Computations of electron-molecule collisions: Prototype case of $\text{H}_2^+ + e$ reactions

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Outline

**Lecture 1** : Monday 23 January 2012, 11:15 – 12:00

1. General introduction
2. MQDT and R-matrix approaches in atomic physics
3. Atomic data

**Lecture 2** : Thursday 26 January 2012, 08:30 – 10:00

1. Electron-molecular ion collisions : H$_2^+$ prototype
2. The halfium model
3. Molecular data : Results for H$_2$
4. Ro-vibronic dynamics using frame transformation method
5. Further systems (HeH+, alkali dimers, …)
Computations of electron-molecule collisions : Lecture 2

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5. Further systems (HeH+, LiH, alkali dimers, …)
Hydrogen molecular ion reactions

• \( H_2^+(v)+e \rightarrow H_2^+(v)+e \) (elastic collision)
• \( H_2^+(v)+e \rightarrow H_2^+(v')+e \) (inelastic collision \( v'>v \))
• \( H_2^+(v)+e \rightarrow H_2^+(v')+e \) (superelastic collision \( v'<v \))
• \( H_2^+(v)+e \rightarrow H+H \) (DR)
• \( H_2^+(v)+e \rightarrow H^++H+e \) (DE)
• \( H_2^+(v)+e \rightarrow H^++H^+ +2e \) (DI)
Hydrogen molecular ion reactions

$\text{H}_2^+(v) + e \rightarrow \text{H}_2^* / \text{H}_2^{**}$

Need for \textit{ab initio} characterization of excited and doubly-excited molecular hydrogen
Hydrogen molecule

Erwin Schrödinger
(1887-1961)

$\text{H}_2 = \text{2 protons} + \text{2 electrons}$

stable four-body system

Schrödinger equation

$H_{\text{mol}} \Psi_{\text{mol}} = E_{\text{mol}} \Psi_{\text{mol}}$
Born-Oppenheimer approximation

Max Born
(1882-1970)

Julius Robert Oppenheimer
(1904-1967)

Separation between electronic (fast) and nuclear (slow) motions

\[ H_{\text{mol}} = H_{\text{nuc}} + H_{\text{elec}} \]

\[ \Psi_{\text{mol}}(R, \vec{r}_1, \vec{r}_2) = \Psi_{\text{nuc}}(R)\Psi_{\text{elec}}(\vec{r}_1, \vec{r}_2) \]
ab initio calculations

• Heitler and London (1927)
  W. Heitler
  (1904-1981)

• Hartree and Fock (1926/1927)
  D. Hartree
  (1897-1958)
  V. A. Fock
  (1895-1974)

• James et Coolidge (1933) (breakthrough): Ground state energy improved by 5500 cm⁻¹

5500 cm⁻¹  
1933

• Further improvements (Wolniewicz et al) lowering ground state energy by 222 cm⁻¹

222 cm⁻¹

X¹Σ⁺

1995
ab initio calculations

- Principal molecular symmetries:
  \[ ^1\Sigma_u, ^1\Sigma_g, ^1\Pi_u, ^1\Pi_g, ^1\Delta_u \text{ et } ^1\Delta_g \text{ (singlet)} \]
  \[ ^3\Sigma_u, ^3\Sigma_g, ^3\Pi_u, ^3\Pi_g, ^3\Delta_u \text{ et } ^3\Delta_g \text{ (triplet)} \]

- High quality theoretical data up to \( n = 4 \text{ à } 5 \) (including adiabatic, non-adiabatic, relativistic, radiative corrections,…)\]
  \[ \Delta E(X^1\Sigma_g) = 0.05 \text{ cm}^{-1} \]

For \( n > 5 \) (Rydberg states) and doubly-excited states (resonances) results are scarce!

