Atomic and Molecular Processes in Fusion Edge Plasmas

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Outline of the lecture

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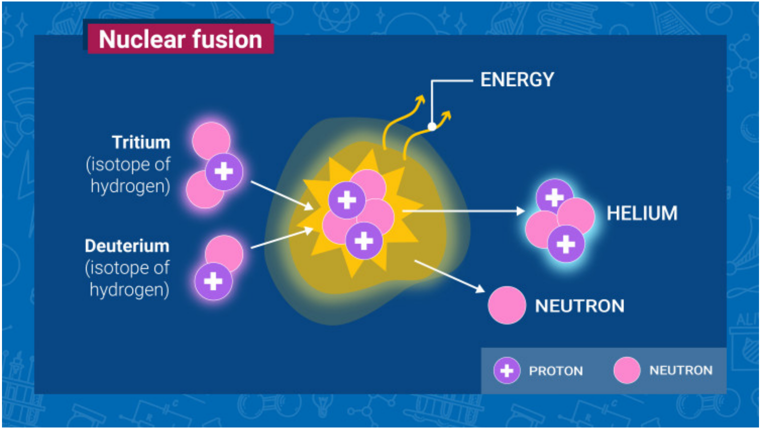
Nuclear fusion

- Lecture by Dr. Ayman Al-Bataineh : Nuclear Reactions and Nuclear Fusion



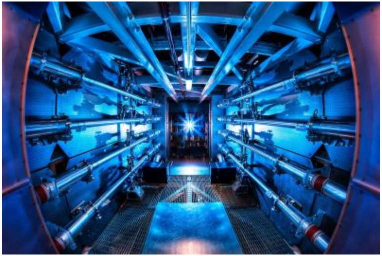
- Credits : Matteo Barbarino, IAEA

Why is nuclear fusion so important?

- Limitless energy production, available all over the world, not subject to local or seasonal variations;
- No greenhouse gas emissions;
- No accidents such as melt-downs or explosions, due to an intrinsically safe physical process;
- No production of radioactive waste with long half-lives;
- No or only a modest proliferation risk.

How to implement nuclear fusion ?

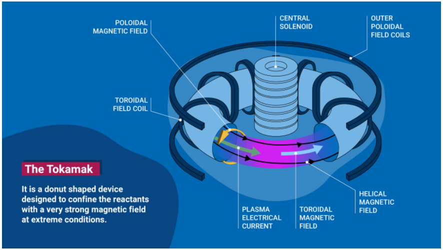
Inertial confinement fusion



Credits: National Ignition Facility, LLNL

This approach is based on maximizing density by the rapid compression and heating of a small solid DT pellet through the use of lasers or particle beams.

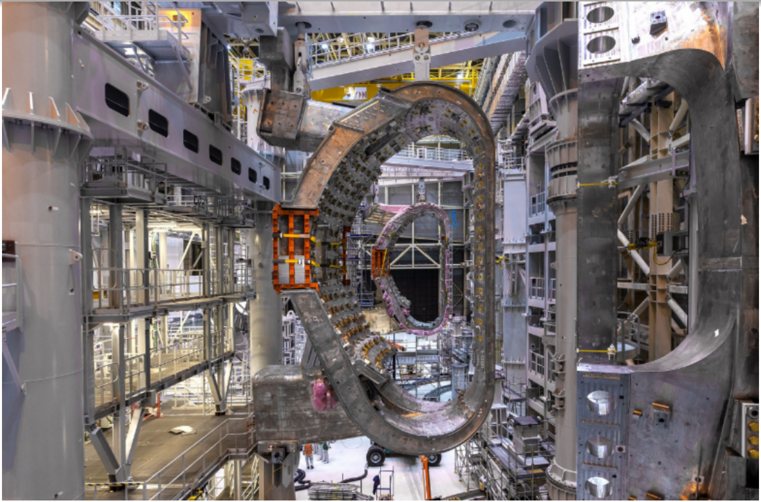
Magnetic confinement fusion



Credits : Matteo Barbarino, IAEA

Magnetic confinement fusion is based on the fact that ions and electrons forming the hot plasma can be confined by strong magnetic fields.

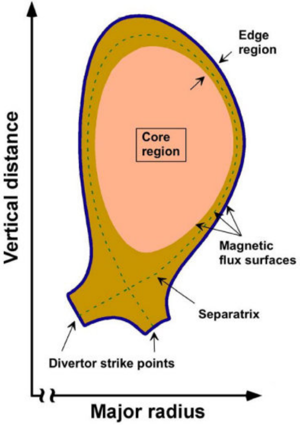
Plasma fusion devices



credits: www.iter.org

Lecture by Dr. Amro Bader : Plasma Technology and the ITER Project

Plasma regions in tokamaks



Credits: M. Tillack, et al, Nuclear Fusion, 53(2), 027003 (2013)

- The core region is where the plasma is fully confined.
- The separatrix, separates the confined plasma from the Edge region.
- The x-point, which is where the separatrix reconnects on itself,
- the divertor which is used for a controlled energy deposition to the outside at the strike points.

Key role of the Edge plasma region

- The Egde plasma region is an interface between the hot burning deuterium-tritium plasma and the cold material walls of the reactor vessel.
- It has to protect the Tokamak walls from the intense particle and power fluxes generated in the reactor burning zone.
- It has to secure the protection of the central plasma from contamination by non-hydrogenic wall impurities (which dilute the thermonuclear fuel and degrade the burn conditions)
- It should exhaust of the thermal plasma power and the reactor ash (thermalized helium), etc.
- Reference : Atomic and molecular processes in Fusion edge plasmas, edited by R. K. Janev, Springer (1995)

Key role of the Edge plasma region

- Because of the low temperatures prevailing in the plasma edge region, the edge plasma composition contains significant fractions of neutral hydrogen and low-charged atomic and molecular impurities produced in plasma-wall interactions.
- The range of collision processes involving plasma electrons and ions, hydrogenic neutrals, and wall impurities is extremely large.
- These processes, affect the plasma edge properties and behavior (e.g., ionization balance, plasma energy and momentum losses, plasma transport, etc.)
- In-depth understanding of atomic and molecular processes in the edge plasma region is necessary for a realistic modelling of the fusion device functioning.

Outline of the lecture

Atomic and molecular processes in Fusion edge plasmas

- The most important of these processes, from the standpoint of their effects on plasma edge are :
    - the electron impact excitation and ionization of plasma edge atoms, ions, and molecules,
    - electron-ion recombination, elastic and momentum transfer collisions of plasma electrons and ions with the plasma edge neutrals,
    - dissociative processes in electron-molecule (molecular ion) collisions
    - Electron capture in ion-atom (molecule) collisions, and energy transfer and reactive ion-molecule collisions.
- In the following, we focus on electron-molecule collisions

Molecular data for electron collisions plasma physics

- International Thermonuclear Experimental Reactor (ITER) : (H-K Chung 2012)
  - Neutrals and molecules are present at the edge of the plasma ($T = 0.1 - 200\ eV$ and $n = 10^{19} - 10^{21}\ m^{-3}$
  - Important molecular systems : H_2, H_2^*, H_2^+, H_3^+, H_2O, CO, CO_2, CH_4, CH, C_2, BeH,BeD,BeT, oxids, nitrats, hydrocarbons nd radicals including hydrogen isotopic variants,
  - Plasma-surface interaction: BeW, BeC, BeN, WF_6, ...
- Cryogenic Storage Ring (CSR) : (www.mpi-hd.mpg.de)
  - So far the stored ion beam energies for singly charged ions, molecules and clusters are in the range from 35 to 280 keV.
  - The following positive and negative ions were stored in the past five years: HD^+, H_3^+, D_2^+, H_2D^+, HeH^+, C^-, CH^+, O^-, OH^+, OH^-, F^{6+}, C_2^-, Si^-, Ar^+, C_4O^-, TiO^+, Al_4^-, Ni_2^-, Co_2^-, Co_3^-, Au^-, Ag_2^-, Co_4^+.

