A Multiquantum State-To-State Model For The Fundamental States Of Air And Application To The Modeling Of High-Speed Shocked Flows

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16 October 2012
Objectives of the Presentation

General Objective: Presentation of a Complete State-Specific, Multiquantum, High-Temperature model for the ground states of $N_2$, $O_2$, and NO: The STELLAR database.

Outline of the Talk:

- Model capabilities for the prediction of high-temperature rates.
- Description of the rates database for the $N_2(X,v)$, $O_2(X,v)$, and NO($X,v$) states. Application for a sample calculation (Fire II 0D calculation)
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- Description of the Forced Harmonic Oscillator Method (FHO) for \( \text{V} \rightarrow \text{T} \), \( \text{V} \rightarrow \text{V} \rightarrow \text{T} \), and \( \text{V} \rightarrow \text{D} \) transitions modeling.
- Model capabilities for the prediction of high-temperature rates.
- Description of the rates database for the \( \text{N}_2(X,v) \), \( \text{O}_2(X,v) \), and \( \text{NO}(X,v) \) states. Application for a sample calculation (Fire II 0D calculation)
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Progresses in Quantum chemistry have introduced increasingly accurate atom-diatom and diatom-diatom potentials. Trajectory methods over such potentials can provide very detailed state-specific data. But these methods remain very intensive for the systematic production of rate databases. Over the last decades, FOPT methods (Such as the SSH approach) have been utilized, with a relative degree of success, for the modeling of heavy-impact processes in low-T plasmas. FHO model proposed at the same time than FOPT models (Rapp&Sharp:1963, Zelechow:1968), but only systematically deployed much later due to computational constraints (Adamovich:1995, LinodaSilva:2007).
An Accurate, Physically-Consistent, Semianalytic Model for the prediction of V–T, V–V–T and V–D Processes

- **FHO model** nicely reproduces results from more sophisticated approaches (QCT methods, etc...), and is physically consistent at high T.

- **SSH model** also nicely scales at low T, but fails at high T.

- For a large range of plasma sources, VT and VD processes can only be properly simulated through the FHO model or sophisticated methods.

- The FHO model provides an interesting bridging theory for the modeling of "contemporary" plasma sources.

1→0, 9→8, and 20→19 N2–N2 V–T rates. Comparison between Billing’s QCT rates (×) and the FHO model (−)
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The Forced Harmonic Oscillator Model in 2 Slides

– V–T transition probabilities for collinear atom-diatom non-reactive collisions are given by Kerner and Treanor

\[ P(i \rightarrow f, \varepsilon) = i!f!\varepsilon^{i+f} \exp(-\varepsilon) \left| \sum_{r=0}^{n} \frac{(-1)^r}{r!(i-r)!(f-r)!\varepsilon^r} \right|^2 \]

with \( n = \text{min}(i, f) \).

– V–V–T transition probabilities for collinear diatom-diatom collisions are given\(^1\) by Zelechow

\[ P(i_1, i_2 \rightarrow f_1, f_2, \varepsilon, \rho) = \left| \sum_{g=1}^{n} (-1)^{(i_12-g+1)} C_{i_12}^{i_2} C_{f_12}^{f_2} \frac{1}{2} (i_12+f_12-2g+2) \exp(-\varepsilon/2) \right|^2 \]

\[ \times \sqrt{(i_12-g+1)!(f_12-g+1)! \exp[-i(f_12-g+1)\rho]} \sum_{l=0}^{n-g} \frac{(-1)^l}{(i_12-g+1-l)!(f_12-g+1-l)!\varepsilon^l} \]

with \( i_{12} = i_1 + i_2, \ f_{12} = f_1 + f_2 \) and \( n = \text{min}(i_1 + i_2 + 1, f_1 + f_2 + 1) \).

In these equations \( \varepsilon \) and \( \rho \) are related to the two-state FOPT transition probabilities, with \( \varepsilon = P_{\text{FOPT}}(1 \rightarrow 0) \) and \( \rho = [4 \cdot P_{\text{FOPT}}(1, 0 \rightarrow 0, 1)]^{1/2} \).