Alternative method for excited states: the \textit{halfium} model

- The halfium model is based on a combination of two complementary theoretical approaches:
  (i) Variational eigenchannel R-matrix method
  (ii) Generalized multichannel Quantum Defect Theory (GMQDT)
- Need for a simple one-electron reference system: the \textit{halfium} particle
- Two-center symmetry: use of prolate spheroidal coordinates
$H_2$ molecule

$Z_A = +e$  $Z_B = +e$
\( \text{H}_2 \) molecule

\( Z_A = 0 \quad Z_B = +e \)
H$_2$ molecule

$Z_A = +e$, $Z_B = 0$
This is \( \text{HALFIIUM} \)
The halfium is a fictive neutral « particle » intermediate between hydrogen atom and hydrogen molecule.
Prolate spheroidal coordinates

Prolate spheroidal coordinates $(\xi, \eta, \varphi)$

\[
\begin{align*}
\xi &= \frac{r_A + r_B}{R} \\
\eta &= \frac{r_A - r_B}{R}
\end{align*}
\]

\[
\begin{align*}
R &\rightarrow 0 & \frac{2r}{R} & \text{« radial » coordinate} \\
\cos \theta & \rightarrow & \text{« angular » coordinate}
\end{align*}
\]
Generalized Quantum Defect Theory

Two-center Coulomb potential, separable in spheroidal coordinates

\[ \Psi(\xi, \eta, \phi) = \frac{\chi(\xi)}{\sqrt{\xi^2 - 1}} \frac{\zeta(\eta)}{\sqrt{1 - \eta^2}} \frac{1}{\sqrt{2\pi}} \exp i \lambda \phi \]

Generalized Coulomb functions, phase-amplitude formalism

\[ \begin{align*}
  f(\xi) &= \alpha(\xi) \sin \phi(\xi) \\
  g(\xi) &= -\alpha(\xi) \cos \phi(\xi)
\end{align*} \]

Milne equation (1930)

\[ \alpha'' + k^2 \alpha = \frac{1}{\alpha^3} \]

Accumulated phase

\[ \beta = \phi(\infty) \]

\[ \beta = \pi (\nu - \ell) \]

Coulomb potential
Generalized Quantum Defect Theory

\[
\chi(\xi) = f(\xi) \cos(\pi \mu) - g(\xi) \sin(\pi \mu)
\]

The effect of the ionic core electrons is to introduce a phase shift in the radial wave function of the electron by the quantity \(\delta = \pi \mu\), where \(\mu\) is the quantum defect. Any combination of Coulomb functions \(f\) and \(g\) is a solution of radial Schrödinger equation.

- Boundary conditions: \(\lim_{\xi \to \infty} \chi(\xi) = 0\)
- The energy of the Rydberg states converging to the ionization threshold \(A^+\) is given by:

\[
E_n = E_{A^+} - \frac{R_M}{(n - \mu)^2} = E_{A^+} - \frac{R_M}{\nu^2}
\]
The halfium model

Adaptation of the variational eigenchannel R-matrix method

In spheroidal coordinates

Generalized multi-channel quantum defect theory

The halfium model
Interactions inside the reaction volume

Born-Oppenheimer Approximation: fixed geometry

\[ H = H_1 + H_2 + \frac{1}{r_{12}} \]

- Mono-electronic Hamiltonians
- Coulomb Interaction (electron-electron correlation)
electron-electron correlation

\[ \frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \sum_{\mu=-\ell}^{\ell} (-1)^{|\mu|} (2\ell + 1) \left[ \frac{(\ell - |\mu|)!}{(\ell + |\mu|)!} \right]_{|\mu|} P_{\ell}^{(|\mu|)}(\xi_<) Q_{\ell}^{(|\mu|)}(\xi_>) P_{\ell}^{(|\mu|)}(\eta_1) P_{\ell}^{(|\mu|)}(\eta_2) \exp i \mu (\phi_1 - \phi_2) \]

avec
\[
\begin{cases} 
\xi_> = \max(\xi_1, \xi_2) \\
\xi_< = \min(\xi_1, \xi_2)
\end{cases}
\]

First and second kind associated Legendre functions

\[ \frac{1}{r_{12}} = \sum_{k=0}^{\infty} P_{\ell}(\cos \theta) \frac{r_<^k}{r_>^{k+1}} \]
Variational calculation

Expansion of the wavefunction on the variational basis

\[ \Psi(r_1, r_2) = \sum_k c_k y_k(r_1, r_2) \]

Kohn variational principle

\[ \delta b = 0 \iff \frac{\partial b}{\partial c_k} = 0 \]

Generalized eigensystem

\[ \Gamma c = b \Lambda c \]