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Molecules versus Atoms

- Characteristics of the electron-molecule collisions as distinct from those of the electron-atom collisions are as follows:
- Molecules have rotational and vibrational degrees of freedom which can be excited by a small amount of energy as compared with the electronic excitation (below the first ionization threshold).
- The electron-molecule interaction is essentially multicentered and nonspherical. The polarizability of the target molecule is anisotropic, and molecules have various permanent electric multipole moments.
- These features make the theoretical study of electron-molecule collisions more difficult than that of the electron-atom collisions.

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Main electron-molecule collisional processes (case of diatomic molecule)

- Elastic Scattering : $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{AB} + \mathrm{e}^-$
- Rotational Excitation : $\mathrm{AB}\ (j) + \mathrm{e}^- \rightarrow \mathrm{AB}\ (j' > j) + \mathrm{e}^-$
  where j denotes the rotational state of the molecule.
- Vibrational Excitation : $\mathrm{AB}\ (v = 0\ ) + \mathrm{e}^- \rightarrow \mathrm{AB}\ (v' > 0) + \mathrm{e}^-$
  where v denotes the vibrational state of the target.
- Electronic Excitation : $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{AB}^* + \mathrm{e}^-$
  where the asterisk labels an electronically excited state.
- Dissociative Attachment: $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{A}^- + \mathrm{B}$ or $\mathrm{A} + \mathrm{B}^-$
- Dissociative Recombination for a cation : $\mathrm{AB}^+ + \mathrm{e}^- \rightarrow \mathrm{A} + \mathrm{B}$.
- Impact Dissociation: $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{A} + \mathrm{B} + \mathrm{e}^-$
  which in practice usually goes via electronic excitation.

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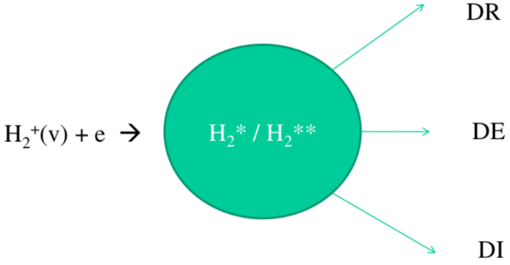
Intermediate compound

- All these processes generally occur via a common compound AB (or AB^-). An accurate description of this intermediary system is crucial for the quality of any theoretical method.



Energy ranges

- The energy range can be roughly divided into three domains :
    - low-energy regime (below the ionization threshold of the target)
    - intermediate energy regime (threshold and energies just above it)
    - high-energy region : (far above threshold)
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Low and intermediate energy range

- At low-energy collisions and related processes such as photoionization, the physics is complicated with many subtle effects and many possible outcomes.
- The cross sections can show very-complicated patterns of sharp resonances. We already emphasized the importance of the intermediate compound.
- The main ab initio methods are based on :
  - Schwinger multi-channel theory.
  - Complex Kohn variational method.
  - $R-$matrix method (with its various versions).
- In general highly excited states (Rydberg) play an important role in the processes (e.g. : indirect DR process). The Multichannel Quantum Defect Theory (MQDT) provides a very convenient framework for the analysis of the system.

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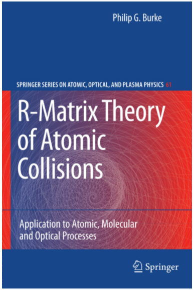
The R−matrix Theory

- The R−matrix method was originally invented by Wigner and Eisenbud (1947) in the context of nuclear collisions.
- It was adapted to atomic physics by Burke *et al.* and later to molecular physics.
- The UK R−matrix code (Tennyson *et al.*) is widely used today and is very successful in the study of electron-molecule collisions, including polyatomic systems.



Philip G. Burke

SPRINGER SERIES ON ATOMIC, OPTICAL, AND PLASMA PHYSICS 61

R-Matrix Theory of Atomic Collisions

Application to Atomic, Molecular and Optical Processes

Springer

- In the following, I will present a specific version of R−matrix (Halfium), for diatomic systems.

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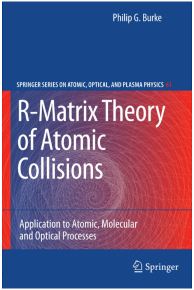
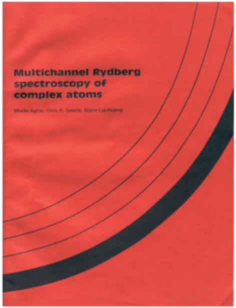


- In the following, I will present a specific version of $R-$matrix (Halfium), for diatomic systems.

Outline of the lecture

1. Introduction: Nuclear fusion and plasma
2. Atomic and Molecular Processes in Fusion Edge Plasmas
3. Theoretical models: Halfium R-matrix method
4. Molecular processes and spectroscopy
5. Conclusion

Eigenchannel $R-$matrix Theory for Atoms



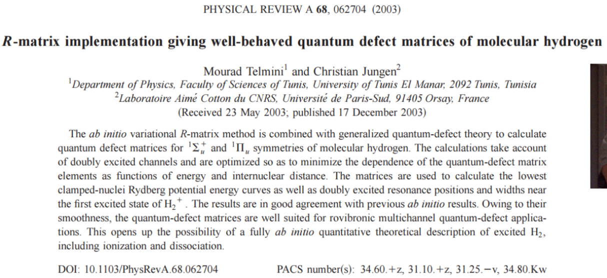
Multichannel Rydberg spectroscopy of complex atoms

Mireille Aymar, Chris H. Greene, Eliane Luc-Koenig

M. Aymar, C.H. Greene and E. Luc-Koenig, Rev. Mod. Phys. **68** 1015 (1996)

- Applied successfully to Alkaline-earth atoms
- Adapted to diatomic molecules (Telmini and Jungen) : Halfium $R-$matrix

Halfium model : R-matrix + MQDT



PHYSICAL REVIEW A **68**, 062704 (2003)

R-matrix implementation giving well-behaved quantum defect matrices of molecular hydrogen

Mourad Telmini[1] and Christian Jungen[2]
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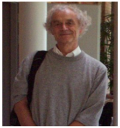
[2]*Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France*

(Received 23 May 2003; published 17 December 2003)

The *ab initio* variational *R*-matrix method is combined with generalized quantum-defect theory to calculate quantum defect matrices for $^1\Sigma_u^+$ and $^1\Pi_u$ symmetries of molecular hydrogen. The calculations take account of doubly excited channels and are optimized so as to minimize the dependence of the quantum-defect matrix elements as functions of energy and internuclear distance. The matrices are used to calculate the lowest clamped-nuclei Rydberg potential energy curves as well as doubly excited resonance positions and widths near the first excited state of H_2^+. The results are in good agreement with previous *ab initio* results. Owing to their smoothness, the quantum-defect matrices are well suited for rovibronic multichannel quantum-defect applications. This opens up the possibility of a fully *ab initio* quantitative theoretical description of excited H_2, including ionization and dissociation.

