

The Full Quantum Mechanical Three Body Problem of H_2^+ (Non-Adiabatic R-Matrix Calculations For Proton-Hydrogen Scattering)

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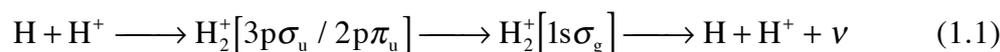
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Abstract

A model describing the full quantum mechanical three body problem of the hydrogen molecular ion is presented, and some of the numerical results are subsequently discussed. The overall numerical scheme is based on a variation principle for the matrix representation of the scattering problem set up using grid-methods (e.g. finite element method) and associated quadrature-schemes (a discrete variable representation).

1. Introduction

We have performed full quantum mechanical three body scattering calculations to form overall “reactions” of the type:



The hydrogen molecular ion, H_2^+ , comprising two protons and one electron, is the simplest molecule of all. If we neglect all effects coming from the spin of the particles and if in addition the motion of the protons is disregarded, we are faced with the problem of an electron moving in the presence of two fixed Coulomb centers of attraction - the so-called Born-Oppenheimer approximation (1). In this from, the analysis of H_2^+ has attended considerable attention over the years; thus, Burrau (2) in 1927, Hylleraas (3) in 1931 and many others have performed Born-Oppenheimer approximate calculations on both the ground state and some of the excited states. The separability of the electronic Schrödinger’s equation in the so-called spheroidal coordinates enables solutions of almost unlimited accuracy to be computed. The full three-body problem of H_2^+ on the other hand, forms a much bigger theoretical as well as computational task - in fact it is well-known that there does not exist any analytical or even “exact” numerical solution to this problem. Further since the Born-Oppenheimer approximation in general terms is acknowledged as being a very good approximation one could ask “why bother to try and solve the full three-body problem of H_2^+ ?”

2. Astrophysical motivation

Like atomic hydrogen, the molecular ion plays a fundamental role in the understanding and interpretation of light emitted from a large number of stars. H line absorption is proportional to the absorber density, but in the H_2^+ -system the absorber density is proportional to the square of the H density, and hence a greater sensitivity to the pressure

in the stellar atmosphere is found in the absorption features of H_2^+ then in H. In an atmosphere in equilibrium the pressure is given by the temperature and the gravity of the star so that it becomes possible to accurately study these parameters in stars that show H_2^+ absorption.

The stars in question are the Hydrogen rich white dwarfs (WD). At a certain temperature (near 16,000K) these WD's show UV absorption features from H_2^+ on the wings of the Lyman α -line. The main interests in studying these WD's lies in the generally interesting role WD's have as end-products of nearly all stellar evolution; 90% of all stars are believed to end up as WD's (4). Of particular interest to some astrophysics (4) is the presence of stellar oscillations in the so-called DA WD's in a temperature range that coincides with the range of temperature in which the H_2^+ features can be seen. Stellar oscillations can be used to study the stellar interior, and important insight into stellar evolution can be obtained if the most accurate information about the star can be gathered from analysis of the observed light-spectrum and collated with the information available from the analysis of the oscillations (5).

A study of the absorption due to transitions among states of H_2^+ , begins with the problem of obtaining a good representation of the transition dipole moment, which expresses the amplitude for the given transition. So far the study of transition dipole moments for H_2^+ has only been done in the adiabatic or Born-Oppenheimer approximation (1) using classical or semi-classical arguments. A good example of such an approach is the work by Bates (6), which is based on the adiabatic potential energy curves for H_2^+ . This and related models do not, however, give the right absorption-coefficients; it is believed that this is due to the neglect of non-adiabatic effects, i.e., the coupling of the nuclear and electronic motions.

