated as above with \(U(R)\) and \(U^+(R)\) (the latter is taken here to correspond to the \(1s\sigma\) \(H_2^+\) state). Figure 2 contains the same information as the familiar potential energy curve representations (cf. figure 2 of [4]), but highlights particular aspects not easily visible in the potential curve diagrams. All the Rydberg states represented in figure 2 are strongly mixed with the core-excited \((2p\sigma)^2\) state in certain ranges of \(R\). The figure shows that their evolution in fact follows two distinct patterns. The quantum defects of the two states labeled d rise by nearly unity as \(R\) increases to 5 Bohr. The quantum defects labeled s on the other hand exhibit a significant but less pronounced evolution.

Figure 2. Effective quantum defects for the five lowest excited \(^1\Sigma_g^+\) states of \(H_2\). Solid lines: \textit{ab initio} results from [8]. Symbols connected with thin dashed lines: present results. The \(n\ell\lambda\) notation is valid for small \(R\).
4. Conclusion
In this paper we have used the halfium model to examine the role of the \((2p\sigma)^2 \Sigma_g^+\) core-excited state of molecular hydrogen. We have shown that our approach yields an accurate description of this state above as well as below threshold. The quantum defects which result from the halfium/R-matrix treatment are smooth functions of energy and internuclear distance as is required by rovibronic multichannel quantum defect theory [14]. This opens up for the first time the possibility of a realistic fully \textit{ab initio} global study of H\(_2\) DR, photoionization and photodissociation [15] dynamics including the rotational degree of freedom.

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