THE CHESS DATABASE OF *Ab Initio* RATE COEFFICIENTS

A GUIDE THROUGH THE DATA

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SECTION 1

CHESS Database of *Ab Initio* Rate Coefficients

1.1 List of Chemical Systems in the Database

The CHESS database contains *ab initio* rate coefficients resulting from the following types of collisions.

1.1.1 N_2+N, NASA Ames PES

The rate coefficients have been computed by Panesi *et al.* [1] based on the PESs from Jaffe *et al.* [2].
Notes:

- Set of translational temperatures: $T_{Tran} = \{ 1\,000, 2\,500, 3\,500, 7\,500, 10\,000, 12\,500, 15\,000, 20\,000, 25\,000, 30\,000, 40\,000, 50\,000 \}$ K
- Compared to the original database, the ro-vibrational levels and the corresponding processes have been resorted based on their internal energies;
- Rate coefficients for the inelastic processes are not differentiated from the ones for exchange reactions. The `Inel` objects in the .hfd5 file are rate matrices obtained by summing the coefficients for the two processes. The `Exch_1` matrix has not been reported;
- Only endothermic rate coefficients have been reported, computed trough micro-reversibility from the exothermic rates resulting from QCT.
- The odd-even splitting quantum rule has been imposed to the rotational mode.

1.1.2 O_2+O, UMN PESs

The rate coefficients have been computed by Venturi *et al.* [3] based on the PESs from Varga *et al.* [4].
Notes:

- Set of translational temperatures: $T_{Tran} = \{ 1500, 2500, 5000, 6000, 8000, 10000, 12000, 14000, 15000, 20000 \}$ K.
- The rate coefficients are the result of a Monte Carlo average of all the 9 PESs. Each of the surfaces has been weighted by its correspondent degeneracy;
- Both exothermic and endothermic rate coefficients have been reported, as they directly result from QCT calculations. In order to improve the accuracy, we recommend to extract only the exothermic rates from the database, and recompute the endothermic ones by invoking micro-reversibility;
- The dissociation rate coefficients have been reported as they directly result from QCT calculations, and they have not been corrected by means of the 16/3 factor.

1.1.3 CO+O, NASA Ames PESs

The rate coefficients have been computed by Venturi *et al.* [5] based on the PESs from Schwenke *et al.* [6].
Notes:

- Set of translational temperatures: $T_{Tran} = \{ 2500, 5000, 7500, 10000, 12500, 15000, 20000 \}$ K.
- The rate coefficients are the result of a Monte Carlo average of all the 3 PESs. Each of the surfaces has been weighted by its correspondent degeneracy;
- Both exothermic and endothermic rate coefficients have been reported, as they directly result from QCT calculations. In order to improve the accuracy, we recommend to extract only the exothermic rates from the database, and recompute the endothermic ones by invoking micro-reversibility.
- The `Exch_1` matrix contains the exchange reaction rate coefficients for the processes CO_i+O=CO_k+O.
  The `Exch_2` matrix contains the exchange reaction rate coefficients for the processes CO_i+O=O_{2_l}+C.

1.1.4 O_2+C, NASA Ames PESs

The rate coefficients have been computed by Venturi *et al.* [5] based on the PESs from Schwenke *et al.* [6].
Notes:

- Set of translational temperatures: $T_{Tran} = \{\, 2500,\ 5000,\ 7500,\ 10000,\ 12500,\ 15000,\ 20000 \,\}$ K.
- The rate coefficients are the result of a Monte Carlo average of all the 3 PESs. Each of the surfaces have been weighted by its correspondent degeneracy;
- Both exothermic and endothermic rate coefficients have been reported, as they directly result from QCT calculations. In order to improve the accuracy, we recommend to extract only the exothermic rates from the database, and recompute the endothermic ones by invoking micro-reversibility.

1.2 HDF5 Files Content

We recommend the use of Panoply (`https://www.giss.nasa.gov/tools/panoply/`) for a quick visualization of the objects stored in each of the .hdf5 files.

The .hdf5 files contain:

- One folder for each of the molecules composing the chemical system, containing its own collection of level properties. As an example, for the N_2+N system, the .hdf5 contains a `N2` directory including a number of arrays characterizing the levels' energies, their quantum numbers, etc
- One folder for each of the translational temperatures; inside are located the corresponding rate coefficients.

