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Fitting Analytic Expressions to Atomic Collision Cross Sections

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Abstract

From our work done under contracts with JAERI, the followings are described:

- Functional forms useful for fits to atomic collision (including charge transfer) cross sections
- A method to optimize adjustable parameters.

Introduction

- Different purposes of fitting equations to data
  - To determine an unknown value in a theoretical relation
  - To analyze experimental data to identify material components, etc. under study (material analysis, etc.)
  - To establish a semiempirical or an empirical relation, or to give recommended values of data, for quantities obtainable only by elaborate study: effective use of data to give most probable values, interpolated and extrapolated values

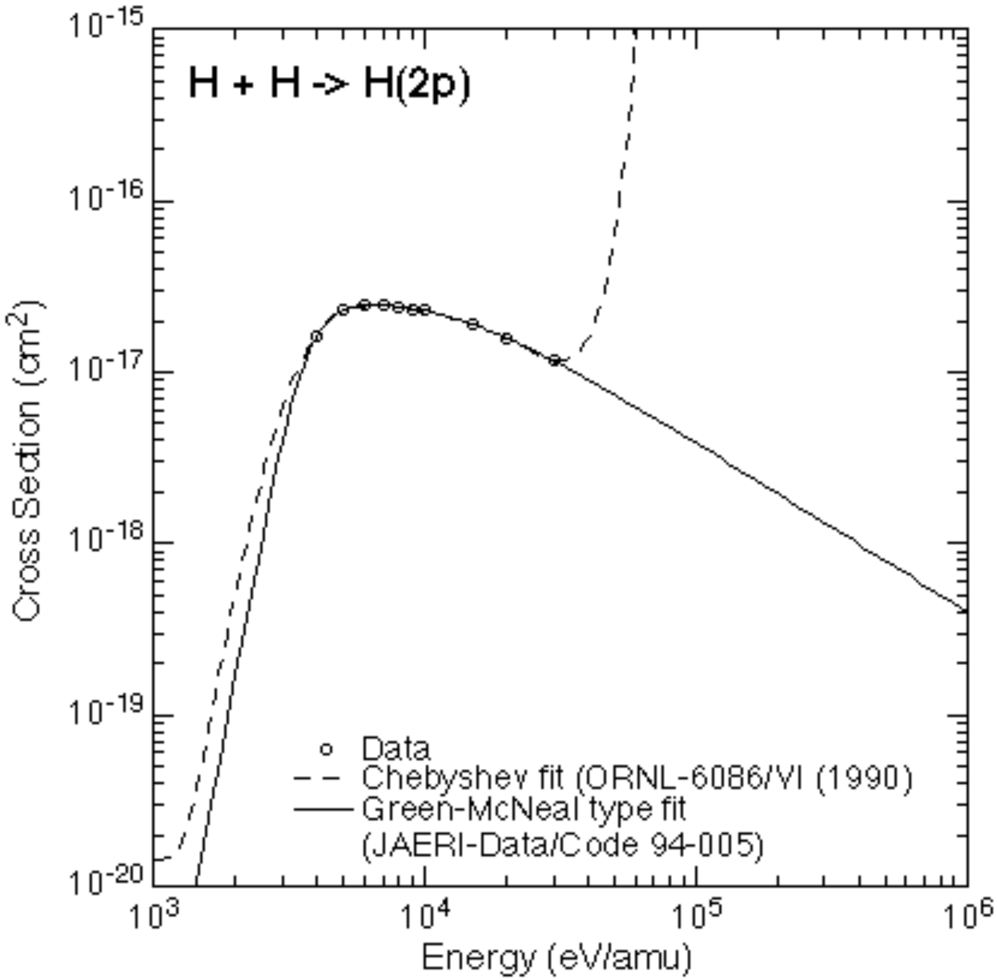
    However, . . .

Introduction (2)

- When a misbehaving function is used, extrapolation even to the smallest extent fails.

Dashed line: Chebyshev fit, ORNL -6086/VI (1990); 7 parameters
Solid line: Our fit, JAERI-Data/Code 94-005; (1994); 6 parameters

[Figure adapted from: T. Tabata and R. Ito, “Report on JAERI Contract Work: Study on Collisions of Atoms, Molecules and Ions” (1991).]



