The $\sigma_v$ reflection symmetry in variational R-matrix theory: Application to Rydberg and doubly-excited states of $^1\Sigma^+_g$ and $^1\Sigma^-_g$ symmetries in diatomic hydrogen

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Abstract. The $\sigma_v$ reflection symmetry for diatomic molecules is discussed in the context of variational R-matrix theory applied to the H$_2$ molecule ("halfium model"). It is shown that explicit use of the reflection symmetry in the R-matrix calculations improves the results of singly and doubly excited $^1\Sigma^+_g$ states and resonances. R-matrix calculations of non-autoionizing $^1\Sigma^-_g$ doubly-excited states of H$_2$ situated 27 eV above the ground state are also presented and compared with existing ab initio data obtained by other methods.

1. Introduction
Singly and doubly excited Rydberg states of neutral hydrogen H$_2$ are known to play a key role in the DR process of H$_2^+$ ions with slow electrons [1]-[4]. They act as intermediate resonances which promote the conversion of electron energy into nuclear kinetic energy during the reactive collision process. The theoretical description of the collision process requires a good knowledge of the electronic structure of both the hydrogen ion H$_2^+$ and the neutral molecule H$_2$, in terms of potential energy curves and/or quantum defects. In particular, the doubly-excited states may autoionize or dissociate into neutral hydrogen atom fragments. Numerous papers [5]-[9] have been published which are dealing with the so-called $Q_1$ and $Q_2$ resonance series converging towards the H$_2^+$ $2p\sigma$ and $2p\pi$ thresholds respectively, and particular attention has been paid to the lowest $Q_1$ resonance of $^1\Sigma^+_g$ symmetry, because its Born-Oppenheimer potential energy curve crosses the threshold not far from the equilibrium position and therefore dominates the DR process.

In recent years we have developed an ab initio R-matrix approach [10] which enables bound states and core-excited scattering states of H$_2$ to be calculated for fixed nuclei. Our work is based on the pioneering ideas of Greene and Yoo [11][12], which it adapts such as to yield quantum defect matrices that evolve smoothly throughout the bound and continuous energy regions, and which also vary relatively mildly as functions of the molecular geometry (internuclear distance...
Our "halfium model" combines the variational eigenchannel R-matrix method [13] with the Generalized Multichannel Quantum Defect Theory (GMQDT) implemented using prolate spheroidal electron coordinates [14]. The approach has been used to investigate singlet ungerade symmetries (\(^1\Sigma_u, ^1\Pi_u\)) [10] and gerade symmetries (\(^1\Sigma_g, ^1\Pi_g, ^1\Delta_g\)) [15], both for the bound and the continuum (autoionization) regions.

It is interesting to note that even the most recent quantum chemical calculations [16], while following individual potential energy curves out to large internuclear distances, are still limited to the lowest excited states since they do not exceed \(n \approx 5\) (where \(n\) is the principal quantum number). On the other hand, the halfium model is limited to relatively small \(R\)-values (\(R \approx 10\,\text{a.u.}\)), and at this stage is not capable of describing double ionization. One of the advantages of the "halfium model" however is that it produces quantum defects which can be used directly for the calculation of the nuclear-electronic dynamics in the framework of multichannel quantum defect theory (MQDT). The halfium scheme together with the MQDT framework leads to a global analysis of the interactions as no distinction is made between "open" and "closed" channels at the outset, but instead all channels are treated on the same footing irrespective of their corresponding channel thresholds. In this picture doubly excited states are included explicitly as electron-ion collision channels in their own right. It has further been shown [17] how MQDT can describe competing ionization and dissociation processes, and include ro-vibrational dynamics via the frame transformation technique [18]. Therefore MQDT possesses all the ingredients to address the problem of dissociative recombination and, when combined with the halfium model, it is capable to yield \textit{ab initio} predictions of DR processes as well. It thus represents an alternative to the more traditional approach to DR, where the dissociative state (corresponding in \(\text{H}_2\) to the lowest \(Q_{1}\,\,^1\Sigma^+_g\) resonance) is treated as a valence state rather than as part of an electron-ion channel [1][2].