1.2.1 Properties of the Ro-Vibrational Levels

- `LevelEEh`: Ro-vibrational energy, in Hartree;
- `LevelEeV`: Ro-vibrational energy, in Electronvolt;
- `Levelvqn`: Vibrational quantum number;
- `Leveljqn`: Rotational quantum number;
- `Levelg`: Degeneracy;
- `LevelrIn`: Inner turning point, in Bohr;
- `LevelrOut`: Outer turning point, in Bohr;
- `LevelTau`: Vibrational time period, in Atomic Units;
- `LevelVMin`: Minimum of the J-dependent diatomic potential, in Hartree;
- `LevelVMax`: Maximum of the J-dependent diatomic potential, in Hartree;
- `LevelrMin`: Atomic distance corresponding to LevelVMin, in Bohr;

- `LevelrMax`: Atomic distance corresponding to LevelVMax, in Bohr;
- `LevelEgam`: Width of resonance, in Atomic Units:
- `LevelToGroupIn`: Mapping Level-to-Group. It applies only in case the original rate coefficients database has been computed based on the CG-QCT method.

1.2.2 Rate Coefficients

In general, we can define N_{Mol} as the number of distinct molecules in the system (e.g., in the N_2+O_2, the N_2, O_2, and NO molecules can be formed. Therefore, N_{Mol}=3). Moreover, we can indicate with N_{Exch} the number of distinct types of exchange reactions in the system (e.g., for N_2+O_2, N_{Exch}=1: only the type of exchange N_2+O_2=NO+NO is possible. On the contrary, for NO+NO N_{Exch}=2. Indeed, when the NOs break, N can form with the remaining two atoms either a new NO or an N_2).

For a system composed by 3 Atoms, A, B, and C (i.e., AB+C):

- **`Diss`**: The matrix contains the dissociation rate coefficients corresponding to the reactions AB_i+C = A+B+C, where i represents the initial level/group of the molecule.
  - The matrix has dimensions $N_{AB} \times (2 + N_{Exch})$, where N_{AB} indicates the number of levels/groups in the AB molecule;
  - The 1-st column of the matrix contains AB_i's overall dissociation rate coefficients;
  - The 2-nd column contains the rate coefficients corresponding to AB_i dissociating without temporarily forming either AC or BC.
  - The $(2+i_{Exch})$-th column contains the rate coefficients corresponding to AB_i dissociating after having temporarily produced the i_{Exch}-th exchange reaction.
- **`Inel`**: The matrix contains the inelastic rate coefficients, corresponding to the reactions AB_i+C = AB_j+C, where i and j represent the initial and final levels/groups, respectively.
  - The matrix has dimensions $N_{AB} \times N_{AB}$.
- **`Exch_`**i_{Exch}: The matrix contains the exchange reaction rate coefficients. For i_{Exch}=1, the matrix corresponds to the reactions AB_i+C = AC_k+B; for i_{Exch}=2, to AB_i+C = BC_l+A.
  - `Exch_` has dimensions $N_{AB} \times N_{AC}$, while `Exch_2` has dimensions $N_{AB} \times N_{BC}$;
  - If A=B (e.g., O_2+C), then only a single Exch_i_{Exch} matrix is reported, and it results from `Exch_1` + `Exch_2`.

For a system composed by 4 Atoms, A, B, C, and D (i.e., AB+CD):