\( C_{ij}^k \) is a transformation matrix calculated according to the expression\(^1\)

\[ C_{ij}^k = 2^{-n/2} \left( \begin{array}{c} k \\ i-1 \end{array} \right)^{-1/2} \left( \begin{array}{c} k \\ j-1 \end{array} \right)^{1/2} \times \sum_{v=0}^{j-1} (-1)^v \left( \begin{array}{c} k-i+1 \\ j-v-1 \end{array} \right) \left( \begin{array}{c} i-1 \\ v \end{array} \right). \]

\(^1\) Corrected from typographic errors

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STELLAR Database, RHTGAE5
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\]

\[
\times \sqrt{(i_12 - g + 1)!(f_12 - g + 1)! \exp[-i(f_12 - g + 1)\rho] \sum_{l=0}^{n-g} \frac{(-1)^l}{(i_12 - g + 1 - l)!(f_12 - g + 1 - l)!!\varepsilon^l}}
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with \( i_{12} = i_1 + i_2, f_{12} = f_1 + f_2 \) and \( n = \min(i_1 + i_2 + 1, f_1 + f_2 + 1) \).

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The Forced Harmonic Oscillator Model in 2 Slides

For a purely repulsive intermolecular potential $V(r) \sim \exp(-\alpha r)$, expressions for $\varepsilon$ and $\rho$ are given by Zelechow

$$\varepsilon = \frac{8\pi^3 \omega \left( \frac{m^2}{\mu} \right)^2 \gamma^2}{\alpha^2 h} \sinh^{-2} \left( \frac{\pi \omega}{\alpha \bar{v}} \right), \quad \rho = 2 \left( \frac{m^2}{\mu} \right) \gamma^2 \alpha \bar{v} / \omega.$$  

For a Morse intermolecular potential $V(r) \sim E_m \left( 1 - \exp(-\alpha r) \right)^2$, the expression for $\varepsilon$ is given by Cottrell (the expression for $\rho$ remains identical)

$$\varepsilon = \frac{8\pi^3 \omega \left( \frac{m^2}{\mu} \right)^2 \gamma^2}{\alpha^2 h} \cosh^2 \left[ \frac{(1+\phi) \pi \omega}{\alpha \bar{v}} \right] \sinh^2 \left( \frac{2\pi \omega}{\alpha \bar{v}} \right), \quad \phi = (2/\pi) \tan^{-1} \sqrt{\frac{2E_m}{\bar{m}\bar{v}^2}}.$$  

$E_m$ represents the potential well, $\omega$ denotes the oscillator frequency, and $\mu, \gamma,$ and $\bar{m}$ are mass parameters.

Adamovich and Macheret summarized and introduced a few improvements for generalizing the FHO theory for arbitrary molecular collisions:

- Symmetrization of the collision velocity to enforce detailed balance (median collision velocity $\bar{v} = (v_i + v_f) / 2$);
- Accounting for the anharmonicity of the oscillator potential curve using an average frequency $\omega = \frac{|(E_i - E_f)/(i - f)|}{i \neq f},$ and $\omega = |E_{i+1} - E_i|$ if $i = f$;
- Generalization of the model for nonresonant V–V–T transitions and V–V–T transitions between different species, by replacing $\rho \rightarrow \rho \times \xi / \sinh(\xi)$, with $\xi = \pi^2 (\omega_1 - \omega_2) / 4 \alpha \bar{v}$;
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The Forced Harmonic Oscillator Model in 2 Slides

For a purely repulsive intermolecular potential \( V(r) \sim \exp(-\alpha r) \), expressions for \( \varepsilon \) and \( \rho \) are given by Zelechow

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\varepsilon = \frac{8\pi^3 \omega (\tilde{m}^2 / \mu) \gamma^2}{\alpha^2 h} \sinh^{-2} \left( \frac{\pi \omega}{\alpha \tilde{v}} \right), \quad \rho = 2 \left( \tilde{m}^2 / \mu \right) \gamma^2 \alpha \tilde{v} / \omega.
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At high $T$, multiquantum V–V–T transitions have to be accounted for. This is impractical as the number of transitions becomes $N^4$ where $N$ is the number of vibrational levels (ex. $N=61$ for $N_2$).