Interaction matrix

\[ \Gamma = 2(EO - H - L) \]

Surface matrix

\[ \Lambda \]

For each given energy \( E \)

Solutions having stationary logarithmic derivative \( b_\beta \) on the reaction surface.
Matching on the reaction surface

Outside ($\xi < \xi_0$)

$$\Psi_{\beta} = \sum_{i=1}^{N} c_k^\beta y_k$$

Outside ($\xi > \xi_0$)

$$\Psi_{\alpha} = \sum_{i=1}^{N} \Phi_i(\omega) U_i^{\alpha} \frac{1}{\sqrt{\xi^2-1}} \left[ f_i(\xi)\cos\pi\mu_\alpha - g(\xi)\sin\pi\mu_\alpha \right]$$

Projection over the surface harmonics $\Phi_i(\omega)$

Short-range reaction matrix $K$

$$K_{ij} = \sum_{\alpha=1}^{N} U_{i\alpha} \tan \pi\mu_\alpha U^+_{\alpha j}$$

Eigenquantum defects
Quantum defects

• Bound states: below the ionization threshold ($\varepsilon < 0$)

$$\det \left| U_{i\alpha} \sin \left( \beta_i + \pi \mu_{\alpha} \right) \right| = 0$$ Secular equation

Adiabatic potential curves

• Resonances: above the ionization threshold ($\varepsilon > 0$)

State density

$$ds(E) = \frac{d}{dE} \sum_{\rho} \tau_{\rho}$$ Breit-Wigner lorentzian shape

Positions and widths of the resonances

Positions and widths of the resonances
Applications to H₂


• *gerade* $^1\Sigma_g^+$, $^1\Pi_g$ and $^1\Delta_g$ symmetries S. Bezzaouia, M. Telmini and Ch. Jungen, *Phys. Rev A* 70 012713 (2004)


**ung erad e** $^1\Sigma_u^+$ and $^1\Pi_u$ symmetries


- **Goal:** unified *ab initio* description of both bound spectrum and continuum.

- **Criteria:**
  
  - (i) *smooth* quantum defects as functions of energy and bond length
  
  - (ii) energies with *good accuracy* (prototype calculation)

- $^1\Sigma_u^+$ Symmetry

  Four channels calculation

  $R=1$ to 5 u.a. and $E=-0.2$ à 0.1 u.a
ungerade $^{1}\Sigma_{u}^{+}$ and $^{1}\Pi_{u}$ symmetries


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R=1 to 5 u.a. and E= -0.2 à 0.1 u.a
Radial mono-electronic functions closed-type

\[ R=2 \text{ a.u. } \xi_0=8.5 \]

- \( \lambda \): good quantum number
- \( \ell \): number of nodes of the angular function \( (\ell - \lambda) \)
- \( n \): number of nodes of the radial function \( (n - \ell - 1) \)

\[ \Psi(\xi, \eta, \varphi) = \frac{\chi(\xi)}{\sqrt{\xi^2 - 1}} \frac{\zeta(\eta)}{\sqrt{1 - \eta^2}} \frac{1}{\sqrt{2\pi}} \exp i\lambda\varphi \]

0 1 2 3 4 5 6 7 8 9
-3
-2
-1
0
1
2
3
\( \chi(\xi) \)

\( \xi \)
Radial mono-electronic functions closed-type

$R=2$ a.u. $\xi_0=8.5$

$\lambda$: good quantum number

$\ell$: number of nodes of the angular function $(\ell - \lambda)$

$n$: number of nodes of the radial function $(n - \ell - 1)$
Radial mono-electronic functions closed-type

\[ R = 2 \text{ a.u.} \quad \xi_0 = 8.5 \]
Radial mono-electronic functions closed-type

$R = 2$ a.u. $\xi_0 = 8.5$
Radial mono-electronic functions closed-type

$R=2 \text{ a.u.} \quad \xi_0=8.5$
Radial mono-electronic functions closed-type

R=2 a.u. $\xi_0=8.5$
Molecular symmetry and good quantum numbers

- $H_2$ symmetry quantum numbers can be expressed easily with one-electron quantum numbers:
  - $\Lambda = |\lambda_1 + \lambda_2|$
  - parity: u/g is the parity of $(\ell_1 + \ell_2)$