Functional Forms for Fitting

- Finding functional forms of equations
  - Theoretical approach
    - Derive from a simple model
    - Use the prediction of an asymptotic theory
    - Use a scaling law
    - Replace some constants in a theoretical equation (based on a simple model) by adjustable parameters
    - Replace a theoretical equation by a simple equation with similar behavior
  - Empirical approach
    - Find a possible functional form by plotting data
  - Combined approach

Functional Forms for Fitting (2)

- An earlier work to express atomic collision cross sections by analytic expressions
  - Green and McNeal, J. Geophys. Res. **76**, 133 (1971)
    Total cross section for electron capture by H^+:

$$\sigma = \sigma_0 \frac{(Za)^{\Omega}(E - E_{\mathrm{t}})^{\nu}}{J^{\Omega+\nu} + E^{\Omega+\nu} + (Za)^{\Omega} E^{\nu} (E/C)^{\Lambda}} \quad (1)$$

$\sigma_0 = 1 \times 10^{-16}\ \mathrm{cm}^2$

Z = number of electrons in the target atom or molecule

E = projectile energy

E_{t} = threshold energy

$a, \Omega, \nu, J, C, \Lambda$: adjustable parameters

Functional Forms for Fitting (3)

- Justification of Green–McNeal formula
  - Low and intermediate energy region: approaches to Rapp–Francis formula
  - High energy region: approaches the result of Born approximation
- Modifications of Green–McNeal formula for various charge transfer cross sections
  - Charge transfer of hydrogen atoms and ions colliding with gaseous atoms and molecules: At. Data Nucl. Data Tables **37**, 69 (1987)
  - The same with metal vapors: Nucl. Instr. Meth. B **31**, 375 (1988)

Functional Forms for Fitting (4)

- Modified formula, Eq. (2)

$$\sigma = \sigma_0 \left\{ f(E_1) + a_7 f(E_1 / a_8) \right\} \qquad (2)$$

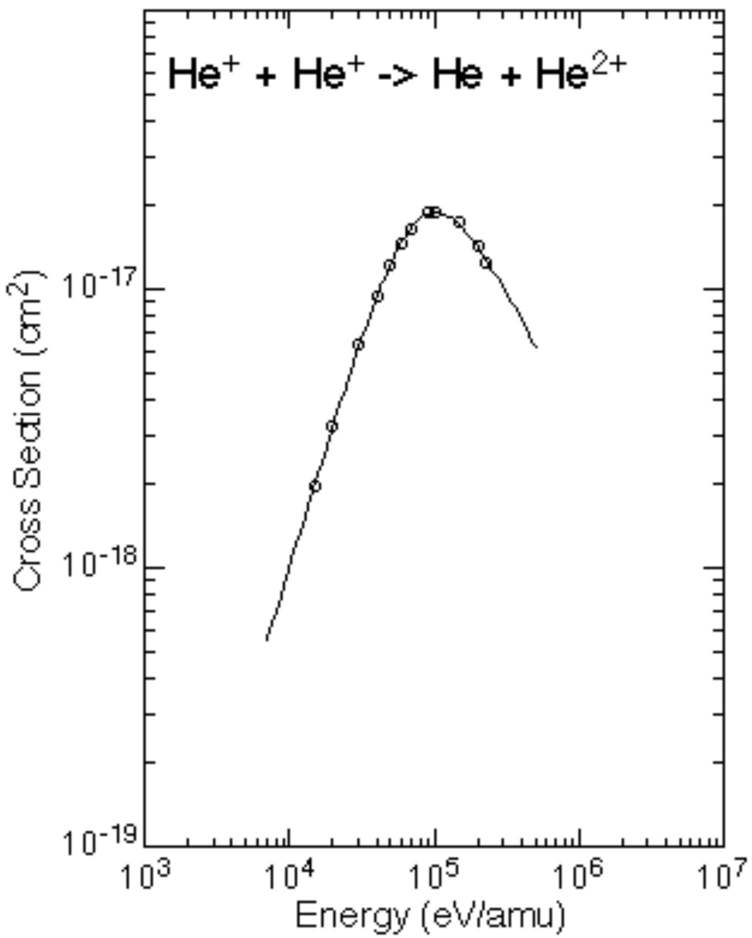
$$f(E) = \frac{a_1 (E/E_\mathrm{R})^{a_2}}{1 + (E/a_3)^{a_2+a_4} + (E/a_5)^{a_2+a_6}} \qquad (3)$$