DOI: 10.1103/PhysRevA.68.062704 PACS number(s): 34.60.+z, 31.10.+z, 31.25.−v, 34.80.Kw



Development from scratch of a code (HALFIUM)
for Rydberg and continuum states of H_2

Diatomic molecule : Interactions and Hamiltonian

- The standard non-relativistic electronic Hamiltonian is (in a.u.):

$$H = -\frac{1}{2}\sum_{i=1}^{n}\Delta_i - \sum_{i=1}^{n}(\frac{Z_A}{r_A} + \frac{Z_B}{r_B}) + \sum_{j>i}\sum_{i=1}^{n}\frac{1}{r_{ij}}$$

with :

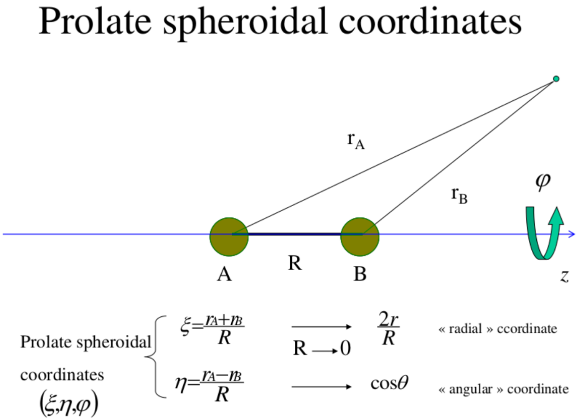
$$\frac{1}{r_{ij}} = \sum_{\ell=0}^{\infty}\frac{r_<^{\ell}}{r_>^{\ell+1}}P_\ell(\cos\theta_{ij})$$

where $r_< = min(r_1, r_2)$ and $r_> = max(r_1, r_2)$.

- Electronic Hamiltonian (one-electron system):

$$H = -\frac{1}{2}\Delta - \left[\frac{Z_A}{r_A} + \frac{Z_B}{r_B}\right]$$

One-electron case



Prolate spheroidal coordinates

Prolate spheroidal coordinates (ξ,η,φ)

$$\begin{cases} \xi = \frac{r_A+r_B}{R} \xrightarrow[R\to 0]{} \frac{2r}{R} & \text{« radial » ccordinate} \\ \eta = \frac{r_A-r_B}{R} \xrightarrow{} \cos\theta & \text{« angular » coordinate} \end{cases}$$

Schrödinger equation

- The hamiltonian becomes :

$$H = -\frac{1}{2}\Delta - \frac{2}{R}\Big[\frac{(Z_A + Z_B)\xi + (Z_B - Z_A)\eta}{\xi^2 - \eta^2}\Big]$$

- The Coulomb two-center Schrödinger equation :

$$\Psi(\xi, \eta, \phi) = E\Psi(\xi, \eta, \varphi)$$

  is separable in prolate spheroidal coordinates and the wavefunction is factorized as :

$$\Psi(\xi, \eta, \phi) = \frac{\chi(\xi)}{\sqrt{\xi^2 - 1}} \frac{\zeta(\eta)}{\sqrt{1 - \eta^2}} \frac{Z(\varphi)}{2\pi}$$

- The azimuthal function $Z(\varphi) = e^{i\lambda\varphi}$, where $\lambda = 0, \pm 1, \pm 2, \cdots$ is a good quantum number associated to the projection of the electronic angular momentum on the internuclear axis, and will serve in labelling the molecular orbitals.

Radial and Angular functions

- The "radial" function $\chi(\xi)$ and the "angular" function $\zeta(\eta)$ are solution of the following equations :

$$\frac{d^2\chi}{d\xi^2} + \Big[\frac{A + (Z_A + Z_B)R\xi - p^2\xi^2}{\xi^2 - 1} + \frac{1-\lambda^2}{(\xi^2-1)^2}\Big]\chi(\xi) = 0$$
$$\frac{d^2\zeta}{d\eta^2} + \Big[\frac{-A + (Z_A - Z_B)R\eta + p^2\eta^2}{1 - \eta^2} + \frac{1-\lambda^2}{(1-\eta^2)^2}\Big]\zeta(\eta) = 0$$

  which are analogous to the radial and angular equations of the hydrogen atom, in spherical coordinates ($R \longrightarrow 0$).

- However, a main difference is that the separation constant A depends on energy, while it does not in the spherical case $(A = -\ell(\ell+1))$.
- Analytical exact expressions of $\chi(\xi)$ and $\zeta(\eta)$ exist (in series of powers of ξ or η). Also, these equations are very easily integrated numerically.

Angular functions

- For given λ, the angular function satisfies the boundary conditions $\zeta(\eta = \pm 1) = 0$. So only quantized eigensolutions with given number of nodes $(\tilde{\ell} - \lambda)$ are allowed , which defines the "angular" quantum number $\tilde{\ell} = \lambda, \lambda + 1, \cdots$.
- The notation $\tilde{\ell}$ is used to avoid any confusion with the standard angular momentum ℓ which is a good quantum number associated with L^2 operator, only in the spherical case.

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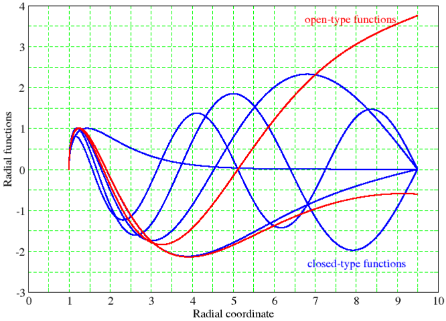
Radial functions

- For given λ and $\tilde{\ell}$, the radial equation gives rise to a series of quantized eigenfunctions with $(n - \tilde{\ell} - 1)$ nodes, when a boundary vanishing condition is imposed to $\chi(\xi)$ at infinity (or at a finite distance as well). $n = \tilde{\ell} + 1, = \tilde{\ell} + 2, \cdots$ is a good quantum number associated with the eigenenergy.



One-electron wavefunctions

- The one-electron two-center Coulomb problem is well mastered and can serve as a reliable ingredient for more complex systems.
- The eigenstates of the system are characterized by a set of 3 quantum numbers :
  - the azimuthal quantum number $\lambda = 0, \pm 1, \pm 2, \cdots$
  - the "angular" quantum number $\tilde{\ell} = \lambda, \lambda + 1, \cdots$
  - the principal quantum number $n = \tilde{\ell} + 1, \tilde{\ell} + 2, \cdots$
- These 3 quantum numbers serve to label the eigenstates of the one-electron system as $|n\tilde{\ell}\lambda\rangle$.
- Used for spectroscopic notations in analogy with atomic case, *e.g.*, the fundamental state of H_2^+ is $1\tilde{s}\sigma$, etc.

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- Used for spectroscopic notations in analogy with atomic case, *e.g.*, the fundamental state of H_2^+ is $1\tilde{s}\sigma$, etc.

One-electron wavefunctions

- The one-electron two-center Coulomb problem is well mastered and can serve as a reliable ingredient for more complex systems.
- The eigenstates of the system are characterized by a set of 3 quantum numbers :
  - the azimuthal quantum number $\lambda = 0, \pm 1, \pm 2, \cdots$
  - the "angular" quantum number $\tilde{\ell} = \lambda, \lambda + 1, \cdots$
  - the principal quantum number $n = \tilde{\ell} + 1, \tilde{\ell} + 2, \cdots$
- These 3 quantum numbers serve to label the eigenstates of the one-electron system as $|n\tilde{\ell}\lambda\rangle$.
- Used for spectroscopic notations in analogy with atomic case, *e.g.*, the fundamental state of H_2^+ is $1\tilde{s}\sigma$, etc.

Two-electron diatomic system

- The hamiltonian can be written as :

$$\mathbf{H} = \mathbf{H_1} + \mathbf{H_2} + \frac{1}{r_{12}}$$

where $\mathbf{H_i}; i = 1, 2$ is the one-electron hamiltonian already presented, which has eigenenergies $E_{n\tilde{\ell}\lambda}$ and associated eigenstates $|n\tilde{\ell}\lambda\rangle$, or equivalent wavefunctions $\Psi_{n\tilde{\ell}\lambda}(\xi, \eta, \varphi)$.