The previous implementations of the molecular variational R-matrix method [10]-[12] made no distinction between channels of \(\Sigma^+\) and \(\Sigma^-\) symmetry, in other words, the symmetry property of the electron wavefunction obtained by a reflection of all electron coordinates at a plane containing the two nuclei (symmetry operation \(\sigma_v\)) was not considered explicitly. In this paper, we show how the halfium model may be reformulated such as to include this symmetry property. We show how the convergence in the calculation of \(^1\Sigma^+_g\) states is improved by this extension, and we also present initial results on doubly excited states of \(\text{H}_2\) of \(^1\Sigma^-_g\) symmetry which occur 27 eV above the ground state. These turn out to be non-autoionizing despite their high energy. To our best knowledge, only two previous theoretical studies of \(\Sigma^-\) states in \(\text{H}_2\) have been made [19][20], and no experimental evidence for their existence appears to have been found so far.

2. Theory

In the halfium model, the two-electron configuration space is devided into two regions: (i) a reaction volume where the variational R-matrix method is used, and (ii) the remaining space, called asymptotic zone, where GMQDT is used. The connection of the inner zone and outer zone wavefunctions yields the desired reaction matrix or the equivalent quantum defect matrix.

In the original formulation of the halfium model [10][12] each calculation was performed separately for each molecular symmetry defined by the standard quantum numbers \(\Lambda\) (projection of the angular momentum on the internuclear axis, taken positive), electron spin \((S = 0, 1)\), and gerade/ungerade \((p = 0 \text{ or } 1)\). From elementary molecular theory [21] we know that in a diatomic molecule the symmetry operation \(\sigma_v\) corresponding to a reflection of all electron coordinates at any plane containing the two nuclei also commutes with the electronic Hamiltonian so that an additional quantum number arises: the electronic wavefunction has \(-\) symmetry \((q = 1)\) or + symmetry \((q = 0)\) depending on whether it changes sign or not upon reflection.

The only symmetry for which the \(q\) quantum number is relevant at the electronic stage of calculation, is \(\Sigma\) symmetry \((\Lambda = 0)[22][23]\). As far as molecular hydrogen is concerned, the \(\sigma_v\),
symmetry may in practice be disregarded even for $\Sigma$ states as long as energies below $2p\sigma$ ion threshold are considered. The reason is that only $\Sigma^+$ states arise in this range. Indeed, the lowest $\Sigma^-$ state occurs associated with the $(2p\pi)^1(e\pi)$ configuration and is expected to lie at around 27 eV above the ground state. The $\Sigma^-$ states are thus well separated from $\Sigma^+$ states, and for many practical purposes need not be taken into consideration.

In what follows we give a brief description of the main modifications required in the halflum model in order to take account of the $\sigma_v$ symmetry. Each two-electron basis function corresponding to a configuration $i, j$ (cf. [10],[12]) is defined in the reaction zone ($\xi_1, \xi_2 \leq \xi_0$) and is specified by the set of quantum numbers $\{S, \Lambda, \nu, q\}$:

$$\Psi_{ij}(r_1^-, r_2^-) = \mathcal{N}_{ij} \left[ y_{ij}^+ - (r_1^-, r_2^-) + (-1)^q y_{ij}^+(r_1^-, r_2^+) \right].$$

$r_1^-$ and $r_2^-$ are the position vectors of each electron defining the corresponding spheroidal coordinates $(\xi, \eta, \varphi)$. The functions $y_{ij}^\pm$ are products of one-electron orbitals characterized by signed orbital angular momentum components:

$$y_{ij}^+(r_1^-, r_2^-) = N_{ij} \left[ \phi_i^+(r_1^-) \phi_j^-(r_2^-) + (-1)^S \phi_j^+(r_1^-) \phi_i^-(r_2^-) \right],$$
$$y_{ij}^-(r_1^-, r_2^-) = N_{ij} \left[ \phi_i^+(r_1^-) \phi_j^-(r_2^-) + (-1)^S \phi_j^+(r_1^-) \phi_i^-(r_2^-) \right],$$

where $\phi_i^\pm(r)$ is a one-electron wavefunction associated with the eigenstate $|i\pm\rangle = |n_i \ell_i \lambda_i^\pm\rangle$ of $\mathsf{H}^+_0$ with $\lambda_i^\pm = |\Lambda_i|$ and $\lambda_i^- = -|\Lambda_i|$. $N_{ij}$ and $N_{ij}$ in the preceding equations are normalization factors, and it is understood that $\ell_i$ is the generalized orbital angular momentum quantum number arising when spheroidal coordinates are used [10].