$E_1 = E_0 - E_\mathrm{t}$
E_R = 25.0 keV (Rydberg energy multiplied by the ratio of the atomic hydrogen mass to the electron mass)
$a_1, a_2, \ldots, a_8$ = adjustable parameters

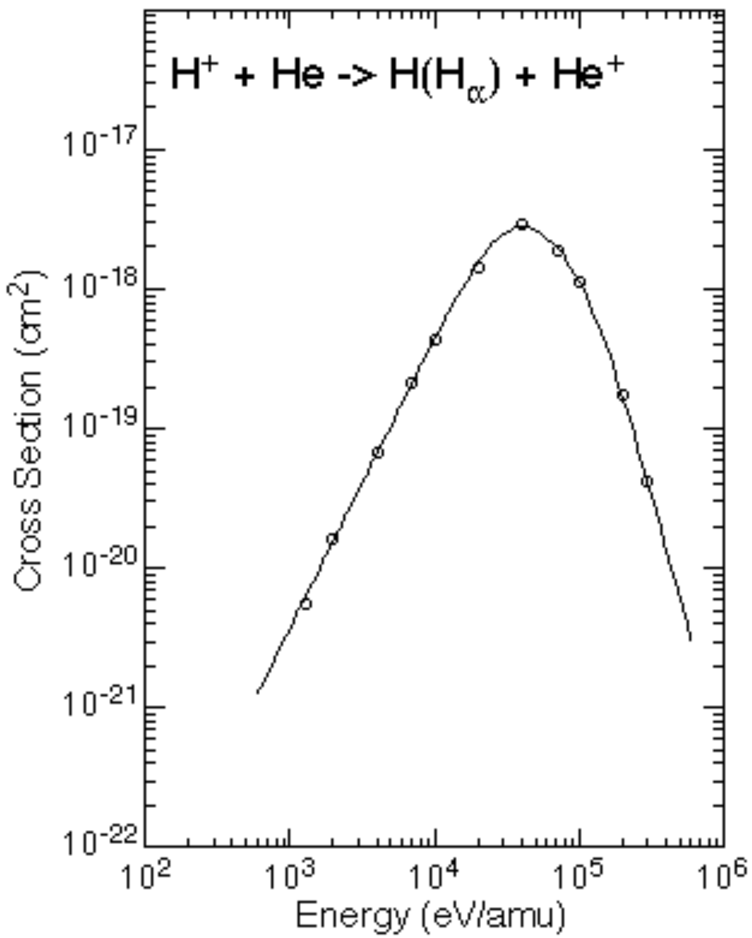
Functional Forms for Fitting (5)

- Examples of fits by Eq. (2) (n: number of parameters)