- The electron-electron term is the master piece in the problem and should be handled with caution. In prolate spheroidal coordinate, we use the Von Neuman expasion :

$$\frac{1}{r_{12}} = \frac{2}{R}\sum_{\ell=0}^{\infty}\sum_{\mu=-\ell}^{\ell}(-1)^{|\mu|}(2\ell+1)\Big(\frac{(\ell-|\mu|)!}{(\ell+|\mu|)!}\Big)^2 \times P_\ell^{|\mu|}(\xi_<)Q_\ell^{|\mu|}(\xi_>)P_\ell^{|\mu|}(\eta_<)P_\ell^{|\mu|}(\eta_>)e^{i\mu(\varphi_2-\varphi_1)}$$

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$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{\ell=0}^{\infty} \sum_{\mu=-\ell}^{\ell} (-1)^{|\mu|} (2\ell + 1) \left(\frac{(\ell - |\mu|)!}{(\ell + |\mu|)!} \right)^2 \times P_\ell^{|\mu|}(\xi_<) Q_\ell^{|\mu|}(\xi_>) P_\ell^{|\mu|}(\eta_<) P_\ell^{|\mu|}(\eta_>) e^{i\mu(\varphi_2 - \varphi_1)}$$

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- Note the analogy of the same term in the spherical coordinates:

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$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{4\pi}{2\ell+1}\frac{r_<^\ell}{r_>^{\ell+1}}Y_{\ell m}(\theta_1,\varphi_1)Y_{\ell m}^*(\theta_2,\varphi_2)$$

- Indeed, the first kind $P_\ell^\mu(\xi)$ and second kind $Q_\ell^\mu(\xi)$ associate Legendre functions have the following asymptotic spherical limit:

$$P_\ell^\mu(\xi) \simeq \frac{(2\ell)!}{2^\ell(\ell-\mu)!\ell!}\xi^\ell$$

$$Q_\ell^\mu(\xi) \simeq \frac{2^\ell(\ell+\mu)!\ell!}{(2\ell+1)!}\frac{1}{\xi^{\ell+1}}$$

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R-matrix calculations

- It is possible to proceed with CI calculation in spheroidal coordinates [Harris,...]. However, the same drawbacks will be eventually faced (huge configuration space)
- Alternative : $R-$matrix treatment, where the full CI calculations are performed in a finite volume and a simplified physics is assumed outside.
- In the asymptotic region where a major assumption is made : only one electron can escape from the R-matrix volume. This means that the size of the volume should contain the wavefunction of the remaining core.
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R-matrix in prolate spheroidal coordinates

- Halfium $R-$matrix method is based on the use of prolate spheroidal coordinates and the the raction volume is an ellipsoid with focii A and B.
- Moreover, the outermost electron is assumed to evolve in a two-center Coulomb field created by two effective charges (Z_A and Z_B) placed on A and B, and defined so that they describe the screening of the nuclei by the inner electron(s).
- In the case of H_2, the symmetry imposes that $Z_A = Z_B = e/2$, so that the molecule is modelled with the fictive neutral system having fractional nuclear charges; the so-called Halfium system.

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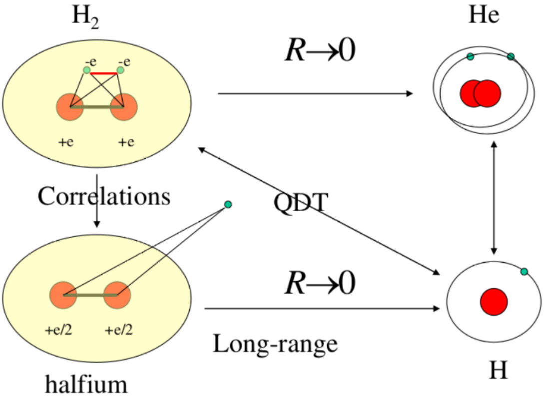
The halfium model

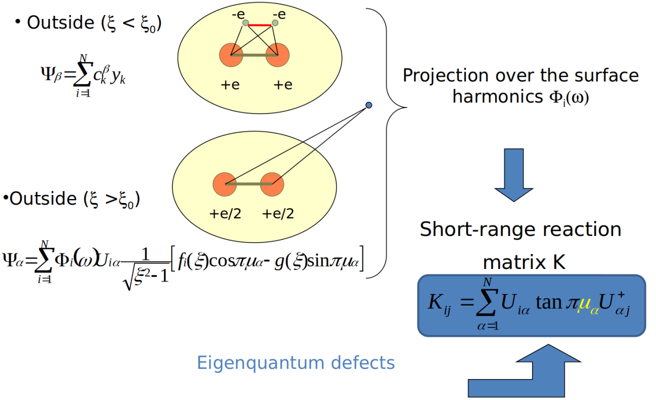


Robert S. Mulliken

(1896-1986)

« Demi- H_2^+ »

Halfium R-matrix method



- 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

Outline of the lecture

Main processes (case of diatomic molecule)

- Elastic Scattering : $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{AB} + \mathrm{e}^-$
- Rotational Excitation : $\mathrm{AB}\ (j) + \mathrm{e}^- \rightarrow \mathrm{AB}\ (j' > j) + \mathrm{e}^-$
  where j denotes the rotational state of the molecule.
- Vibrational Excitation : $\mathrm{AB}\ (v = 0\ ) + \mathrm{e}^- \rightarrow \mathrm{AB}\ (v' > 0) + \mathrm{e}^-$
  where v denotes the vibrational state of the target.
- Dissociative Attachment: $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{A}^- + \mathrm{B}$ or $\mathrm{A} + \mathrm{B}^-$
- Dissociative Recombination for a cation : $\mathrm{AB}^+ + \mathrm{e}^- \rightarrow \mathrm{A} + \mathrm{B}$.
- Electronic Excitation : $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{AB}^* + \mathrm{e}^-$
  where the asterisk labels an electronically excited state.
- Impact Dissociation: $\mathrm{AB} + \mathrm{e}^- \rightarrow \mathrm{A} + \mathrm{B} + \mathrm{e}^-$
  which in practice usually goes via electronic excitation.

Interface with stepwise MQDT

- Dissociative recombination of H_2^+ and HD^+ (work done in collaboration with Ioan Schneider).
- Necessity to take into account both direct and indirect processes

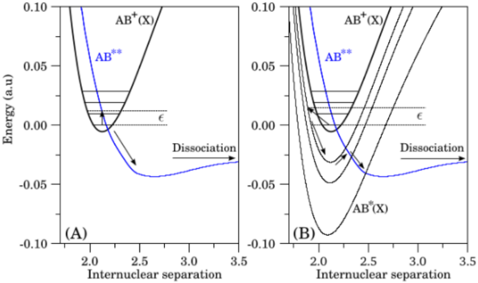
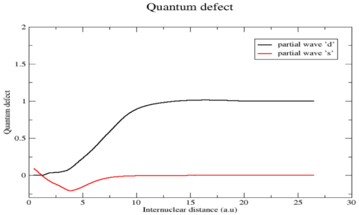
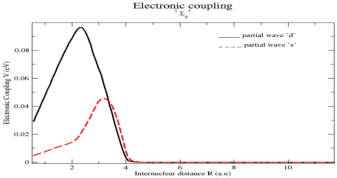


Figure 3.2: Dissociative recombination mechanisms: **(A)** Direct mechanism: A dissociative state of the neutral (blue line) crossing the ion potential energy curve (black line). The electron is captured into this state and then dissociation occurs. **(B)** Indirect mechanism: The electron is first captured on a vibrational level of the neutral state belonging to a Rydberg series which converges to the ground state of the ion, coupled to the resonant state leading to dissociation.