Adamovich verified that for $E_{tr} \gg E_{vib}$, V–V–T processes occur as two independent V–T processes, and pure V–V exchanges can be neglected (roughly for $T > 10,000K$). We then have:

$$P_{VVT}(i_1, i_2 \rightarrow f_1, f_2, \varepsilon, \rho) \approx P_{VT}(i_1 \rightarrow f_1, \varepsilon) \cdot P_{VT}(i_2 \rightarrow f_2, \varepsilon)$$

$$P_{VT}(i_1, \text{all} \rightarrow f_1, \text{all}, \varepsilon, \rho) = P_{VT}(i_1 \rightarrow f_1, \varepsilon)$$

which leads to a more practical calculation of $N^2$ rates.

V–D processes such as $AB(i) + M \rightleftharpoons A + B + M$ are modeled according to the approach proposed by Macheret and Adamovich. The probability for dissociation as the product of the transition probability to a quasi-bound state such that $v > v_{diss}$, times the probability of the subsequent decay of the energetic complex

$$P(i \rightarrow, \varepsilon) = P(i \rightarrow v_{qbound}, \varepsilon) \cdot P_{\text{decay}}$$

with $P_{\text{decay}} \sim 1$. 

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STELLAR Database, RHTGAE5
Factorials in denominators/numerators of probabilities expressions lead to overflows/underflows for high quantum numbers.

**Factorial → Bessel**

\[ P(i \rightarrow f, \varepsilon) = J_s^2 \left( 2 \sqrt{n_s \varepsilon} \right) \]

for \( i, f \gg s = |i - f| \), and \( n_s = [\max(i, f)! \min(i, f)!]^{-s} \), and

\[ P(i_1, i_2 \rightarrow f_1, f_2, \varepsilon, \rho) = J_s^2 \left[ 2 \left( n_s^{(1)} n_s^{(2)} \rho_s^2 / 4 \right)^{1/2} \right] \]

for \( i_1 + i_2 = f_1 + f_2 \), and \( i_1 + i_2 + f_1 + f_2 \gg s = |i_1 - f_1| \).

**Bessel → Polynom**

\[ J_s^2 \left( 2 \sqrt{n_s \varepsilon} \right) \simeq \frac{(n_s)^s}{(s!)^2} \varepsilon^s \exp \left( -\frac{2n_s \varepsilon}{s + 1} \right) ; \]

\[ J_s^2 \left[ 2 \left( n_s^{(1)} n_s^{(2)} \rho_s^2 / 4 \right)^{1/2} \right] \simeq \left( \frac{n_s^{(1)} n_s^{(2)}}{(s!)^2} \right)^s \left( \frac{\rho_s^2}{4} \right)^s \exp \left( -\frac{n_s^{(1)} n_s^{(2)}}{s + 1} \frac{\rho_s^2}{4} \right) \]
Factorials in denominators/numerators of probabilities expressions lead to overflows/underflows for high quantum numbers.

Exact (bold) and asymptotic probability (light) for a $5 \rightarrow 4 \text{N}_2$--$\text{N}_2$ V–T collision (upper figure) and maxwellian velocity distribution functions at 10,000 K and 100,000 K (lower figure).

Nikitin (light) and Exact (bold) asymptotic transition probabilities for a $15 \rightarrow 30 \text{N}_2$--$\text{N}_2$ V–T collision as a function of the colliding velocity (upper figure) and corresponding reaction rates against the translational temperature (lower figure).
Numerical Implementation of the FHO Model

Factorials in denominators/numerators of probabilities expressions lead to overflows/underflows for high quantum numbers.

Only the Bessel approximation can be recommended for low-intermediate temperatures.
The Question of Accurate Level Energies Calculations

- Typical level energies calculations rely on polynomial expansions. These are not accurate outside their initial fit range.

- Potential reconstruction methods (+ solving the radial Schrödinger equation) allow accurate extrapolations up to the dissociation energy.

- For \( \text{N}_2(\text{X}) \), a RKR method and a more sophisticated DPF method both yield \( v_{\text{max}} = 60 \) instead of the traditional \( v_{\text{max}} = 45-47 \). The 2D limit of the Lagana \( \text{N}_3 \) potential considered by the Bari team yields \( v_{\text{max}} = 67 \).