A narrow peak, n = 4



A broad peak, n = 6

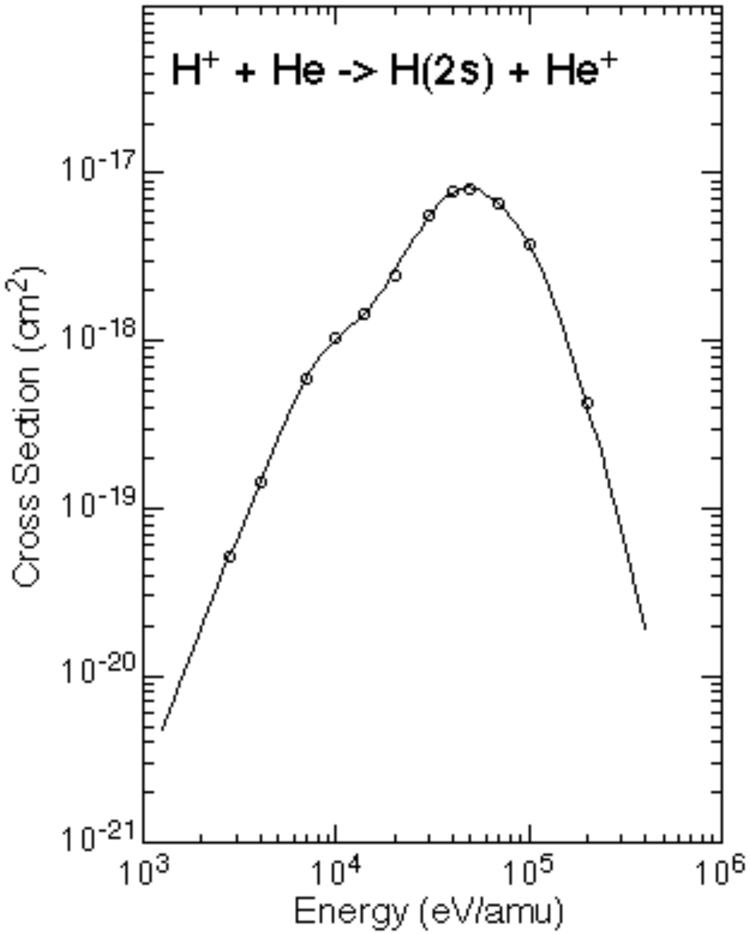


Figures adapted from JAERI-M 93-117

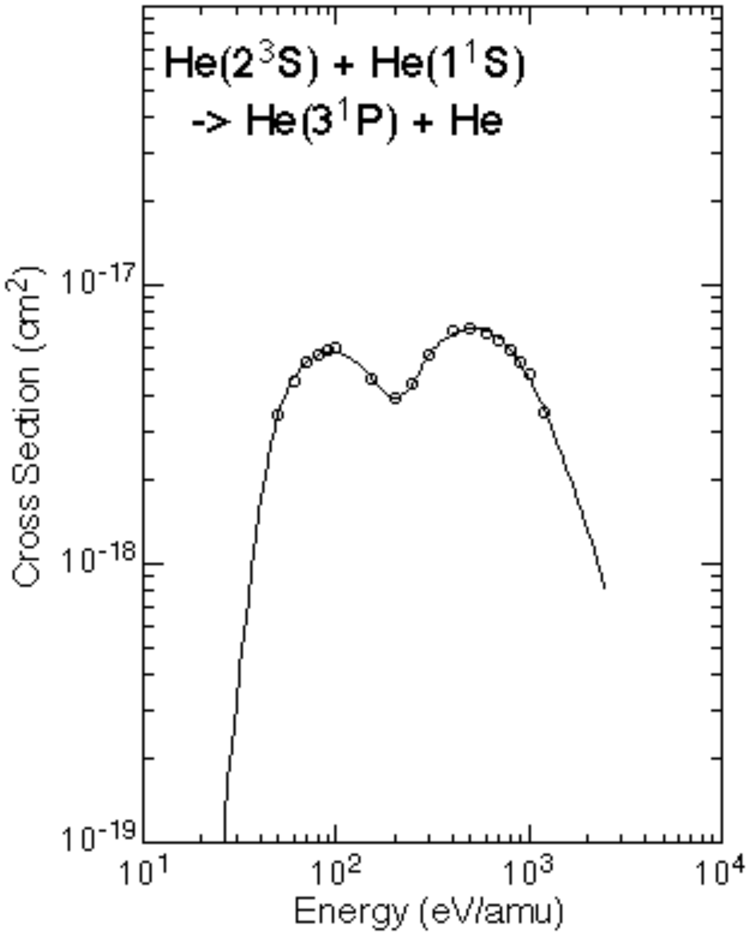
Functional Forms for Fitting (6)

- Examples of fits by Eq. (2) (Continued)