The two-electron basis functions are used to solve the Schrödinger equation inside the reaction surface in terms of so-called "surface harmonics" $\Phi_k(\omega)$ (where $\omega$ stands for all coordinates except the radial coordinate of the outermost electron) for each asymptotic channel $k = ij$ (see [10]). Taking account of the reflection symmetry we write these surface harmonics as:

$$\Phi_k(\omega) = \overline{N_{\Phi_k}} \left[ \Phi_k^+ - (\omega) + (-1)^q \Phi_k^+ + (\omega) \right],$$

where

$$\Phi_k^+ - (\omega) = N_{\Phi_k} \phi_i^+(r^-) Y_{\ell_k \lambda^-} (\eta_>, \varphi_>)$$
$$\Phi_k^+ + (\omega) = N_{\Phi_k} \phi_i^-(r^-) Y_{\ell_k \lambda^-} (\eta_>, \varphi_>) ,$$

and $\overline{N_{\Phi_k}}$ and $N_{\Phi_k}$ are normalization factors. Here the indexes $<$ and $>$ designate the inner and outermost electron respectively; they arise from the indiscernability of the electrons. $Y_{\ell_k \lambda_\nu}(\eta, \varphi)$ are spheroidal harmonics analogous to the standard spherical harmonics.

The matching of the inner zone solutions to those obtained outside the reaction volume yields short-range reaction matrix $\mathbf{K}$ and equivalent quantum defect matrix $\mu$. The energies of bound and doubly-excited states are finally obtained by standard MQDT procedures as in the standard halfium model [10].
3. Results

3.1. Singly excited bound $^1\Sigma^+_g$ states: the ns$\sigma$ Rydberg series

Although $\Sigma^+$ states in H$_2$ are generally well separated from $\Sigma^-$ states, a slight improvement of the bound state energies of the $\Sigma^+$ states nevertheless occurs due to improved convergence properties of the calculation when the symmetrized version of the code is used. A $\Sigma$ symmetry two-electron variational basis typically is composed of $\sigma\sigma$, $\pi\pi$, $\delta\delta$ ... configurations. The two first ion thresholds are of $\sigma-$type ($1s\sigma$ and $2p\sigma$), so that the majority of the basis functions will naturally correspond to $\sigma\sigma$ configurations. These have $\Sigma^+$ symmetry and consequently are not affected by the basis set symmetrization. By contrast, $\pi\pi$ and $\delta\delta$ configurations yield both $\Sigma^+$ and $\Sigma^-$ symmetry functions. For a given size of the basis set, the symmetrization of the basis function will therefore effectively optimize the basis, pushing down the lowest roots of the Hamiltonian, although the improvement is expected to be small as stated earlier. We have verified that two calculations done, respectively, with and without symmetrization, but including exclusively $\sigma\sigma$ configurations, do give exactly the same results as required. The calculations have been carried out by using reaction boundaries corresponding to $\xi_0 = 25/R + 1$.

Figure 1 displays differences $\Delta\nu = \nu - \nu_{ab\text{ initio}}$ as a function of the internuclear distance $R$ for the $^1\Sigma^+_g$ ns$\sigma$ series of H$_2$ (principal configuration [1s$\sigma$]ns$\sigma$, $n = 2 - 4$). The effective principal quantum number is defined by the Rydberg equation as $\nu = 1/\sqrt{E_{1s\sigma} - E_n}$, where $E_n$ is the bound state eigen-energy and $E_{1s\sigma}$ the first ionization threshold energy in rydbergs. The effective quantum numbers $\nu_{ab\text{ initio}}$ have been extracted from quasi-exact state-of-the-art quantum chemical calculations [24]. Open symbols in Figure 1 show the differences obtained in a non-symmetrized R-matrix calculation, whereas full symbols designate the differences obtained when a calculation with a symmetrized basis of the same size was carried out. The improvement obtained with the symmetrized code is obvious, particularly for small $R$ values.