credits : A. Abdulanziz, PhD thesis 2021

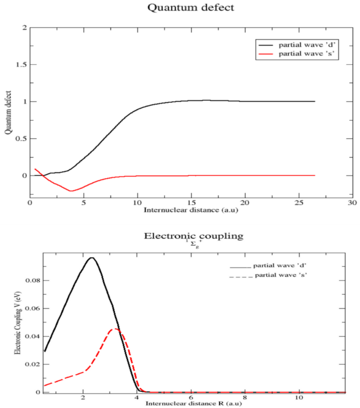
Prototype calculation: $e+H_2^+$ DR





Halfium input: Quantum defects & resonance widths (couplings)

Prototype calculation: e+H_2^+ DR



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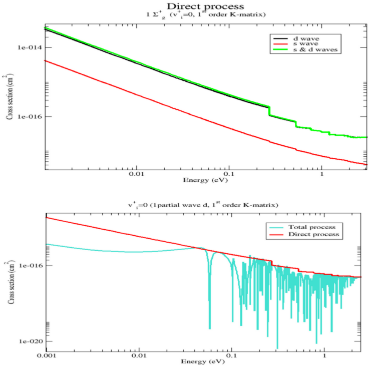
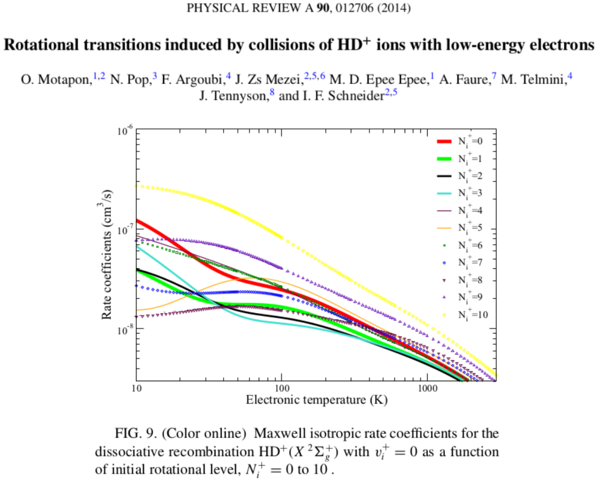


Stepwise MQDT output: Cross sections and rates

Rotational excitations in HD^+



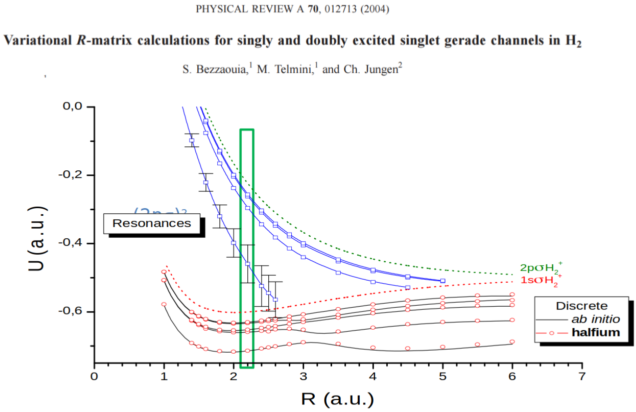
PHYSICAL REVIEW A **90**, 012706 (2014)

Rotational transitions induced by collisions of HD^+ ions with low-energy electrons

O. Motapon,[1,2] N. Pop,[3] F. Argoubi,[4] J. Zs Mezei,[2,5,6] M. D. Epee Epee,[1] A. Faure,[7] M. Telmini,[4]
J. Tennyson,[8] and I. F. Schneider[2,5]

FIG. 9. (Color online) Maxwell isotropic rate coefficients for the dissociative recombination $HD^+(X\,^2\Sigma_g^+)$ with $v_i^+=0$ as a function of initial rotational level, $N_i^+=0$ to 10 .

Spectroscopy and accuracy assessment



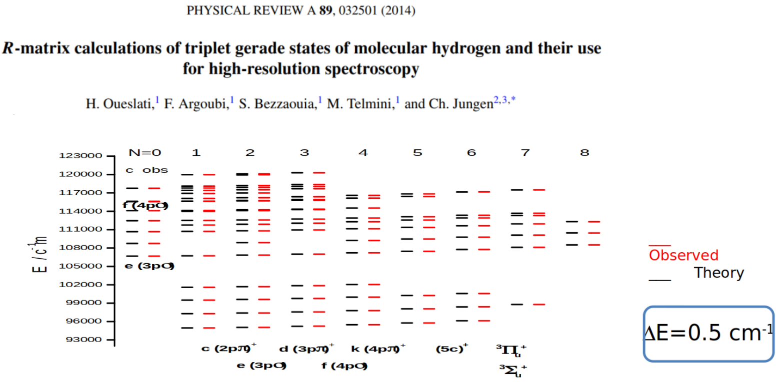
PHYSICAL REVIEW A **70**, 012713 (2004)

Variational *R*-matrix calculations for singly and doubly excited singlet gerade channels in H_2

S. Bezzaouia,[1] M. Telmini,[1] and Ch. Jungen[2]

Halfium model : unified treatment of bound and continuum spectra

Ro-vibronic dynamics: Frame transformation



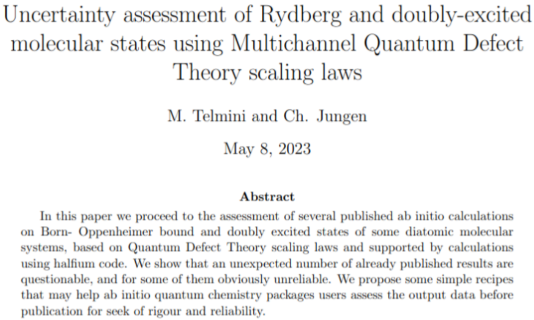
PHYSICAL REVIEW A **89**, 032501 (2014)

***R*-matrix calculations of triplet gerade states of molecular hydrogen and their use for high-resolution spectroscopy**

H. Oueslati,[1] F. Argoubi,[1] S. Bezzaouia,[1] M. Telmini,[1] and Ch. Jungen[2,3,*]

- Using frame-transformation technique (Fano, Jungen, Atabek)
- H_3^+ DR (Kokooouline and Greene)

Accuracy assesement of ab initio calculations: H_2



Uncertainty assessment of Rydberg and doubly-excited molecular states using Multichannel Quantum Defect Theory scaling laws

M. Telmini and Ch. Jungen

May 8, 2023

Abstract

In this paper we proceed to the assessment of several published ab initio calculations on Born- Oppenheimer bound and doubly excited states of some diatomic molecular systems, based on Quantum Defect Theory scaling laws and supported by calculations using halfium code. We show that an unexpected number of already published results are questionable, and for some of them obviously unreliable. We propose some simple recipes that may help ab initio quantum chemistry packages users assess the output data before publication for seek of rigour and reliability.

H_2 $^1\Sigma_g^+$ excited states

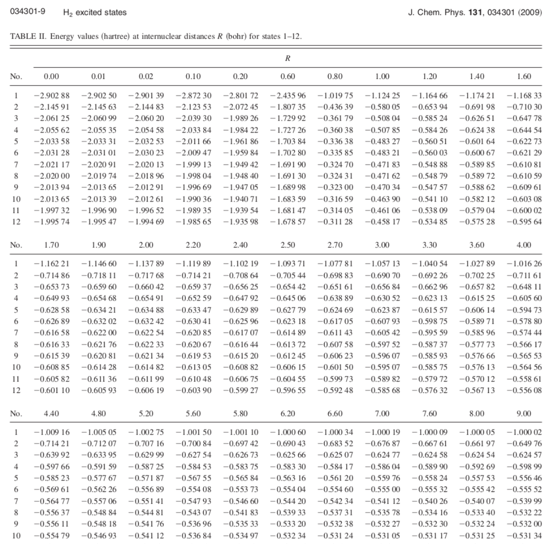


TABLE II. Energy values (hartree) at internuclear distances R (bohr) for states 1–12.