- Spin symmetrization

$$ y_{ij}(\vec{r}_1, \vec{r}_2) = N_{ij} \left[ \phi_i(\vec{r}_1)\phi_j(\vec{r}_2) + (-1)^S \phi_j(\vec{r}_1)\phi_i(\vec{r}_2) \right] $$

- $\sigma_v$ symmetrization (for $\Sigma$ symmetries $\Lambda=0$)

$$ \overline{y}_{ij}(\vec{r}_1, \vec{r}_2) = \overline{N}_{ij} \left[ y_{ij}^+(\vec{r}_1, \vec{r}_2) + (-1)^I y_{ij}^+(\vec{r}_1, \vec{r}_2) \right] $$
Matrix elements

- Hamiltonian matrix:

\[
H_{ij,i'j'} = \langle \psi_{ij} | H | \psi_{i'j'} \rangle = (E_j + E_{j'}) O_{ij,i'j'} + \langle \psi_{ij} | \frac{1}{r_{12}} | \psi_{i'j'} \rangle
\]

- electron-electron interaction:

\[
\frac{1}{r_{12}} = \frac{2}{R} \sum_{\ell=0}^{\infty} \sum_{\mu=-\ell}^{\ell} (-1)^{|\mu|} (2\ell + 1) \left[ \frac{(\ell - |\mu|)!}{(\ell + |\mu|)!} \right]^{\mu|} P_{\ell}^{\mu|} (\xi_\ell) Q_{\ell}^{\mu|} (\xi_\ell) P_{\ell}^{\mu|} (\eta_1) P_{\ell}^{\mu|} (\eta_2) \exp i \mu (\varphi_1 - \varphi_2)
\]

where

\[
\begin{aligned}
\xi_\ell &= \max(\xi_1, \xi_2) \\
\xi_\ell &= \min(\xi_1, \xi_2)
\end{aligned}
\]

For more details: PRA 68 062704 (2003)
Matching solutions

- **On the reaction surface** ($\xi = \xi_0$): Set of orthogonal surface harmonics $\Phi_i(\omega)$

- **From inside** ($\xi < \xi_0$): Variational R-matrix solution
  
  \[ \Psi_\beta = \sum_{k=1}^{n} C_k^\beta y_k \]

  \[ y_{ij}(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^{N} \Phi_i(\omega) \frac{1}{\sqrt{\xi_0^2 - 1}} u_j(\xi_0) \]

- **From outside** ($\xi > \xi_0$):

  \[ \Psi_\beta(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^{N} \Phi_i(\omega) \frac{1}{\sqrt{\xi_0^2 - 1}} \left[ f_i(\xi_0) I_{i\beta} - g_i(\xi_0) J_{i\beta} \right] \]

- **Matching** : projection of $\Psi_\beta$ on $\Phi_i$

  \[
  \begin{align*}
  u_{i\beta}(\xi_0) &= \langle \Phi_i | \Psi_\beta \rangle \Sigma = f_j(\xi_0) I_{ij} - g_j(\xi_0) J_{ij} \\
  u'_{i\beta}(\xi_0) &= \langle \Phi_i | \Psi'_\beta \rangle \Sigma = -b_{\beta} u_{i\beta} = f'_j(\xi_0) I_{ij} - g'_j(\xi_0) J_{ij}
  \end{align*}
  \]
**ungerade** $^1\Sigma_u^+$ et $^1\Pi_u$ symétries


Previous attempts did not overcome this challenge (Greene et Yoo 1995)

**eigenquantum defects** $\mu_\alpha(E,R)$ are smooth functions of $R$ and $E$
ungerade $^1Σ_u^+$ and $^1Π_u$ symmetries


Effective quantum number:

\[
\nu = n - \delta
\]

\[
U_n(R) = U^+(R) - \frac{1}{\nu^2(R)}
\]

Comparison best available theoretical *ab initio* data (Wolniewicz et al.)