A more quantitative analysis of these results is presented in Table 1. For each of the three Rydberg states represented in Fig. 1, we have averaged the deviations over $R$ and evaluated the rms value of $\Delta\nu$. The last column contains the average of the rms value for all three states. This quantity is a global measure of the improvement obtained: the value decreases from 0.023 (for non symmetrized calculations) to 0.015 (for symmetrized calculations), showing that the overall improvement amounts to 35%. Furthermore, by averaging the $\Delta\nu$ values for each state separately, we see that the symmetrized energies are systematically lower than non-symmetrized energies, confirming once again the improvement of the calculations. In terms of averages, the deviation is reduced by a factor 2 ($\langle \Delta\nu_{\text{non-sym}} \rangle = 0.019$ and $\langle \Delta\nu_{\text{sym}} \rangle = 0.010$).

3.2. Doubly excited $^1\Sigma^+_g$ resonances: the $Q_1$ resonance series

The $Q_1$ resonance series are situated above threshold and therefore have the character of autoionizing series. It must therefore be stressed that the Ritz variational principle does not

Table 1. $^1\Sigma^+_g$ ns$\sigma$ Rydberg series in H$_2$. Root mean squares and averaged values of symmetrized (● in Fig 1) and non-symmetrized (○ in Fig. 1) deviations of effective principal quantum numbers with respect to quantum chemical data [24] (cf. the text).

| state | 2s$\sigma$ | 3s$\sigma$ | 4s$\sigma$ | average |
|-------|-----------|-----------|-----------|---------|
| rms$_{\text{non-sym}}$ | 0.024 | 0.025 | 0.020 | 0.023 |
| rms$_{\text{sym}}$ | 0.014 | 0.014 | 0.016 | 0.015 |
| $\Delta\nu_{\text{non-sym}}$ | 0.021 | 0.021 | 0.016 | 0.019 |
| $\Delta\nu_{\text{sym}}$ | 0.011 | 0.010 | 0.010 | 0.010 |
Figure 1. $^1\Sigma^+_g$ $ns\sigma$ Rydberg series in H$_2$. Deviations $\Delta\nu = \nu - \nu_{ab\text{ initio}}$ of calculated effective principal quantum numbers obtained without (○) and with (●) symmetrization, from the corresponding quantum chemical results [24], plotted as function of the internuclear distance $R$ (in bohr) for (a) $2s\sigma$, (b) $3s\sigma$ and (c) $4s\sigma$. $\nu$ is the effective principal quantum number.

apply in this situation as a consequence of the fact that the core excited states are embedded in the open ionization continua. This means that we have no unique criterion at our disposal in order to assess the quality of the calculations. Of course we may expect that the results obtained with symmetrized and with non-symmetrized bases should be basically comparable, and as a rule of thumb we can hope that a lowering of the resonance positions is a sign that the calculation has been improved. The calculations have been carried out as described in Ref. [15].

Tables 2, 3 and 4 list effective principal quantum numbers for the core excited $^1\Sigma^+_g$ states $nQ_1$ ($n = 1, 2, 3$) resonances. The notations have the same meaning as in Table 1, except that $\nu_{ab\text{ initio}}$ here refers to the R-matrix calculations from Ref. [6]. As before, the last row of each Table displays the averages of the principal quantum number differences. We can see a significant improvement for the lowest resonance (in the sense defined above), whereas the two higher resonances are hardly affected.

3.3. Doubly excited non-autoionizing states of $^1\Sigma^-_g$ symmetry

We have evaluated $^1\Sigma^-_g$ states corresponding to the doubly-excited Rydberg series $(2p\pi)(n'p\pi)$ $n' \geq 3$ and $(2p\pi)(n''f\pi)$ $n'' \geq 4$ converging to $2p\pi$ ion threshold. This kind of calculation had not been possible with the old version of our R-matrix code and is conducted here for the first time. To underline the non-autoionizing character of these metastable states, we denote them as $nP_2$ $^1\Sigma^-_g$. This notation is inspired by Bottcher’s notation $nQ_2$ for autoionizing doubly-excited states lying in the same energy range [25].
Table 2. Effective principal quantum numbers of the $1Q_1^{1}\Sigma_g^+$ core excited resonance. Values $\nu_{\text{sym}}$ and $\nu_{\text{non-sym}}$ correspond to symmetrized and non-symmetrized calculations, respectively, and $\nu_{\text{ab initio}}$ are derived from Ref. [6]. The internuclear distance $R$ is in bohr.

