State-to-State Kinetics of Molecular and Atomic Hydrogen Plasmas

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MOLECULAR DYNAMICS

\[ \text{state-resolved} \]
\[ \text{elementary process probability} \]

KINETIC MODELS

\[ \text{non-equilibrium distributions} \]
\[ \text{on internal degrees of freedom} \]

FLUID DYNAMICS
MOLECULAR DYNAMICS

- Electron-impact induced processes
- Atom-molecule collision processes
- Gas-surface interaction processes

KINETIC MODELS

- State-resolved elementary process probability

FLUID DYNAMICS

- Non-equilibrium distributions on internal degrees of freedom
Electron-Impact Induced Processes

✓ Processes
  ✓ vibronic excitation
  ✓ direct dissociation

✓ Theoretical Approaches
  ✓ semiclassical impact parameter method

✓ Input Data
  ✓ molecular potential of involved electronic states
  ✓ transition moment
  ✓ Born high-energy cross section value

✓ Dynamical Information
  ✓ energy and vibrational dependence of cross sections (complete set)
  ✓ isotopic effect investigation
  ✓ state-resolved and macroscopic rate coefficients
  ✓ radiative-decay vibrational excitation cross sections (EV)

✓ Features
  ✓ satisfactory accuracy (agreement with experimental data within the error of other methods)
  ✓ low computational load (except in the ab-initio step)
  ✓ suitable only for dipole-allowed transitions
  ✓ no treatment of resonances
GAMESS
(General Atomic and Molecular Electronic Structure System)

FAUST
BORN Cross Section

IMPACT
Cross Section

Radiative-Decay Vibrational Excitation

Rate Coefficients

maxwellian eedf distribution

Einstein coeffs of spontaneous emission

DYNAMIC CALCULATION
solution of the radial Schroedinger equation for quantum vibrational levels and estimation of structural and dynamical factors (evaluation of integrals)

AB-INITIO CALCULATION
potentials, transition dipole moments and GOS (Multi Reference Configuration Interaction)
GAMESS
(General Atomic and Molecular Electronic Structure System)

FAUST
BORN Cross Section

SIMILARITY APPROACH
Cross Section

IMPACT Cross Section

Rate Coefficients

maxwellian eeaf distribution

INTERFACING SCHEME of DIFFERENT CODES

AB-INITIO CALCULATION

DYNAMIC CALCULATION
rapid estimation of cross sections from oscillator strength and transition energy
electron-impact induced VIBRONIC EXCITATION CROSS SECTIONS for H$_2$
comparison of different approaches

D’Ammando, in preparation
Celiberto et al., ADNDT, 77 (2001)
VIBRATIONALLY-RESOLVED CROSS SECTIONS for H$_2$

$X^1\Sigma_g^+ (\nu_i) \rightarrow B^1\Sigma_u^+$

Impact Parameter Method
Celiberto 2001

similarity approach
\[ \chi^1\Sigma_g (v_i) \rightarrow C^1\Pi_u \]

**Impact Parameter Method**
Celiberto 2001

**similarity approach**

VIBRATIONALLY-RESOLVED CROSS SECTIONS for H\(_2\)
RESONANT PROCESSES in e- H₂ collisions

✓ PROCESSES
  ✓ dissociative attachment
  ✓ resonant vibrational excitation (eV processes)

✓ THEORETICAL APPROACH
  ✓ local resonance theory

✓ INPUT DATA
  ✓ molecular potential of involved electronic states
  ✓ resonance characterization (width and energy dependence)

✓ DYNAMICAL INFORMATION
  ✓ angular, energy and vibrational dependence of cross sections (complete set)
  ✓ isotopic effect investigation

✓ FEATURES
  ✓ excellent agreement with experimental data
  ✓ reasonable computational load
ATOM-MOLECULE COLLISIONS: from PES to complete sets of rovibrational CROSS SECTIONS and RATES

PES from literature

LIVX
Calculation of complete rovibrational ladders relative to all the possible reactants/products, including quasibound states by WKB method

DINX
Quasiclassical dynamics of atom-diatom collision processes. Distribution of computations on a wide computational grid with periodic check of results, automatic re-calculations for uncompleted jobs and collection of good ones
QCTX
Trajectory analysis and cross section results for reactive and non-reactive processes as well as dissociation. The quasibound states are here considered as bound states. Various reactant and product weight functions can be used to analyze the trajectory results.

XRATE
From translational energy dependent rovibrational cross sections to rate coefficients. This module includes the possibility of selecting and mixing rate coefficients on the base of lifetime of initial/final states and of the level of detail requested (e.g. total thermal rate, sum of rates on final rotation, dissociation summed to state-to-state rate coefficients with low lifetime, etc.)

Recombination can be obtained in this module by two methods: detailed balance applied to dissociation rates and orbiting resonance applied to rovibrational state-to-state rates.
Two possible mechanisms: *orbiting resonance* theory and *direct three body* recombination (by detailed balance of dissociation data)

✓ the two mechanisms can be used in a *complementary way*, by choosing accurately the states involved in the calculations

✓ a detailed database of rate coefficients including initial and final rotation and state selected dissociation for H+H₂ collision process is necessary
normalized recombination vs final vibrational quantum number

recombination rates vs final rotational quantum number

ION-MOLECULE COLLISION PROCESSES

\[
\text{H}^++\text{H}_2(v, j) \rightarrow \begin{cases} 
\text{H}^+\text{H}_2^+(w, k) \\
\text{H}^++\text{H}_2(w, k) \\
\text{H}+\text{H}+\text{H}^+ 
\end{cases}
\]

✓ PES used:

✓ couplings calculated from the potential matrix, with particular care for sign consistency of eigenvectors
*Esposito, in preparation*

✓ a vibrationally detailed database of rate coefficients should be calculated, using trajectory surface hopping, including initial/final rotation and dissociation
*Esposito, in preparation*
This method is useful when, for a given chemical process, there are not cross sections data, but there are information about rate coefficients in a given range of temperatures (Minelli, to be published). The only data required are a good functional form for cross section and a temperature dependent rate. The reference rate coefficients are input to a standard nonlinear optimization algorithm (Downhill Simplex Method, DSM (Nelder and Mead, Computer Journal 7 (1965)) to give reconstructed cross sections that satisfy a convergence criterion.