We have obtained $\Delta \nu \sim 0.02$

Scale law:

\[
\Delta E = \frac{\Delta \nu}{\nu^3}
\]

\[
\begin{align*}
  n = 2 & \quad \Delta E = 540 \text{ cm}^{-1} \\
  n = 10 & \quad \Delta E = 4 \text{ cm}^{-1}
\end{align*}
\]
Interpolation of quantum defects and state density


Diagonal quantum defects $\mu_{ii}(E,R)$

$^1\Pi_u$ symmetry (3 open channels)
Interpolation of quantum defects and state density


Off-diagonal quantum defects $\mu_{ii}(E,R)$

$^1\Pi_u$ symmetry (3 open channels)
Interpolation of quantum defects and state density

Interpolation of quantum defects and state density


$R = 2$ a.u.  **Resonances**
Interpolation of quantum defects and state density

Interpolation of quantum defects and state density


R=4 a.u.  Resonances
Gerade Symmetries $^{1}\Sigma_{g}^{+}$, $^{1}\Pi_{g}$ et $^{1}\Delta_{g}$


• Goal: *unified* *ab initio* description of both bound spectrum and continuum.

• Criteria:
  
  - (i) *smooth* quantum defects as functions of energy and bond length
  
  - (ii) Reproduce the double-well structure in the adiabatic potential energy curves
  
  - (iii) Positions and widths of resonances

$^{1}\Sigma_{g}^{+}$ Symmetry

Four channels calculation

$R=1$ to 5 a.u. and $E= -0.2$ to 0.1 a.u
Gerade Symmetries $^{1}\Sigma_g^+ , ^{1}\Pi_g \text{ et } ^{1}\Delta_g$


Unified treatment of bound spectrum and continuum
Photoionisation

Calculation dipolar transition momenta and photoionization cross sections

Photoionization ground state \( X \, ^1\Sigma_g^+ \)

Beutler-Fano profile around \( 2p\sigma 3d\pi \, ^1\Pi_u \) resonance
Highly-excited resonances


\[ U(R) \text{ (u.a.)} \]

\[ R(u.a.) \]

\[ n=3 \, H_2^+ \]

\[ X^1\Sigma_g^+ \]

\[ Q_4 \text{ and } Q_5 \text{ resonances } ^1\Pi_u \text{ @ } R=1.4 \text{ u.a.} \]
$1,3\Sigma_{u/g}^{-}$ metastable states

- Electronically stable states at high energy (~26eV)
- Scarce theoretical results:
  - Komasa: PCCP 10 3383 (2008) Lowest state in each symmetry
- Lack of experimental spectra (spectroscopy, storage rings ?)
- Assessment of the accuracy of the halfium code ($\sigma_v$ symmetrization)
- This symmetrization is expected to improve the accuracy of the code for $\Sigma^+$ doubly-excited states known to be important for $\text{H}_2^+$ dissociative recombination ($Q_1$ and $Q_2$ resonances)
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

Soumaya Bezzaoui¹, Fatma Argoubi¹, Mourad Telmini¹,² and Christian Jungen³,⁴

Deviations $\Delta v = v - v_{ab}$ of effective quantum numbers before (0) and after (●) symmetrization with respect to ab initio quantum chemistry codes results [1] as function of bond length $R$ in atomic units for (a) 2s$\sigma$, (b) 3s$\sigma$ et (c) 4s$\sigma$ states of $1\Sigma^+_g$ symmetry.

Schematic view at fixed R

Bound states

Rydberg series

Four $\Sigma^-$ symmetries: $^1\Sigma_g^-$, $^3\Sigma_g^-$, $^1\Sigma_u^-$, $^3\Sigma_u^-$

Non-autoionizing states

Resonances

continuum

1s$\sigma$

2p$\sigma$

2p$\pi$
BO energy curves: $^{1,3}\Sigma_{g/u}^-$ symmetries
BO energy curves: $^1,^3\Sigma^-_{g/u}$ symmetries
Eigenquantum defect as a function of energy and bond length

$1\Sigma_g^-$ symmetry

Two-channel calculation

Quite smooth dependence of quantum defects with $E$ and $R$
Rydberg series: \(^1\Sigma_g^-\) states