A peak with a shoulder, n = 8



Two peaks, n = 8



Figures adapted from JAERI-M 93-117 and JAERI-Data/Code 94-005

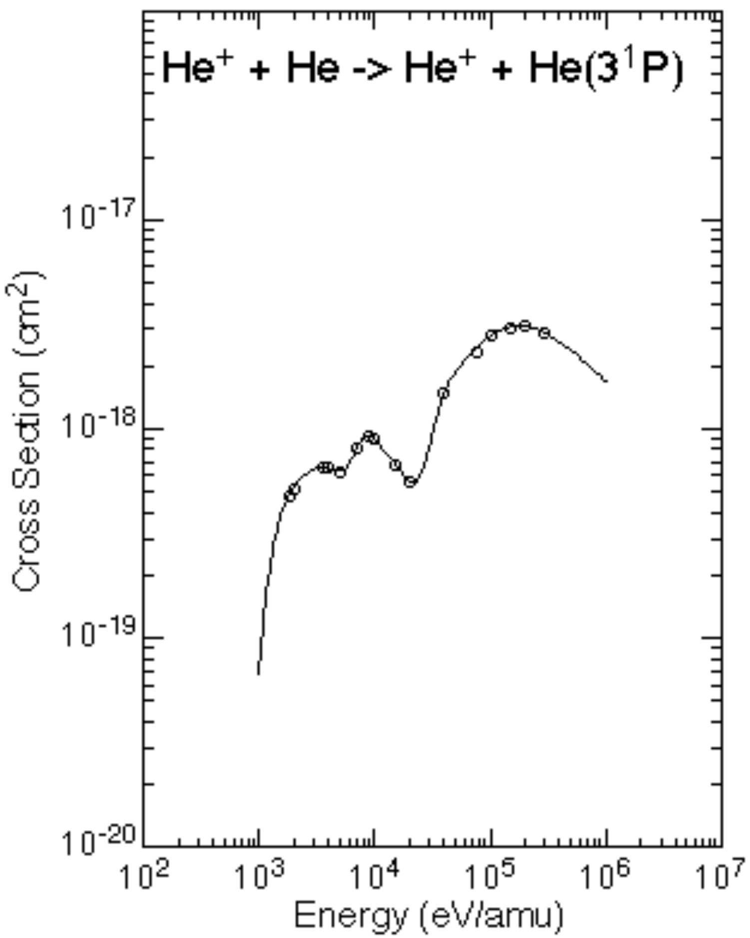
Functional Forms for Fitting (7)

- Cross sections with more structures
  - Summation of more terms of the form of Eq. (3)
    Collisions of H, H_2, He and Li atoms and molecules,
    I, JAERI-M 93-117 (1993); II, JAERI-Data/Code 94-005; III, ibid 95-008; IV, ibid 96-024
  - Similar treatment:
    Rudd et al. [Phys. Rev. A **28**, 3244 (1983)]
    fitted cross sections of electron capture by H^+
    colliding with gaseous atoms and molecules
    by the use of summation of the terms similar to
    Eq. (3) over (outer most) subshells

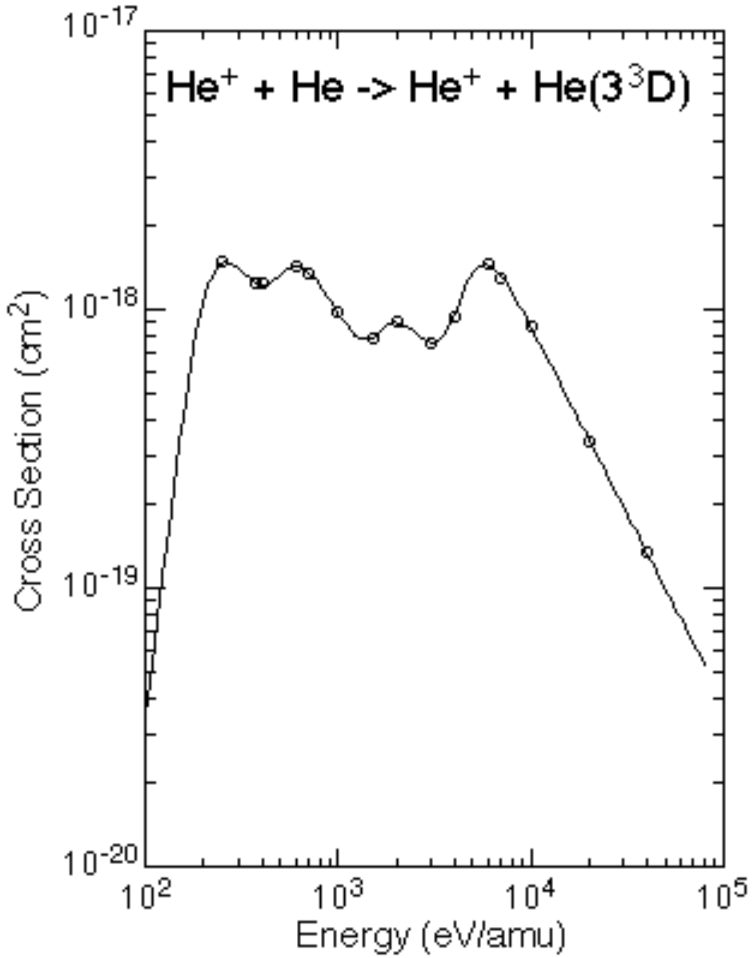
Functional Forms for Fitting (8)