- `Diss`: The matrix contains the dissociation rate coefficients, corresponding to the reactions AB_i+CD_j = A+B+C+D, where i and j represent the initial levels/groups of the molecules.
  - The matrix has dimensions $N_{AB} \times N_{CD} \times (2 + N_{Exch})$;
  - The (:,:,1) elements of the matrix represent the AB_i+CD_j's overall dissociation rate coefficients;
  - The (:,:,2) elements of the matrix correspond to the rate coefficients of AB and CD dissociating without temporarily forming any other molecule.
  - The (:,:,2+i_{Exch}) elements of the matrix correspond to the rate coefficients of AB and CD dissociating after having temporarily produced the i_{Exch}-th exchange reaction.
- `DissInel`: The matrix contains the rate coefficients corresponding to the reactions AB_i+CD_j = $Molecule_k$+Atom+Atom.
  - The matrix has dimensions $N_{AB} \times N_{CD} \times N_{MAX} \times N_{Mol}$, where $N_{MAX} = \arg\max(N_{AB}, N_{AC}, N_{AD}, N_{BC}, N_{BD}, N_{CD})$.
  - The (i, j, k, i_{Mol}) element of the matrix correspond to the reaction AB_i+CD_j = $Molecule_k^{i_{Mol}}$+Atom+Atom, producing the i_{Mol}-th molecule in the k-th state.
- `Inel`: The matrix contains the inelastic rate coefficients, corresponding to the reactions AB_i+CD_j = AB_k+CD_l, where k and l represent the final levels/groups, respectively.
  - The matrix has dimensions $N_{AB} \times N_{CD} \times N_{AB} \times N_{CD}$.
- `Exch_`i_{Exch}: The matrix contains the reaction rate coefficients. For i_{Exch}=1, the matrix corresponds to the reactions AB_i+CD_j = AC_m+BD_n; for i_{Exch}=2, to AB_i+CD_j = AD_o+BC_p.
  - `Exch_1` has dimensions $N_{AB} \times N_{CD} \times N_{AC} \times N_{BD}$, while `Exch_2` has dimensions $N_{AB} \times N_{CD} \times N_{AD} \times N_{BC}$;
  - If A=B and C=D (e.g., N_2+O_2), then only a single Exch_i_{Exch} matrix is reported, and it results from `Exch_1` + `Exch_2`.

1.3 References

[1] M. Panesi, R. L. Jaffe, D. W. Schwenke, and T. E. Magin, "Rovibrational internal energy transfer and dissociation of N(4 S u) + N 2 (1 + g) sytem in hypersonic flows," J. Chem. Phys 138, 044312 (2013).

[2] R. L. Jaffe, D. W. Schwenke, G. Chaban, and W. Huo, "Vibrational and rotational excitation and relaxation of nitrogen from accurate theoretical calculations," AIAA Paper 2008–1208 (2008) 46th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV.

[3] S. Venturi *et al.*, In preparation

[4] Z. Varga, Y. Paukku, and D. G. Truhlar, "Potential energy surfaces for O + O 2 collisions," J. Chem. Phys. 147, 154312/1–17 (2017).

[5] S. Venturi *et al.*, In preparation

[6] D. W. Schwenke, R. L. Jaffe, and G. M. Chaban, "Collisional dissociation of CO: ab initio potential energy surfaces and quasiclassical trajectory rate coecients," NASA Technical Report ARC-E-DAA-TN30024 (2016) NASA Ames Research Center; Moffett Field, CA United States.

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SECTION

PyCoarseAIR: A Python Postprocessing of *Ab initio* Databases

PyCoarseAIR is a collection of Phyton scripts for postprocessing the databases of *ab initio* rate coefficients resulting from the CoarseAIR code [1] (https://github.com/simoneventuri/CoarseAIR) implementing the quasi-classical trajectories (QCT) method.

2.1 Quickstart

2.1.1 Requirements

1. The following Python libraries need to be installed:

   - `numpy`, fundamental package for scientific computing (https://numpy.org/);
   - `matplotlib`, for static, animated, and interactive visualizations (https://matplotlib.org/);
   - `pandas`, data analysis and manipulation tool (https://pandas.pydata.org/);
   - `csv`, implementing classes to read and write tabular data in CSV format (https://docs.python.org/3/library/csv.html);
   - `h5py`, a Pythonic interface to the HDF5 binary data format (https://www.h5py.org/).

   All these libraries can be easily installed through pip3 (i.e., by typing: "`pip3 install numpy`" from the terminal).

2. The PyCoarseAIR code can be cloned as a GitHub repository: https://github.com/simoneventuri/PyCoarseAIR (i.e., from the terminal, type:

"git clone https://github.com/simoneventuri/PyCoarseAIR").
For the remaining part of this manual, the path to the local PyCoarseAIR folder will be referred to as
PyCoarseAIRFldr.

3. The .hdf5 file corresponding to the *ab initio* database for the desired chemical system needs to be downloaded from https://www.chess.aerospace.illinois.edu/databases. For the remaining part of this manual, the path to the folder containing the downloaded file will be referred to as DtbHDF5Fldr, while SystOI will be used for indicating the name of the desired chemical system.