3. Quantum mechanical motivation

At the very heart of practically all ab initio quantum mechanical calculations for molecular systems lies either the Born-Oppenheimer (1) or the adiabatic approximation. The philosophy of these approaches is a separation (complete or partial) of the electronic and nuclear motions, taking point of reference in the large difference in the masses. Solving ab initio quantum mechanical calculations for many particle systems in this picture of a clamped nucleus Hamiltonian is difficult enough, and hence it is unlikely that calculations will be made at a higher level of approximation in the near future. There are, however, and this is of course the basis of this study, systems like H_2^+ (and its isotopes) for which this statement is definitely not true. These molecules contain so few particles that one need not make "any" approximations in the solving of Schrödinger's equation. Furthermore, since the nuclei are very light, the corrections to the Born-Oppenheimer (1) or adiabatic results will be greater for these molecules than for most others.

4. Theory

The work takes point of reference in the Wigner-Eisenbud (7) R-matrix theory where the configuration space is divided into two regions, a bounded internal interaction region V and an external region in which the interactions have vanished. The mapping of the

internal scattering wave function onto the asymptotic states, $H + H^+$, on the surface S enclosing V is expressed in terms of log-derivative boundary conditions represented by the R -matrix. The variational formulation of the Schrödinger equation and the above associated scattering boundary conditions is conveniently expressed in the J -functional (8) which reads,

$$\begin{aligned} J(\psi, \phi) \equiv & \int dv \left\{ (E - W(\omega)) |\psi(\omega)|^2 - |\nabla \psi(\omega)|^2 \right\} \\ & + \int ds \left\{ \psi^*(\omega) \phi(\omega) + \phi^*(\omega) \psi(\omega) \right\} \\ & - \int ds ds' \left\{ \phi^*(\omega) R_s(\omega, \omega') \phi(\omega') \right\} \end{aligned} \quad (4.1)$$

where $\psi(\omega)$ denotes the scattering amplitude and $\phi(\omega)$ the asymptotic state, $H + H^+$. To reduce the full 3×3 dimensional problem of H_2^+ to just *three dimensions*, 3 translation and 3 rotation coordinates are separated out to yield the following 3 body fixed spheroidal coordinates

$$\begin{aligned} \xi & \equiv \left[|\vec{r} + R/2\vec{e}_3| + |\vec{r} - R/2\vec{e}_3| \right] / R \quad , \text{where } 1 \leq \xi \leq \infty \\ \eta & \equiv \left[|\vec{r} + R/2\vec{e}_3| - |\vec{r} - R/2\vec{e}_3| \right] / R \quad , \text{where } -1 \leq \eta \leq 1 \\ f & \equiv R/2 \quad , \text{where } 0 \leq f \leq \infty \end{aligned} \quad (4.2)$$

where R denotes the inter-nuclear distance and \vec{r} the vector from the nuclear center of mass to the electron. The full scattering wave function, $\psi(\omega)$, is expanded in a series of Sturmian basis functions (10), $\{u_i(\xi, \eta, f), i = 1, \dots, N\}$, i.e. a basis-set where all the members correspond to the same value of the energy.

$$\psi(\omega) = \psi(\xi, \eta, f) = \sum_{i=1}^N u_i(\xi, \eta, f) \quad (4.3)$$

The Sturmian basis functions, $u_i(\xi, \eta, f)$, are in turn expanded in a series of product-functions of linear *finite element method* (FEM) functions (9), $\{h_i(f), i = 1, \dots, N\}$, and Born-Oppenheimer approximate *channel wave functions*, $\{\varphi_j^i(\xi, \eta), j = 1, \dots, M\}$.

$$u_i(\xi, \eta, f) = h_i(f) \sum_{j=1}^M C_j^i \varphi_j^i(\xi, \eta) \quad (4.4)$$

Finally the channel wave functions, $\varphi_j^i(\xi, \eta)$, are expressed in a product basis-set of associated Legendre functions in η and associated Laguerre functions in the ξ coordinate. This particular choice of primitive basis functions in (ξ, η) allows for a very powerful and convenient 2-dimensional *discrete variable representation* scheme (11) to be used. Inserting these basis-expansions, Eq. (4.3-4), into Eq. (4.1) and using some aspects of variational R -matrix theory that emerge from the FEM representation of $\psi(\xi, \eta, f)$ in the f coordinate, the full scattering problem of the hydrogen molecular ion reduces to the following matrix equation.