- Inaccurate level energies lead to orders of magnitude differences (\( \text{N}_2 \) dissociation rates, Pink Afterglow times. (see LinodaSilva, PSST 2009 & LinodaSilva, ChemPhys 2008)
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Mário Lino da Silva, IPFN–IST

STELLAR Database, RHTGAE5
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Development of Detailed Databases for Multiquantum V–T and V–D transitions in Air

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Model</th>
<th>$\alpha^{-1}$ (Å)</th>
<th>E (K)</th>
<th>N</th>
<th>Ref.</th>
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<td>FHO 4</td>
<td>200</td>
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<td>92</td>
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</table>

These 34148 Rates are compiled in the IST STELLAR 1.0 Database (available at http://esther.ist.utl.pt)
Database for $N_2$–$N_2$ Transitions

Single-quantum V–V rates for $N_2$–$N_2$ $(0, 1\rightarrow1, 0)$ and $(0, 1\rightarrow20, 19)$ transitions and $O_2$–$N_2$ $(0, 1\rightarrow1, 0)$ transitions. − and − − , FHO model. × , calculations of Billing for $N_2$–$N_2$. ◊, interpolation of experimental data for $N_2$–$O_2$ $(1, 0\rightarrow0, 1)$, Taylor:1969.

The STELLAR Database: A Detailed Database for Air Reproduction of Macroscopic Rates

Sample Applications

Database for \( \text{O}_2\text{–O}_2 \) Transitions

Single-quantum V–T rates for \( 1 \rightarrow 0 \) and \( 2 \rightarrow 1 \) transitions (bottom to top). ––, FHO model \((E = 380\text{K})\); α–α, FHO model (repulsive potential); o, calculations of Coletti and Billing.

Reproduction of Equilibrium Dissociation Rates

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\[ \text{N}_2 + \text{N}_2 \rightarrow \text{N} + \text{N} + \text{N}_2 \text{ (LinodaSilva)} \]

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Comparison between FHO (red) and Macroscopic Kinetics Datasets

\[ K_d^{eq} = \frac{Q_v(T)}{\sum Q_v(T) k_d(v, T)} \]

Excellent reproduction of equilibrium dissociation data.

Mário Lino da Silva, IPFN–IST

STELLAR Database, RHTGAE5
Reproduction of Equilibrium Dissociation Rates

\[ \text{N}_2 + \text{N} \rightarrow \text{N} + \text{N} + \text{N} \] (Esposito)

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Reproduction of Equilibrium Dissociation Rates

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Sample Applications and Future Work

Sample Applications
Towards an Adequate Accounting of Excited Levels and V–E Rates

- V–E transitions presented as:
- $N_2(v) + M \rightarrow N_2(A) + M$

Potential curves and first and last vibrational levels for $N_2(X)$ and $N_2(A)$
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- V–E transitions presented as:
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Potential curves and first and last vibrational levels for $N_2(X)$ and $N_2(A)$.
Towards an Adequate Accounting of Excited Levels and V–E Rates

- V–E transitions presented as:
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- Which means:
  \[ N_2(X, \nu = i) + M \rightarrow N_2(A, \nu = f) + M \]
- We replace them by:
  \[ N_2(X, \nu_i) + M \rightarrow N_2(X, \nu_f) + M \]
  \[ N_2(X, \nu_i) + M \rightarrow N_2(A, \nu_f) + M \]
  \[ N_2(A, \nu_i) + M \rightarrow N_2(A, \nu_f) + M \]
0D calculation in the conditions of Fire II

Post-shock average vibrational energies of N₂, O₂ and NO

Mário Lino da Silva, IPFN–IST  STELLAR Database, RHTGAE5
Post-shock excitation of the vibrational levels of N\(_2\), using an N\(_2\)–N\(_2\) (FHO, Lino da Silva) and N\(_2\)–N (QCT, Esposito) multiquantum kinetic dataset.
Conclusions


- A full repulsive 3D FHO approach, including the effects of rotation exists (Macheret & Adamovich) but it is preferred to keep the 1D approach with steric factors, as we can account for repulsive-attractive Morse interactions. Need to carefully tailor the numerical simulation (underflows/overflows) and to select adequate vibrational energies manifolds.

- The diatom-diatom collision databases produced using the FHO model pass all the validation tests (physical consistency, thermodynamic equilibrium consistency, reproduction of available experimental and numerical state-to-state rates from sophisticated models), and provide reliable datasets which will help bridging the transition to full 3D trajectory methods over surface potentials.

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