	R										
No.	0.00	0.01	0.02	0.10	0.20	0.60	0.80	1.00	1.20	1.40	1.60
1	−2.902 88	−2.902 50	−2.901 39	−2.872 30	−2.801 72	−2.435 96	−1.019 75	−1.124 25	−1.164 66	−1.174 21	−1.168 33
2	−2.145 91	−2.145 63	−2.144 83	−2.123 53	−2.072 45	−1.807 35	−0.436 39	−0.580 05	−0.653 94	−0.691 98	−0.710 30
3	−2.061 25	−2.060 99	−2.060 20	−2.039 30	−1.989 26	−1.729 92	−0.361 79	−0.508 04	−0.585 24	−0.626 51	−0.647 78
4	−2.055 62	−2.055 35	−2.054 58	−2.033 84	−1.984 22	−1.727 26	−0.360 38	−0.507 85	−0.584 26	−0.624 38	−0.644 54
5	−2.033 58	−2.033 31	−2.032 53	−2.011 66	−1.961 86	−1.703 84	−0.336 38	−0.483 27	−0.560 51	−0.601 64	−0.622 73
6	−2.031 28	−2.031 01	−2.030 23	−2.009 47	−1.959 84	−1.702 80	−0.335 85	−0.483 21	−0.560 03	−0.600 67	−0.621 29
7	−2.021 17	−2.020 91	−2.020 13	−1.999 13	−1.949 42	−1.691 90	−0.324 70	−0.471 83	−0.548 88	−0.589 85	−0.610 81
8	−2.020 00	−2.019 74	−2.018 96	−1.998 04	−1.948 40	−1.691 30	−0.324 31	−0.471 62	−0.548 79	−0.589 72	−0.610 59
9	−2.013 94	−2.013 65	−2.012 91	−1.996 69	−1.947 05	−1.689 98	−0.323 00	−0.470 34	−0.547 57	−0.588 62	−0.609 61
10	−2.013 65	−2.013 39	−2.012 61	−1.990 36	−1.940 71	−1.683 59	−0.316 59	−0.463 90	−0.541 10	−0.582 12	−0.603 08
11	−1.997 32	−1.996 90	−1.996 52	−1.989 35	−1.939 54	−1.681 47	−0.314 05	−0.461 06	−0.538 09	−0.579 04	−0.600 02
12	−1.995 74	−1.995 47	−1.994 69	−1.985 65	−1.935 98	−1.678 57	−0.311 28	−0.458 17	−0.534 85	−0.575 28	−0.595 64

No.	1.70	1.90	2.00	2.20	2.40	2.50	2.70	3.00	3.30	3.60	4.00
1	−1.162 21	−1.146 60	−1.137 89	−1.119 89	−1.102 19	−1.093 71	−1.077 81	−1.057 13	−1.040 54	−1.027 89	−1.016 26
2	−0.714 86	−0.718 11	−0.717 68	−0.714 21	−0.708 64	−0.705 44	−0.698 83	−0.690 70	−0.692 26	−0.702 25	−0.711 61
3	−0.653 73	−0.659 60	−0.660 42	−0.659 37	−0.656 25	−0.654 42	−0.651 61	−0.656 84	−0.662 96	−0.657 82	−0.648 11
4	−0.649 93	−0.654 68	−0.654 91	−0.652 59	−0.647 92	−0.645 06	−0.638 89	−0.630 52	−0.623 13	−0.615 25	−0.605 60
5	−0.628 58	−0.634 21	−0.634 88	−0.633 47	−0.629 89	−0.627 79	−0.624 69	−0.623 87	−0.615 57	−0.606 14	−0.594 73
6	−0.626 89	−0.632 02	−0.632 42	−0.630 41	−0.625 96	−0.623 18	−0.617 05	−0.607 93	−0.598 75	−0.589 71	−0.578 80
7	−0.616 58	−0.622 00	−0.622 54	−0.620 85	−0.617 07	−0.614 89	−0.611 43	−0.605 42	−0.595 59	−0.585 96	−0.574 44
8	−0.616 33	−0.621 76	−0.622 33	−0.620 67	−0.616 44	−0.613 72	−0.607 58	−0.597 52	−0.587 37	−0.577 73	−0.566 17
9	−0.615 39	−0.620 81	−0.621 34	−0.619 53	−0.615 20	−0.612 45	−0.606 23	−0.596 07	−0.585 93	−0.576 66	−0.565 53
10	−0.608 85	−0.614 28	−0.614 82	−0.613 05	−0.608 82	−0.606 15	−0.601 50	−0.595 07	−0.585 75	−0.576 13	−0.564 56
11	−0.605 82	−0.611 36	−0.611 99	−0.610 48	−0.606 75	−0.604 55	−0.599 73	−0.589 82	−0.579 72	−0.570 12	−0.558 61
12	−0.601 10	−0.605 93	−0.606 19	−0.603 90	−0.599 27	−0.596 55	−0.592 48	−0.585 68	−0.576 32	−0.567 13	−0.556 08

No.	4.40	4.80	5.20	5.60	5.80	6.20	6.60	7.00	7.60	8.00	9.00
1	−1.009 16	−1.005 05	−1.002 75	−1.001 50	−1.001 10	−1.000 60	−1.000 34	−1.000 19	−1.000 09	−1.000 05	−1.000 02
2	−0.714 21	−0.712 07	−0.707 16	−0.700 84	−0.697 42	−0.690 43	−0.683 52	−0.676 87	−0.667 61	−0.661 97	−0.649 76
3	−0.639 92	−0.633 95	−0.629 99	−0.627 54	−0.626 73	−0.625 66	−0.625 07	−0.624 77	−0.624 58	−0.624 54	−0.624 57
4	−0.597 66	−0.591 59	−0.587 25	−0.584 53	−0.583 75	−0.583 30	−0.584 17	−0.586 04	−0.589 90	−0.592 69	−0.598 99
5	−0.585 23	−0.577 67	−0.571 87	−0.567 55	−0.565 84	−0.563 16	−0.561 20	−0.559 76	−0.558 24	−0.557 53	−0.556 46
6	−0.569 61	−0.562 26	−0.556 89	−0.554 08	−0.553 73	−0.554 04	−0.554 60	−0.555 00	−0.555 32	−0.555 42	−0.555 52
7	−0.564 77	−0.557 06	−0.551 41	−0.547 93	−0.546 60	−0.544 20	−0.542 34	−0.541 12	−0.540 26	−0.540 07	−0.539 99
8	−0.556 37	−0.548 84	−0.544 81	−0.543 07	−0.541 83	−0.539 33	−0.537 31	−0.535 78	−0.534 16	−0.533 40	−0.532 22
9	−0.556 11	−0.548 18	−0.541 76	−0.536 96	−0.535 33	−0.533 20	−0.532 38	−0.532 27	−0.532 30	−0.532 24	−0.532 00
10	−0.554 79	−0.546 93	−0.541 12	−0.536 84	−0.534 97	−0.532 34	−0.531 24	−0.531 05	−0.531 17	−0.531 25	−0.531 34
11	−0.548 82	−0.540 88	−0.538 54	−0.534 61	−0.532 69	−0.529 45	−0.526 97	−0.525 21	−0.524 09	−0.523 87	−0.523 47