$$\begin{bmatrix} \bar{A}_{11} & \bar{A}_{12} & \bar{0} & \cdots & \bar{0} \\ \bar{A}_{21} & \bar{A}_{22} & \bar{A}_{23} & \bar{0} & \bar{0} \\ \bar{0} & \bar{A}_{32} & \ddots & \bar{A}_{N-1N} & \vdots \\ \vdots & \bar{0} & \bar{A}_{NN-1} & \bar{A}_{NN} & \bar{u}_N^*(\omega') \\ \bar{0}^T & \bar{0}^T & \cdots & \bar{u}_N^T(\omega) & -R(\omega, \omega') \end{bmatrix} \begin{bmatrix} \bar{C}_1 \\ \bar{C}_2 \\ \vdots \\ \bar{C}_N \\ 1 \end{bmatrix} = \bar{0}, \quad \omega, \omega' \in S \quad (4.5)$$

In this equations \bar{A}_{ij} is a square $M \times M$ matrix representation of the first term in Eq. (4.1), \bar{u}_N and \bar{C}_i are column vector of dimension M and $R(\omega, \omega')$ is a real number (i.e. a one-dimensional matrix). The idea is now to apply a recursive procedure that successively computes $R(\omega, \omega')$ starting at the boundary f_{\max} , and then going inwards to f_{\min} , in such a way that it allow us to judge the possible convergence as more and more functions are included in the domain of small f . It can easily be shown that the solution to the matrix equation (4.5) can be expressed as

$$R = \sum_{k=0}^{N-1} \bar{D}_{N-k}^T \bar{R}_{N-k} \bar{D}_{N-k} \quad (4.6)$$

where

$$\left. \begin{aligned} \bar{D}_k &= \bar{B}_k^T \bar{D}_{k+1} \\ \bar{R}_k &= - \left[\bar{A}_{kk} + \bar{A}_{k+1k}^T \bar{B}_k \right]^{-1} \\ \bar{B}_k &= \bar{R}_{k+1} \bar{A}_{k+1k} \end{aligned} \right\}, \quad 1 \leq k \leq N-1 \quad (4.7)$$

with the following initial expressions for \bar{R}_N and \bar{D}_N .

$$\begin{aligned} \bar{D}_N &\equiv \bar{u}_N \\ \bar{R}_N &\equiv -\bar{A}_{NN}^{-1} \\ \bar{B}_{N-1} &\equiv \bar{R}_N \bar{A}_{NN-1} \end{aligned} \quad (4.8)$$

The amplitudes read as

$$\begin{aligned} \bar{C}_1 &= \bar{R}_1 \bar{D}_1 \\ \bar{C}_k &= \bar{R}_k \bar{D}_k + \bar{B}_{k-1} \bar{C}_{k-1}, \quad 2 \leq k \leq N \end{aligned} \quad (4.9)$$

This recursive formula causes the amplitude of the scattering wave function to be *propagated* from f_{\min} to the boundary f_{\max} . The overall numerical scheme for each scattering calculation is then started by initiating the total scattering wave function, $\psi(\omega)$, with a particular electronic state at the boundary f_{\max} - corresponding to fixing \bar{u}_N in Eq. (4.8) to a desired asymptotic electronic wave function in the incoming channel. This situation is illustrated in figure 1 below.

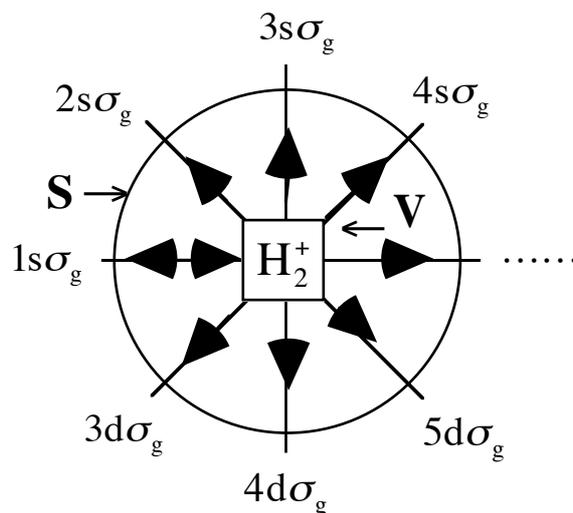


Figure 1 Schematic illustration of a scattering calculation initiated by a $1s\sigma_g$ electronic state. The in- and out-going arrows denote respectively the in- and out-coming channels. All the other channels are assumed to be closed in the calculations.