<table>
<thead>
<tr>
<th>state</th>
<th>(R=1)</th>
<th>(R=2)</th>
<th>(R=3)</th>
<th>(R=4)</th>
<th>(R=5)</th>
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</thead>
<tbody>
<tr>
<td>(3p\pi)</td>
<td>(v^*)</td>
<td>(v(\text{ha}))</td>
<td>(\Delta v)</td>
<td>(v^*)</td>
<td>(v(\text{ha}))</td>
</tr>
<tr>
<td>1</td>
<td>2,534</td>
<td>2,536</td>
<td>0.002</td>
<td>2,597</td>
<td>2,602</td>
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<tr>
<td>(4p\pi)</td>
<td>3,572</td>
<td>3,580</td>
<td>0.008</td>
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<td>3,647</td>
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<tr>
<td>(4f\pi)</td>
<td>3,947</td>
<td>3,976</td>
<td>0.029</td>
<td>3,921</td>
<td>3,959</td>
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<tr>
<td>(5p\pi)</td>
<td>4,594</td>
<td>4,594</td>
<td>0.000</td>
<td>4,659</td>
<td>4,661</td>
</tr>
<tr>
<td>(5f\pi)</td>
<td>4,952</td>
<td>4,966</td>
<td>0.014</td>
<td>4,935</td>
<td>4,946</td>
</tr>
</tbody>
</table>

Higher Rydberg states at will
Rydberg series: $^1\Sigma_g^-$ states, $R>5$ a.u.

<table>
<thead>
<tr>
<th>state</th>
<th>R(a.u.)</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3pπ</td>
<td>2,888</td>
<td>2,952</td>
<td>3,011</td>
<td>3,064</td>
<td>3,117</td>
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<tr>
<td>2</td>
<td>4pπ</td>
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<td>3,679</td>
<td>3,569</td>
<td>3,468</td>
<td>3,365</td>
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<tr>
<td>3</td>
<td>4fπ</td>
<td>3,934</td>
<td>3,992</td>
<td>4,045</td>
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<tr>
<td>4</td>
<td>5pπ</td>
<td>4,749</td>
<td>4,680</td>
<td>4,613</td>
<td>4,564</td>
<td>4,524</td>
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<tr>
<td>5</td>
<td>5fπ</td>
<td>4,945</td>
<td>5,004</td>
<td>5,048</td>
<td>5,104</td>
<td>5,141</td>
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<tr>
<td>6</td>
<td>6pπ</td>
<td>5,747</td>
<td>5,685</td>
<td>5,589</td>
<td>5,581</td>
<td>5,549</td>
</tr>
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<td>6fπ</td>
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<td>7,150</td>
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<td>10</td>
<td>8pπ</td>
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<td>7,689</td>
<td>7,633</td>
<td>7,593</td>
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BO energy curves : $^1\Sigma_g^-$ states
Rydberg series: \(^{1}\Sigma_u^-\) states

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<td>(\Delta v)</td>
<td>(v^*)</td>
<td>(v(\text{ha}))</td>
<td>(\Delta v)</td>
</tr>
<tr>
<td>1 (3d\pi)</td>
<td>2,767</td>
<td>2,766</td>
<td>0,001</td>
<td>2,664</td>
<td>2,662</td>
</tr>
<tr>
<td>2 (4d\pi)</td>
<td>3,775</td>
<td>3,782</td>
<td>0,007</td>
<td>3,695</td>
<td>3,709</td>
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<tr>
<td>3 (5d\pi)</td>
<td>4,79</td>
<td>4,786</td>
<td>0,004</td>
<td>4,711</td>
<td>4,717</td>
</tr>
<tr>
<td>4 (5g\pi)</td>
<td>4,976</td>
<td>4,999</td>
<td>0,023</td>
<td>4,971</td>
<td>4,998</td>
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<tr>
<td>5 (6d\pi)</td>
<td>6,252</td>
<td>5,787</td>
<td>0,465</td>
<td>6,079</td>
<td>5,720</td>
</tr>
<tr>
<td>6 (6g\pi)</td>
<td>5,998</td>
<td>5,996</td>
<td>5,987</td>
<td>5,988</td>
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Comparison with Martin calculation: highest states are questionable.
Rydberg series

\[ n^* \]

\[ R \text{ (a.u.)} \]
BO energy curves: $^1\Sigma_u^-$ states
BO energy curves: $^3\Sigma_u^-$ states