| $R$ | $\nu_{\text{non-sym}}$ | $\nu_{\text{sym}}$ | $\nu_{\text{ab initio}}$ | $\Delta\nu_{\text{non-sym}}$ | $\Delta\nu_{\text{sym}}$ |
|-----|------------------|------------------|------------------|------------------|------------------|
| 1.0 | 1.594            | 1.578            | 1.630            | -0.036           | -0.052           |
| 2.0 | 1.473            | 1.465            | 1.467            | 0.007            | -0.002           |
| average | 1.535          | 1.550            | 1.593            | 0.007            | -0.027           |

Table 3. Same as Table 2 for the $2Q_1^{1}\Sigma_g^+$ core excited resonance.

| $R$ | $\nu_{\text{non-sym}}$ | $\nu_{\text{sym}}$ | $\nu_{\text{ab initio}}$ | $\Delta\nu_{\text{non-sym}}$ | $\Delta\nu_{\text{sym}}$ |
|-----|------------------|------------------|------------------|------------------|------------------|
| 1.0 | 2.783            | 2.775            | 2.821            | -0.038           | -0.046           |
| 2.0 | 2.675            | 2.680            | 2.681            | -0.006           | -0.001           |
| 3.0 | 2.633            | 2.632            | 2.649            | -0.016           | -0.017           |
| 4.0 | 2.724            | 2.723            | 2.705            | 0.019            | 0.018            |
| average | 2.708          | 2.711            | 2.713            | 0.010            | 0.011            |

Table 4. Same as Table 2 for the $3Q_1^{1}\Sigma_g^+$ core excited resonance.

| $R$ | $\nu_{\text{non-sym}}$ | $\nu_{\text{sym}}$ | $\nu_{\text{ab initio}}$ | $\Delta\nu_{\text{non-sym}}$ | $\Delta\nu_{\text{sym}}$ |
|-----|------------------|------------------|------------------|------------------|------------------|
| 1.0 | 3.800            | 3.794            | 3.817            | -0.017           | -0.023           |
| 2.0 | 3.693            | 3.696            | 3.702            | -0.009           | -0.006           |
| 3.0 | 3.663            | 3.662            | 3.672            | -0.009           | -0.010           |
| 4.0 | 3.740            | 3.737            | 3.731            | 0.009            | 0.006            |
| 5.0 | 3.885            | 3.818            | 3.822            | 0.063            | -0.004           |
| average | 3.792          | 3.788            | 3.796            | -0.007           | -0.007           |

Table 5. Energies of the non-autoionizing $1P_2^{1}\Sigma_g^-$ doubly-excited state in $H_2$ for different internuclear distances $R$. $E_S$, this work. $E_K$, Ref. [20]. $E_M$, Ref. [19]. Energies and $R$ are in atomic units. See the text for details.

| $R$ | $E_K$   | $E_M$   | $E_S$   | $\Delta E_{SK}$ | $\Delta E_{SM}$ |
|-----|---------|---------|---------|-----------------|-----------------|
| 1.0 | -0.5523 | -0.5520 | -0.5522 | 0.0001          | -0.0002         |
| 2.0 | -0.5031 | -0.5029 | -0.5030 | 0.0001          | -0.0001         |
| 3.0 | -0.4568 | -0.4566 | -0.4567 | 0.0001          | -0.0001         |
| 4.0 | -0.4176 | -0.4174 | -0.4175 | 0.0001          | -0.0001         |
| 5.0 | -0.3850 | -0.3848 | -0.3848 | 0.0002          | 0.0000          |
Figure 2. Potential energy curves of $nP_2 \, 1\Sigma_g^-$ states. The $2p\pi$ threshold is represented by a dashed line.