4. In PyCoarseAIRFldr/exec/PyCoarseAir.py (i.e., the main file of the program), the following paths need to modified:

   - PyCoarseAIRFldr, based on point 2 of this list;
   - DtbHDF5Fldr, based on point 3 of this list;
   - DtbWriteFldr, pointing to the folder where PyCoareseAIR is required to write the postprocessed kinetics database;
   - OutputWriteFldr, pointing to the folder where PyCoareseAIR is required to save its output files and plots.

2.1.2 Executing PyCoarseAIR

The code can be executed from the PyCoarseAIRFldr/exec/ folder by typing:
"python3 ./PyCoarseAir.py PyCoarseAIRFldr/input/SystOI"
(e.g., "cd /home/venturi/WORKSPACE/PyCoarseAIR/exec/;
python3 ./PyCoarseAIR.py ../input/N3_NASA/").

2.1.3 PyCoarseAIR Output Files

The files containing the desired rate coefficients can be found in the folder PyCoarseAIRFldr/kinetic/SystOI/, while the lists of levels/groups for each of the molecules in the system are located in PyCoarseAIRFldr/thermo/SystOI/.
In PyCoarseAIRFldr/thermo/SystOI/, the code also writes one file for each of the molecules containing the levels / groups distribution functions at the initial temperature. All the output files just mentioned are compatible with the PLATO library by Dr. A. Munafò [2-5] for the solution of the master equation and CFD calculations.

2.2 A Brief List of PyCoarseAIR's Fundamental Input Variables

- TranVec: Vector of translational temperatures for which we are interested in loading the corresponding rate coefficients;
- T0: Initial temperature of further heat bath simulations. The distribution functions corresponding to T0 will be computed and written for all the molecules composing the mixture;

- `WriteDiss_Flg`: With `WriteDiss_Flg=True`, the dissociation rate coefficients will be uploaded from the database and written locally.
- `CorrFactor`: If `CorrFactor` $\neq 1$, the dissociation rates loaded from the database are multiplied by `CorrFactor` before being written;
- `WriteDissInel_Flg`: With `WriteDissInel_Flg=True`, the dissociation-inelastic rate coefficients (e.g., the ones corresponding to the processes AB+CD=AB+C+D) will be uploaded from the database and written locally (only for 4-atoms system).
- `WriteInel_Flg`: With `WriteInel_Flg=True`, the inelastic rate coefficients will be uploaded from the database and written locally.
- `WriteExch_Flg`: With `WriteExch_Flg=True`, the exchange reaction rate coefficients will be uploaded from the database and written locally.
- `WriteExoth_Flg`: With `WriteExoth_Flg=True`, the exothermic rate coefficients will be written locally. With `WriteExoth_Flg=False`, the endothermic rate coefficients will be written locally.
- `WriteQB_IntFlg`: Integer flag for considering the quasi-bound levels. With `WriteQB_IntFlg=0`, only bound levels are considered; with `WriteQB_IntFlg=1`, only quasi-bound levels are considered; with `WriteQB_IntFlg=2`, both bound and quasi-bound levels are considered.
- `WriteFormat`: With `WriteFormat='PLATO'`, the utput data will be produced in PLATO's [2-5] format. With `WriteFormat='csv'`, the utput data will be written in .csv files. With `WriteFormat='custom'`, the user can customize the format by modifying the files `/PyCoarseAIR/src/Objects/Molecule.py` and/or `/PyCoarseAIR/src/Objects/System.py`

2.3 References

[1] Venturi *et al.*, In preparation

[2] A. Munafò, A. Alberti, C. Pantano, J. Freund, and M. Panesi, "Modeling of laser-induced breakdown phenomena in non-equilibrium plasmas," in 2018 AIAA Aerospace Sciences Meeting.

[3] A. Munafò, N. N. Mansour, and M. Panesi, "A reduced-order NLTE kinetic model for radiating plasmas of outer envelopes of stellar atmospheres," Astrophys. J. 838, 126 (2017).

[4] A. Munafò, Y. Liu, and M. Panesi, "Physical models for dissociation and energy transfer in shock-heated nitrogen flows," Phys. Fluids 27, 127101 (2015).

[5] A. Munafò, A. Alberti, C. Pantano, J. Freund, and M. Panesi, "A computational model for nanosecond pulse laser-plasma interactions", J. Comput. Phys. 406, 109190 (2020).