![BO energy curves](image-url)
### Lowest $^{3}\Sigma_g^{-} (2p\pi)^2$ state

<table>
<thead>
<tr>
<th>R(a.u.)</th>
<th>Komasa</th>
<th>Martin</th>
<th>Halfium</th>
<th>H-K</th>
<th>H-M</th>
<th>M-K</th>
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Comparaison of the lowest states

Comparaison

Komasa
(Chimie Quantique)

ABOTJ

$2p\pi$

$1\Sigma_g^-$

$3\Sigma_g^-$

$1\Sigma_u^-$

$3\Sigma_u^-$

$2p\pi$

$1\Sigma_g^-$

$3\Sigma_g^-$

$1\Sigma_u^-$

$3\Sigma_u^-$

$U$(eV)

$R$(a.u.)
Lowest $\ ^3\Sigma_g^-$ $(2p\pi)^2$ state

Frame transformation: rovibronic MQDT (Ch. Jungen)
BO energy curves

\[ \begin{align*}
\text{energy (a.u.)} & \quad \text{internuclear distance (a.u.)} \\
& \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12
\end{align*} \]
Ro-vibronic dynamics of $\text{H}_2$
Rovibronic MQDT : The frame transformation approach combined with QDT

• The foundations of this theory have been advanced by Fano (1970)

• A more complete theory was formulated by Jungen and Atabek (1977)

• The extension to spin has been formulated by Jungen and Raseev (1997)
The rovibronic Hamiltonian

\[
H = \left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 + V \right] + \left[ -\frac{\hbar^2}{8\mu} \sum_{i,j=1}^{n} \nabla_i \nabla_j - \frac{\hbar^2}{2\mu_\alpha} \nabla_R \sum_{i=1}^{n} \nabla_i \right] H_e + H'_e
\]

\[-\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \frac{R^2 \partial}{\partial R} \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} - \frac{i}{\hbar} L_z \cot \theta \right)^2 - \frac{1}{\hbar^2} \left( L_x^2 + L_y^2 \right) \right] H_v
\]

\[-\frac{\hbar^2}{2\mu R^2} \left( -2 \frac{i}{\hbar} L_x \frac{\partial}{\partial \theta} - 2 \frac{i}{\hbar} L_y \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} - \frac{i}{\hbar} L_z \cot \theta \right) \right) \right] \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} - \frac{i}{\hbar} L_z \cot \theta \right) \right] \right] H'_r
\]

Close-coupling method

Theoretical methods

The frame transformation approach
The adiabatic potential energy curves of Rydberg states are obtained by solving the following secular equation:

$$\det \left| \tan(\beta_i) \delta_{ij} + K_{ij}(E) \right| = 0$$

where:

$$K_{ij} = \sum_{\alpha=1}^{N} U_{i\alpha} \tan \pi \mu_{\alpha} U_{\alpha j}^+$$

We then use the frame transformation technique, using the electronic quantum defect matrices, to calculate rovibronic reaction matrix and therefore the rovibronic energy levels:

$$K_{i v_i^+ N_i^+, j v_j N_j^+} = \int dR^{JM} [U K_{ij}^{(R)}]^{JM} U^+$$

S. C Ross and Ch. Jungen, PRA, 49, 6, 1994
The frame transformation elements are a product of a rotational and a vibrational factor:

\[ U_{i\alpha} = \langle i | \alpha \rangle = \langle v^+ | R \rangle^{N^+} \langle N^+ | \Lambda \rangle^{LJ} \]

where:

\[ \langle v^+ | R \rangle^{N^+} = \chi_{v^+}^{(N^+)}(R) \]

and

\[ \langle N^+ | \Lambda \rangle = \frac{1}{(1 + \delta_{\Lambda^0 \Lambda^0})^{1/2}} \frac{1}{(1 + \delta_{\Lambda^+ \Lambda^0})^{1/2}} \]

\[ \ast (2N^+ + 1)^{1/2}(-1)^{N^-} \]

\[ \ast \left[ 1 + \delta_{\Lambda^- \Lambda^0}(-1)^{l-N^+p-q} \right] \]

\[ \ast \left( \begin{array}{ccc} N & l & N^+ \\ \Lambda & \Lambda^+ - \Lambda & \Lambda^+ \end{array} \right) \]