Table 6. Energies of non-auto-ionizing states $nP_2 \, 1\Sigma_g^-$ ($n = 2 - 4$) obtained here, $E_S$, and by Martin [19], $E_M$, and their differences for different internuclear distances $R$. Energies and $R$ are in atomic units.

| $R$ | $E_S$ | $E_M$ | $\Delta E_{SM}$ | $E_S$ | $E_M$ | $\Delta E_{SM}$ | $E_S$ | $E_M$ | $\Delta E_{SM}$ |
|-----|-------|-------|------------------|-------|-------|------------------|-------|-------|------------------|
| 1.0 | -0.5132 | -0.5133 | 0.0001           | -0.5060 | -0.5062 | 0.0002           | -0.4978 | -0.4978 | 0.0000          |
| 2.0 | -0.4664 | -0.4665 | 0.0001           | -0.4610 | -0.4613 | 0.0003           | -0.4518 | -0.4518 | 0.0000          |
| 3.0 | -0.4226 | -0.4227 | 0.0001           | -0.4194 | -0.4195 | 0.0001           | -0.4088 | -0.4087 | -0.0001         |
| 4.0 | -0.3857 | -0.3857 | 0.0000           | -0.3844 | -0.3847 | 0.0003           | -0.3725 | -0.3724 | -0.0001         |
| 5.0 | -0.3563 | -0.3564 | 0.0001           | -0.3548 | -0.3550 | 0.0002           | -0.3432 | -0.3432 | 0.0000          |

Table 5 lists the present results (indexed by $S$ in the Table) obtained for the $1P_2 \, 1\Sigma_g^-$ state for different internuclear distances $R$, and compares them with those of Martin [19] (indexed by $M$) and Komasa [20] (indexed by $K$). To the best of our knowledge, these two papers are the only existing publications reporting $ab\, initio$ calculations of $\Sigma^-$ states of $\text{H}_2$. The Table indicates that there is overall agreement between the different calculations. As expected, the quantum chemical energies of Ref. [20] are lowest ($\Delta E > 0$), but the two other sets of results fall to within a reasonable margin of the order of 50 cm$^{-1}$. Note that the calculations of Ref. [20] are no doubt of benchmark quality. They extend to large $R$ values (not shown in Table 5), but are limited to the lowest state of $1\Sigma_g^-$ symmetry. Ref. [19] on the other hand reports five excited states, but only up to $R \leq 5$ a.u.

The R-matrix method in principle is able to provide $ab\, initio$ data for arbitrarily high principal quantum numbers as well as for internuclear distances up to $R = 10$ a.u. at least. Figure 2 illustrates preliminary calculations of a few higher potential energy curves of metastable non-autoionizing $nP_2 \, 1\Sigma_g^-$ ($n = 1 - 4$) states. These curves are seen to run parallel to the $2p\pi$ ionization threshold as is characteristic for Rydberg states. In Table 6 we list the presently obtained energies $E_S$ along with those of Martin [19], $E_M$, and the differences ($\Delta E_{SM} = E_S - E_M$) for the states $nP_2 \, 1\Sigma_g^-$ ($n = 2 - 4$). The overall agreement is similar as obtained for the lowest $1\Sigma_g^-$ state.
4. Conclusion
We have implemented the \( \sigma_n \) molecular reflection symmetry in the framework of the "halflium" variational R-matrix code and investigated its effect on the calculation of \( \text{H}_2 \, ^1\Sigma_g^+ \) states in the discrete range and in the ionization continuum. Preliminary results on \( ^1\Sigma_g^- \) non-autoionizing doubly-excited states have also been presented, and have been compared with published data from other authors. These states cannot autoionize by electronic interaction (configuration mixing), but they may be weakly autoionized and/or predissociated by rotational-electronic non-adiabatic coupling. Systematic calculations of singlet and triplet \( \text{H}_2 \, \Sigma^- \) states are underway and will be published in a forthcoming paper [26].

Acknowledgements
We thank Drs. S. L. Guberman, I. F. Schneider, C. H. Greene and X. Urbain for stimulating discussions concerning this work. We are grateful to Dr. F. Martin for providing unpublished data on doubly-excited states of \( \text{H}_2 \). M. T. and Ch. J. acknowledge financial support from NSF and NASA. Ch. J. was supported in part by the ANR (France) under Contract No. 09-BLAN-020901. F. A. and Ch. J. have also benefitted from support by the E. Miescher Foundation (Basel, Switzerland).

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