- Cross sections with more structures (Continued)

Three peaks, n=11



Four peaks, n=10



Figures adapted from JAERI-Data/Code 94-005

Functional Forms for Fitting (9)

- Different functional forms used by other authors
  - Electron removal from hydrogen atoms in collisions with positive ions:
    - Olson et al., Phys. Rev. Lett. **41**, 163 (1978)

$$\sigma/q = a(bq/E_0)[1 - \exp(-E_0/bq)]\sigma_0 \quad (4)$$

  - General scaling relations for multiply charged ions
    - Phaneuf et al., Nucl. Fusion, Special Suppl. (1987)

$$\sigma/q = \frac{Aq\ln\left(B\sqrt{q}/E_0\right)}{1 + CE_0^{\ 2}/q + D\left(E_0/\sqrt{q}\right)^{4.5}} \quad (5)$$

Functional Forms for Fitting (10)

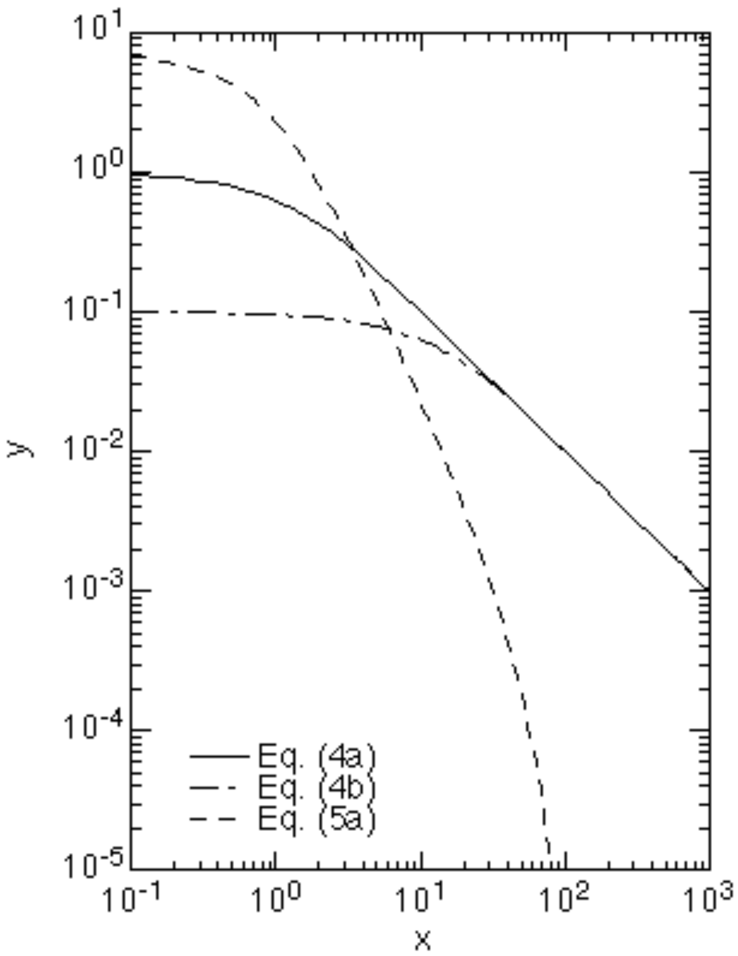
- Behavior of Eqs. (4) and (5)
  - Plot of representative curves:

$$y = (1/x)[1 - \exp(-x)] \qquad (4a)$$

$$y = (1/x)[1 - \exp(-x/10)] \qquad (4b)$$

$$y = \ln(10^2/x)\left[1 + x^2 - \exp(-x/10)^{4.5}\right] \qquad (5)$$

  - Limitations of these equations:
    - Eq. (4), fixed asymptotic behavior
    - Eq. (5), limited energy region