**Case study to test method**

dissociation of the hydrogen molecule by atom impact

\[ \text{H} + \text{H}_2(v, j = 0) \rightarrow 3\text{H} \]

comparison between cross sections obtained by DSM (Downhill Simplex Method - full lines) and by QCT (Quasi Classical Trajectory - symbols)
MOLECULAR DYNAMICS for GAS/SURFACE INTERACTION PROCESSES
ISOTOPIC EFFECT: H/D RECOMBINATION on GRAPHITE

\[ D_{\text{ad}*\text{graphite}} + D_{\text{gas}} \rightarrow D_2(v,j) \]

\[ E_{\text{kin}} = 0.8 \text{eV} \]

\[ T_S = 500 \text{K} \]

M. Rutigliano and M. Cacciatore

M. Cacciatore and M. Rutigliano
Plasma Sources Sci. Technol. 18 (2009) 023002
Topical Review
PLASMA NUMERICAL EXPERIMENTS

**ion sources**
- Electric thrusters
- Negative ion sources
- Plasma shock tube

**plasma-wall transition**
- Divertor region
- Sheath physics:
  - See
  - Instability
  - Electronegativity

**electrostatic probe**
- Ion collection
- Electron collection
- Dusty

**laser-induced plasma**
- LIBS
- Under-water cavitation bubble dynamics

**hypersonic plasma flow**
- MHD bow shock
- Space charge region

**kinetic models** (Vlasov, PIC-MCC)

**fluid models** (CFD, MHD, SPH)
ATOMIC HYDROGEN under SHOCK WAVE

Gas Temperature (K)

upstream

$T_1 = 5000 \text{ K}$
$P_1 = 10^{-2} \text{ atm}$
$u_1 = 5$

downstream

$T_2(x=0) > T_1$
$P_2(x=0) > P_1$
$u_2(x=0) < u_1$

Molar Fractions

thick

$\lambda = 0$

thin

$\lambda = 1$

Euler Equations

CR Master & Electron Boltzmann Equations

Radiative Transfer Equation

H$_2$ kinetics

IAEA TECHNICAL MEETING: SECOND MEETING OF THE INTERNATIONAL CODE CENTRES NETWORK
27–28 SEPTEMBER 2010, IAEA HEADQUARTERS, VIENNA, AUSTRIA
**LOCAL SOURCE FUNCTION**

optically thin plasma ($\lambda=1$)

**upstream condition**

$P_1=10^{-2}$ atm  
$T_1=1000$ K  
$u=20$

**Source function** is the ratio of emissivity over absorption coefficient

$$S_{\nu} = \frac{j_{\nu}}{K_{\nu}}$$

at equilibrium equals the blackbody intensity

$$S_{\nu} = B_{\nu}(T)$$

non-equilibrium distributions of spectral quantities

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MOLECULAR DYNAMICS

- electron-impact induced processes
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collision integrals

state-resolved elementary process probability

THERMODYNAMICS

KINETIC MODELS

non-equilibrium distributions on internal degrees of freedom

TRANSPORT THEORY

FLUID DYNAMICS

transport properties
✓ THERMODYNAMIC PROPERTIES of multicomponent plasmas including Debye-Hückel correction

✓ SIMPLIFIED TWO and THREE-LEVEL PARTITION FUNCTION

✓ ATOMIC HYDROGEN LEVELS in a BOX in the presence of Coulomb and Debye-Hückel potentials
• the method is based on the idea of combining a multitude of atomic energy levels into two or three grouped levels. The partition function for atomic hydrogen can be approximated as

\[ Q(T) = g_0 + g_1 e^{-\varepsilon_1/kT} \]

\[ g_1 = \sum_{n=2}^{n_{\text{max}}} 2n^2 \]

\[ \varepsilon_1 = \frac{1}{g_1} \sum_{n=2}^{n_{\text{max}}} 2n^2 \varepsilon_n \]

• the method has been applied to many atomic and ionic systems

\[ n_{\text{max}} = 10 \]

\[ n_{\text{max}} = 100 \]

ENERGY LEVELS for ATOMIC HYDROGEN in a SPHERICAL BOX

Capitelli & Giordano, Physical Review A, 80 (2009)
**TRANSPORT PROPERTIES**

- DATABASE OF TRANSPORT CROSS SECTION and COLLISION INTEGRALS for He-$H_2$ interactions in a wide temperature range [100-50000 K]
  
  *Bruno et al., Physics of Plasmas (2010) in press*

- EFFECT OF MAGNETIC FIELD (*tensorial reformulation*)

- EFFECT OF ELECTRONICALLY EXCITED STATES (EES)
INTERFACING SCHEME of DIFFERENT CODES

DYNAMICAL CALCULATION
classical collision integrals for elastic collision between species from (accurate, model or phenomenological) interaction potentials

OMEGA

HIERARCHICAL CODE

calculation of the species-concentration as a function of temperature

TRANSPORT PROPERTY CALCULATION
solution of a system of linear equations algebraic equations of order n*K, n being the number of species and K the order of approximation of the expansion in Sonine polynomials

CHAPMAN-ESKOG CODE

heat flux & diffusion

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INTERNAL CONDUCTIVITY for HYDROGEN PLASMA including EES