Accuracy assessment of ab initio calculations

- How to assess the accuracy of *ab initio* calculations ?
  - Ritz variational principle : the lower the better!
  - Ground state : Benchmark, virtually exact.
  - What about excited states ?
  - How to select only converged roots ?
- We propose a simple method based on MQDT scaling laws and Quantum defect analysis

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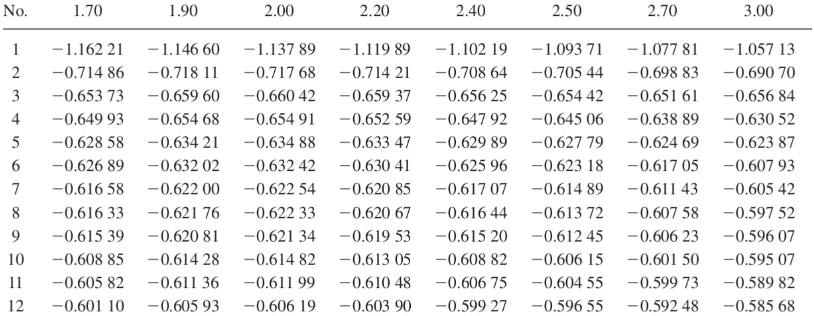
- We propose a simple method based on MQDT scaling laws and Quantum defect analysis

Accuracy assessment of ab initio calculations

- How to assess the accuracy of *ab initio* calculations ?
  - Ritz variational principle : the lower the better!
  - Ground state : Benchmark, virtually exact.
  - What about excited states ?
  - How to select only converged roots ?
- We propose a simple method based on MQDT scaling laws and Quantum defect analysis

H_2 $^1\Sigma_g^+$ excited states



No.	1.70	1.90	2.00	2.20	2.40	2.50	2.70	3.00
1	−1.162 21	−1.146 60	−1.137 89	−1.119 89	−1.102 19	−1.093 71	−1.077 81	−1.057 13
2	−0.714 86	−0.718 11	−0.717 68	−0.714 21	−0.708 64	−0.705 44	−0.698 83	−0.690 70
3	−0.653 73	−0.659 60	−0.660 42	−0.659 37	−0.656 25	−0.654 42	−0.651 61	−0.656 84
4	−0.649 93	−0.654 68	−0.654 91	−0.652 59	−0.647 92	−0.645 06	−0.638 89	−0.630 52
5	−0.628 58	−0.634 21	−0.634 88	−0.633 47	−0.629 89	−0.627 79	−0.624 69	−0.623 87
6	−0.626 89	−0.632 02	−0.632 42	−0.630 41	−0.625 96	−0.623 18	−0.617 05	−0.607 93
7	−0.616 58	−0.622 00	−0.622 54	−0.620 85	−0.617 07	−0.614 89	−0.611 43	−0.605 42
8	−0.616 33	−0.621 76	−0.622 33	−0.620 67	−0.616 44	−0.613 72	−0.607 58	−0.597 52
9	−0.615 39	−0.620 81	−0.621 34	−0.619 53	−0.615 20	−0.612 45	−0.606 23	−0.596 07
10	−0.608 85	−0.614 28	−0.614 82	−0.613 05	−0.608 82	−0.606 15	−0.601 50	−0.595 07
11	−0.605 82	−0.611 36	−0.611 99	−0.610 48	−0.606 75	−0.604 55	−0.599 73	−0.589 82
12	−0.601 10	−0.605 93	−0.606 19	−0.603 90	−0.599 27	−0.596 55	−0.592 48	−0.585 68

J. Chem Phys. (2009) DOI: 10.1063/1.3168506

Accuracy assessment using Rydberg scaling laws

- Effective quantum number ν_k and the quantum defect μ_k :

$$E_k(a.u.) = \mathcal{E}_{ion} - \frac{1}{2\nu_k^2};\ \mu_k = \nu_k - n$$

No	E_k(a.u.)	ν_k	n	ℓ	μ_k
1	-1.13789	0.9665	1	s	0,0335
2	-0.71768	2.0847	2	s	-0.0847
3	-0.66042	2.9416	3	d	0,0584
4	-0.65491	3.0927	3	s	-0.0927
5	-0.63488	3.9378	4	d	0,0622
6	-0.63242	4.0972	4	s	-0.0972
7	-0.62254	5,0119	5	g	-0.0119
8	-0.62233	5.0386	5	d	-0.0386
9	-0.62134	5.1702	5	s	-0.1702
10	-0.61482	6.4058	6	g	-0.4058
11	-0.61199	7.3108	6	d	-1.3108
12	-0.60619	11.8594	6	s	-5.8594
ion	-0.602635	∞	∞		

Quantum defect analysis

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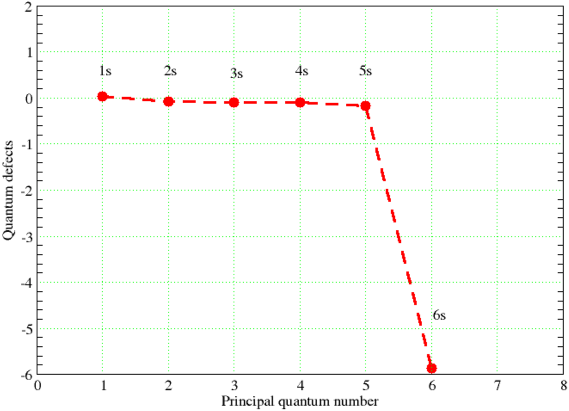
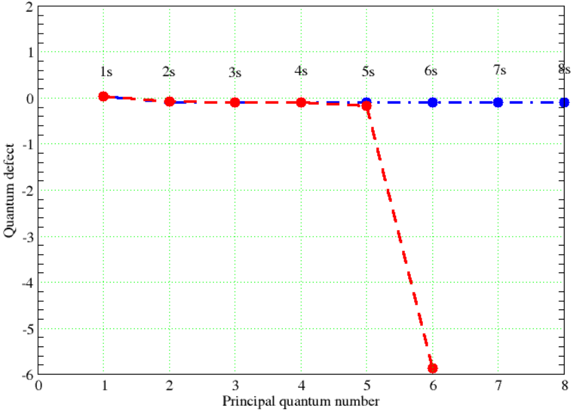
Quantum defect analysis



Quantum defect analysis



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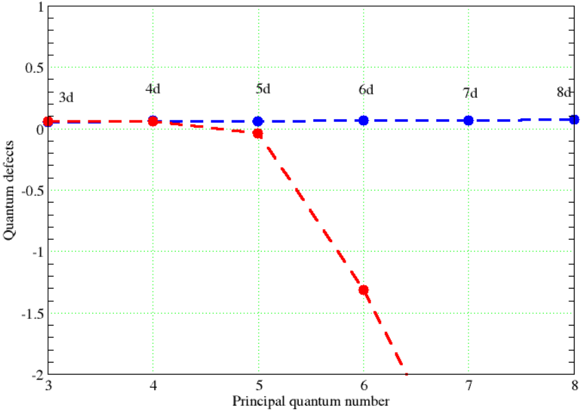

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10	-0.61482	6.4058	6	g	-0.4058
ion	-0.602635	∞	∞		