In the considered scattering calculations the in-coming channels were respectively an electronic $1s\sigma_g$ (as is illustrated in figure 1), $3p\sigma_u$ and $2p\pi_u$ state. Non-adiabatic radial coupling terms were included in the formulation, but angular coupling terms were neglected as a first approximation. Thus coupling between channels with different parity was neglected.

5. Results

As a test of the stability of the overall numerical scheme, the zero order term in the variational functional (i.e. the Born-Oppenheimer term) was evaluated. In table 1 the convergence of the Born-Oppenheimer energy for the $1s\sigma_g$ state with at a fixed nuclear separation ($2.0 a_0$) is shown as the number of grid-points in (ξ, η) is increased.

Table 1

Exact value -0.6026342144949 (12, 13)				
E/au	$N_\xi=5$	10	30	50
$N_\eta=5$	-0.6	-0.6026342	-0.6026342	-0.6026342
10	-0.6	-0.6026342	-0.60263421449	-0.602634214495
30	-0.6	-0.6026342	-0.60263421449	-0.6026342144949
50	-0.6	-0.6026342	-0.60263421449	-0.6026342144949

As suggested by these numbers we found the numerical scheme to be accurate for the zero order term in the functional - down to the floating point precision of the machine. In figure 2 the exact potential energy curves are shown.

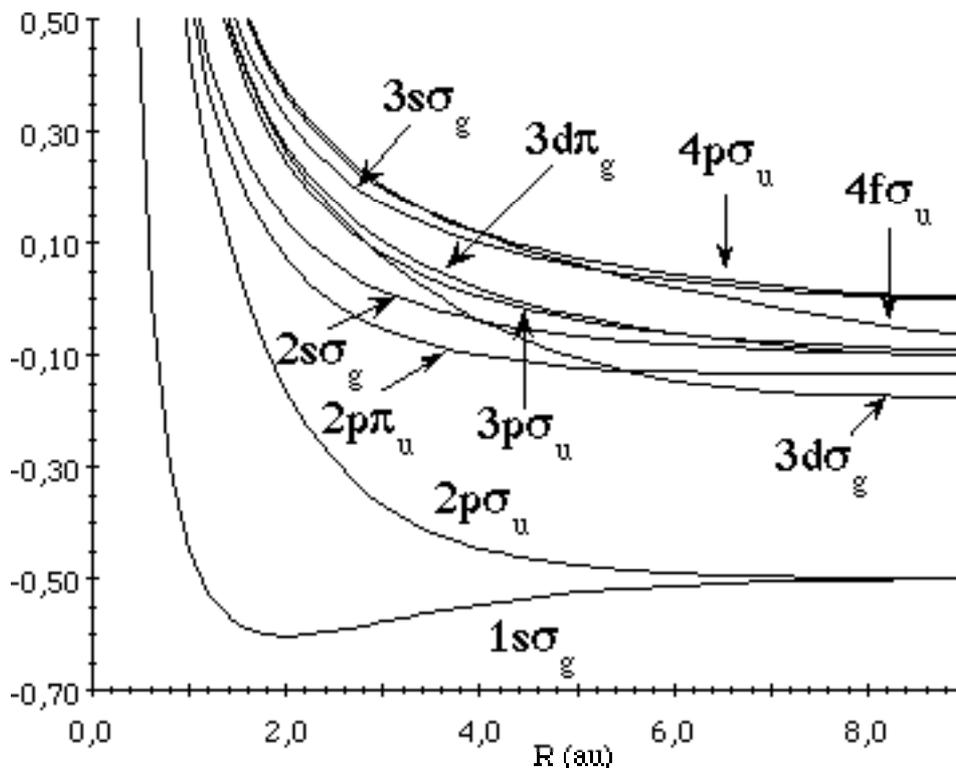


Figure 2 Plot of the electronic potential energy curves for the hydrogen molecular ion.