The expression of the quantum defects is then obtained as:

\[ \mu_{v^+N^+,v^+';N^+'} = \sum \langle N^+ | \Lambda \rangle \left[ \int dR \langle v^+ | R \rangle^{N^+} \mu_{\Lambda}(R) \langle R | v^+ \rangle^{N^+'} \right] \langle \Lambda | i | N^+ \rangle^{LJ} \]
The frame transformation approach

The vibrational core wave functions depend on both the electronic state (implicit in the index \( i \)) and the core rotational quantum number.

\[
\mathbf{K}_{\nu^+ N^+_i \nu'^+ N'^+_j} = \int dR \langle \nu^+_i \, N^+_i \, \nu'^+_j \, N'^+_j \mid \sum_{\Lambda} \langle i\, R\, \Lambda \mid K_{\nu \nu'}^{\Lambda}(R) \mid j\, R\, \Lambda \rangle \rangle
\]
The frame transformation approach

When the Rydberg electron is close to the core:
The Coulomb attraction leads the electron to move very quickly compared to nuclei: BO approximation
• It is coupled to the internuclear axis.
• \( \Lambda \) is well defined.
• The potential energy \( U(R) \) is characterized by \( \{R, \Lambda\} \).

When the Rydberg electron is far from the core:
• The motion of the electron is slow compared to the nuclear motion: BOP.
• It is uncoupled to the internuclear axis.
• The rovibronic molecular wavefunctions of \( H_2 \) is obtained by a products of the adiabatic functions for the ions, characterized by: \( \{v^+, N^+\} \).
Quantum defects of $^3\Pi_u$ and $^3\Sigma_u^+$ symmetries
(The rovibronic MQDT calculation are defined in new manner)

Symétrie $^3\Pi_u$ de H$_2$

$K_{ij}^{\Pi}(R)$

Symétrie $^3\Sigma_u$ de H$_2$

$K_{ij}^{\Sigma}(R)$

R. Gérout, Ch. Jungen, H. Oueslati, S. C. Ross and M. Telmini
Comparison of observed and calculated rovibronic energies levels of $^3\Pi_u$ states of $\text{H}_2$
Comparison of observed and calculated rovibronic energies levels of $^3\Pi_u^-$ states of $H_2$
Comparison of observed and calculated term values for the \( c^- (2p\pi) \) state

<table>
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<tr>
<th>( \nu )</th>
<th>( N=1 )</th>
<th>Ross et al [1]</th>
<th>Our results</th>
<th>( N=2 )</th>
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<th>( N=3 )</th>
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<td>( \text{Exp (cm}^{-1}\text{)} )</td>
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Comparison of observed and calculated rovibronic energies levels of $^3\Pi_u^+$ and $^3\Sigma_u^+$ states of H$_2$
Comparison of observed and calculated term values for the: $c^+ (2p\pi)$ state

<table>
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<th>N=1 Exp (cm$^{-1}$) [2]</th>
<th>Our results</th>
<th>N=2 Exp (cm$^{-1}$) [2]</th>
<th>Our results</th>
<th>N=3 Exp (cm$^{-1}$) [2]</th>
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Comparison of observed and calculated term values for the: e (3pσ) state

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<th>Our results</th>
<th>N=2 Exp (cm⁻¹) [2]</th>
<th>Our results</th>
<th>N=3 Exp (cm⁻¹) [2]</th>
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Generalization to other two-electron molecular systems

- **HeH\(^+\)**: should be straightforward

- **Alkali dimers**: model potentials

```
\begin{align*}
\text{HeH}^+ & : \text{should be straightforward} \\
\text{Li}^+ & : \text{model potentials}
\end{align*}
```

![Diagram of electron configurations](image)
Conclusion

• The halfium model: original theoretical approach to study highly excited (Rydberg) states and doubly excited (resonance) states of molecular hydrogen.

• The halfium code generates molecular data that may be useful in many fields including fusion plasma modelling.

• $\sigma_v$ symmetrization allows for discrimination between $\Sigma^+$ and $\Sigma^-$ states.

• Ro-vibronic dynamics using electronic quantum defects and frame transformation.

• Possible generalization to other molecular systems ($\text{HeH}^{++}, \text{LiH}, \text{Li}_2, \ldots$).