Accuracy assessment: diagnostic

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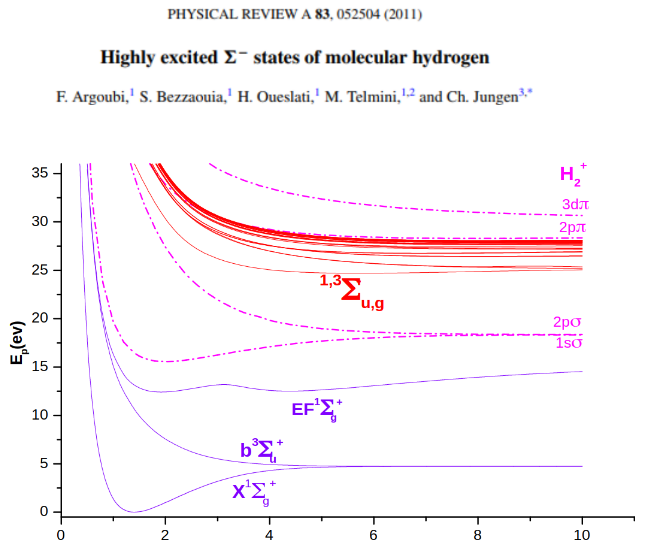
$^1\Sigma^-$ Doubly-excited states

State		R = 1			R = 2	
	ν[1]	ν[TJ]	$\Delta\nu$	ν[1]	ν[TJ]	$\Delta\nu$
$3d\pi$	2.767	2.766	0.001	2.664	2.662	0.002
$4d\pi$	3.775	3.782	0.007	3.695	3.709	0.014
$5d\pi$	4.790	4.786	0.004	4.711	4.717	0.006
$5g\pi$	4.976	4.999	0.023	4.971	4.998	0.027
$6d\pi$	6.252	5.787	0.465	6.079	5.720	0.359
$6g\pi$		5.998			5.996	
$7d\pi$		6.788			6.723	
$7g\pi$		6.997			6.995	

[1] J. Phys. B: At. Mol. Opt. Phys. 32 L181 (1999)

$^1\Sigma^-$ Doubly-excited states

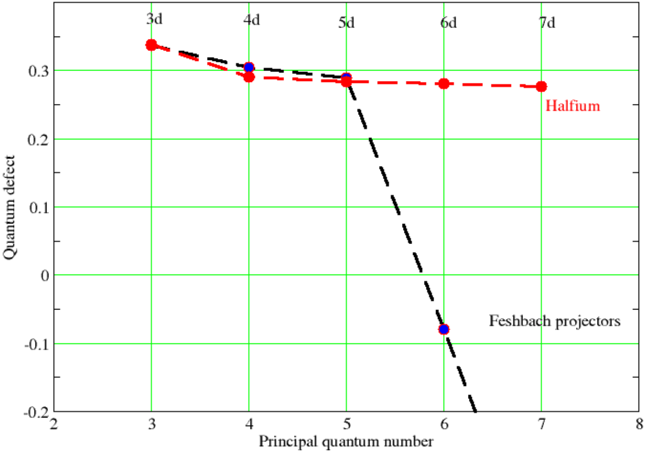


PHYSICAL REVIEW A **83**, 052504 (2011)

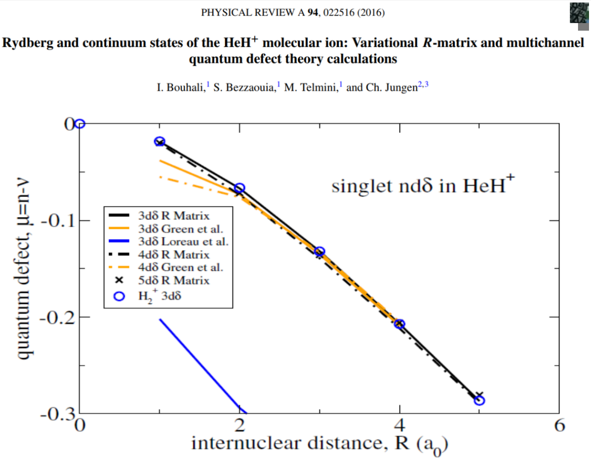
Highly excited Σ^- states of molecular hydrogen

F. Argoubi,[1] S. Bezzaouia,[1] H. Oueslati,[1] M. Telmini,[1,2] and Ch. Jungen[3,*]

Quantum defect analysis



HeH$^+$ molecular ion: $^1\Delta$ $nd\delta$ states



PHYSICAL REVIEW A **94**, 022516 (2016)

Rydberg and continuum states of the HeH$^+$ molecular ion: Variational *R*-matrix and multichannel quantum defect theory calculations

I. Bouhali,[1] S. Bezzaouia,[1] M. Telmini,[1] and Ch. Jungen[2,3]

- MOLPRO calculated energies are too high by about 2000 cm^{-1}.
  Mol. Phys. 43 065101 (2010) DOI 10.1088/0953-4075/43/6/065101

Recent example of ab initio calculations

- Silkowski *et al* (2021)

Accurate Born-Oppenheimer potentials for excited Σ^+ states of the hydrogen molecule

Michał Siłkowski*, Magdalena Zientkiewicz, and Krzysztof Pachucki
Faculty of Physics, University of Warsaw, Warsaw, Poland
*Corresponding author: e-mail address: michal.silkowski@fuw.edu.pl

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https://doi.org/10.1016/bs.aiq.2021.05.012

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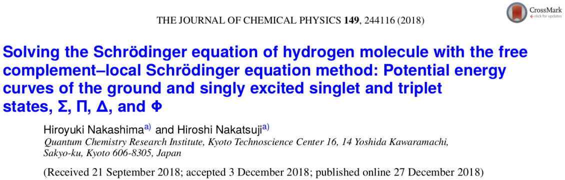
- Nakashima and Nakatsuji (2018)



THE JOURNAL OF CHEMICAL PHYSICS **149**, 244116 (2018)

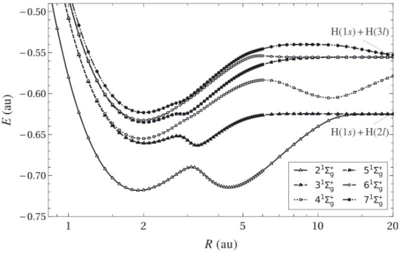
CrossMark

Solving the Schrödinger equation of hydrogen molecule with the free complement–local Schrödinger equation method: Potential energy curves of the ground and singly excited singlet and triplet states, Σ, Π, Δ, and Φ

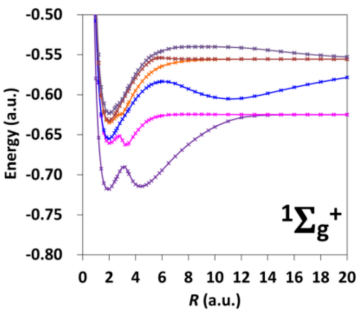
Hiroyuki Nakashima[a] and Hiroshi Nakatsuji[a]
Quantum Chemistry Research Institute, Kyoto Technoscience Center 16, 14 Yoshida Kawaramachi, Sakyo-ku, Kyoto 606-8305, Japan

(Received 21 September 2018; accepted 3 December 2018; published online 27 December 2018)

Quantum defect analysis: simple recipe



Silkowski *et al* (2021)



Nakashima and Nakatsuji (2018)

- Quantum defect analysis : Very good and reliable data (the authors limited themselves to low-lying states $n \leq 5$).
- This simple recipe can help deciding which roots are converged. It is applicable to a wide ensemble of atomic and molecular *ab initio* calculations of excited states.

Outline of the lecture

Conclusion

- Atomic and Molecular processses play an important role in Fusion Egde Plasmas and impact their properties and behavior.
- Electron-molecule collision is a complex and challenging problem, especially at low energy.
- Strong theoretical methods are required for a full understanding of the outcomes os the collisional processes, especially for modelling plasma physics.
- $R-$matrix Theory is one of the best available approaches.
- Hafium $R-$matrix method has a natural interface with MQDT and gives good results for simple two-electron molecular systems.
- Importance of uncertainty assessment for theoretical data.
- Quantum defect analysis is a simple universal tool for excited states.

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