The FORTRAN code for the full scattering problem has been implemented on the Convex 3220 (hccvix) in Lyngby and the Convex 3240 (beta) in Odense. Because of the size of the presented problem, data had to be buffered to the scratch disk. By extracting the shared steps in the algorithms for different scattering calculations, the high I/O performance of the super-computers made the disk buffering practical. Once the shared data had been computed and stored on disk, additional scattering calculations could be computed with a significant speedup. Using 30 grid points in both of the coordinates (ξ, η) (i.e. $M=900$ in Eq. (4.4)) the computation of the shared data takes roughly 1 CPU hour. Thereafter each scattering calculation ran for 1.5 CPU hour using 500 finite element functions in the f coordinate (i.e. $N=500$ in Eq. (4.3)). In figure 3 and 4 the radial variations of the resulting scattering wave functions are plotted for respectively a $1s_g$ and $3p\sigma_u$ initiated calculation. Note that the classical turning-points (i.e. where the amplitudes fade out rapidly for small f) in figure 3 and 4 are in exact agreement with the respective potential energy curves shown in figure 2. The resulting scattering amplitudes are then used to generate the dipole moment function, which takes 1.5 CPU hour. To obtain a reasonable representation of the total transition dipole moment as a function of the frequency and the temperature we expect to require around 50 of these data points, i.e. 225 CPU hours. Finally to obtain absorption-coefficients for H_2^+ we have to apply a modified version of M. Baranger's "simplified quantum-mechanical theory of pressure

broadening” (14). These absorption spectra should then be compared with the absorption spectra recorded in hydrogen-rich white dwarf atmospheres (4, 15).

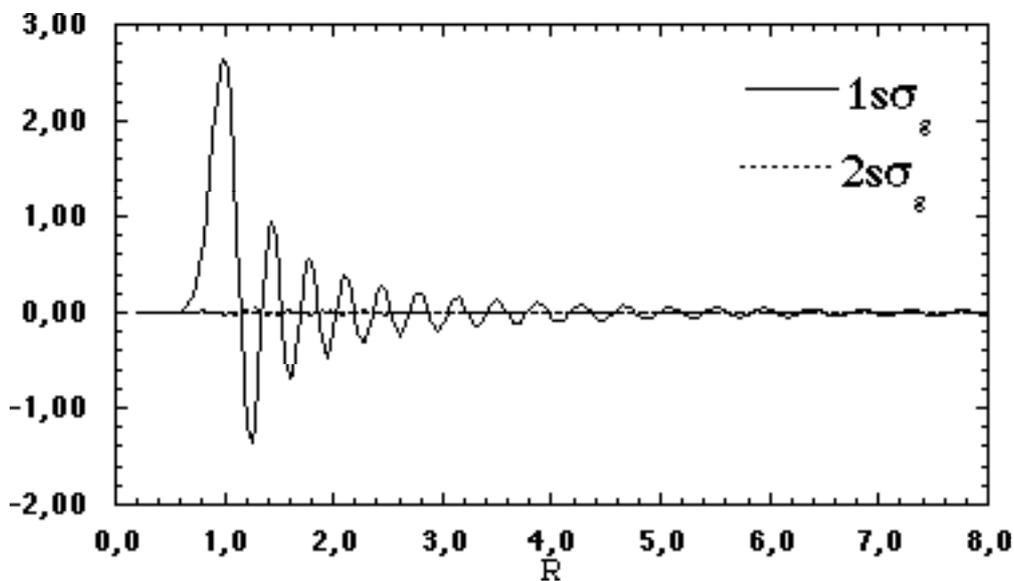


Figure 3 Plot of the radial variation of a scattering wave function initiated by an $1s\sigma_g$ electronic state with energy -0.4000 au.

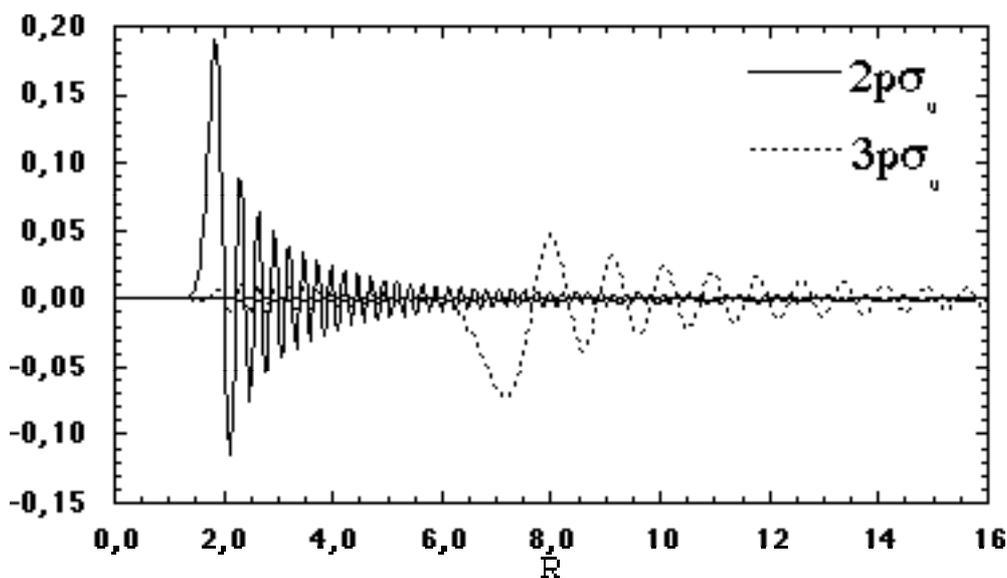


Figure 4 Plot of the radial variation of a scattering wave function initiated by an $3p\sigma_u$ electronic state with energy -0.0745 au.

6. Conclusion

We have demonstrated a new approach to the full quantum mechanical three body problem of the hydrogen molecular ion, using a variational R-matrix method on proton hydrogen scattering. So far this approach has proven to be very versatile and promising,

but it should be emphasized that a conclusive evaluation in terms of comparison with experimental results, still can not be made. However it should be clear from the interim results presented in the previous section that nothing so far indicates that the model suffer from neither numerical instabilities nor subsequent problems with convergence. Actually all the computed wave functions seems to be in excellent agreement with the intuitively expected results using semi-classical arguments. Especially a justification or rather motivation for the Born-Oppenheimer approximation emerge from the calculations. Of the more practical aspects of this project, we would like to stress that it has been a very computationally intensive task to solve this quantum mechanical three body problem, and as such it is not surprising that it has never been attempted before - at least not in this sort of formulation. Besides the fact that the implementation of the variational R-matrix algorithm appears to give correct results, the numerically most exciting aspect of the project was certainly that we obtained exact eigenvalues down to the floating point precision of the computer, for at least the two lowest electronic states of H_2^+ . Thus the developed DVR-scheme has definitely proved practicable and possibly even advantageous to the other numerical schemes used for solving the Born-Oppenheimer approximate states of the hydrogen molecular ion.

As have been pointed out before, the project is not yet completed in terms of obtaining the desired absorption coefficients for H_2^+ . Next we have to compute transition dipole moments from the obtained scattering amplitudes, and from these data the absorption spectra for the hydrogen molecular ion should be generated. Also the development of the non-adiabatic model itself is far from over. Future steps involve inclusion the non-adiabatic angular momentum coupling terms in the variational functional Eq. (4.1). This will introduce coupling between wave functions with difference in unity in the projection angular momentum quantum number, such that states with different parity couples. Consequently many more channels will be open, and the discrete variable representation (DVR) scheme will be complicate by the fact that we must define a new DVR for every value of the projection angular momentum.

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