Optimization of Adjustable Parameters

- Method of least-squares fit
  - Computer code used:
    ALESQ [RIAST OPU TR No. 2 (1997)]
  - Algorithm used in ALESQ:
    Levenberg–Marquardt algorithm (maximum-neighborhood algorithm) [see Bevington, "Data Reduction and Error Analysis for the Physical Sciences" (McGraw-Hill, New York, 1969)]
    with Tabata–Ito strategy [Computer J. **18**, 250 (1975)]

Optimization of Adjustable Parameters (2)

- Weighting data points
  - Ideally:

$$w_i = \frac{N / \sigma_i^2}{\sum_{i=1}^{N} \left(1 / \sigma_i^2 \right)} \qquad (6)$$

  - Practically for data that range over an order of magnitude or more: Assume uncertainties of approximately equal relative magnitude (σ_i = const·y_i):

$$w_i = \frac{N / y_i^2}{\sum_{i=1}^{N} \left(1 / y_i^2 \right)} \qquad (7)$$

However, . . .

Optimization of Adjustable Parameters (3)

- Weighting data points (Continued)
  - For data with large fluctuations:
    Use two-step fitting
    - First step:
      Function (ln y) is fitted to data {ln y_i} with
      $$w_i = 1 \qquad (8)$$
    - Second step:
      Function y is fitted to data {y_i} with
      $$w_i = \frac{N / y^2(\mathbf{x}_i;\ \mathbf{a}_\mathrm{F})}{\sum_{i=1}^{N} \left[1 / y^2(\mathbf{x}_i;\ \mathbf{a}_\mathrm{F}) \right]} \qquad (9)$$

Optimization of Adjustable Parameters (4)

- Finding initial values
  - Example: C^+ production by electron collision with CO

$$\sigma = \sigma_0 \frac{a_1\left[(E_0 - E_t)/E_R\right]^{a_2}}{1+\left(\left[(E_0 - E_t)\right]/a_3\right)^{a_2+a_4}}$$

$E_t = 2.24\times10^{-2}$ keV

$E_R = 1.361\times10^{-2}$ keV

$a_1 = 1.3\times10^{-1}$ (vertical scale of arrow 1)

$a_2 = 1.5$ (gradient of line 2)

$a_3 = 1.0\times10^{-1}$ (keV) (horizontal scale of arrow 3)

$a_4 = 1.0$ (absolute gradient of line 4)

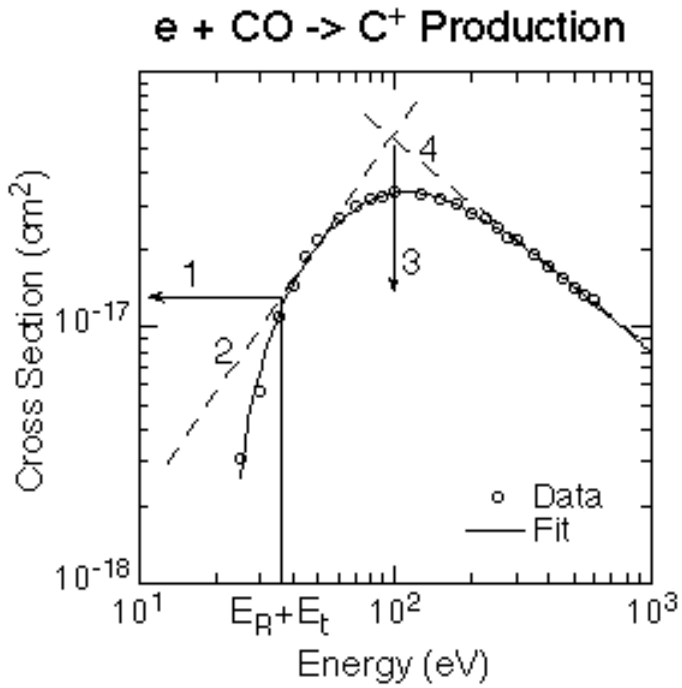
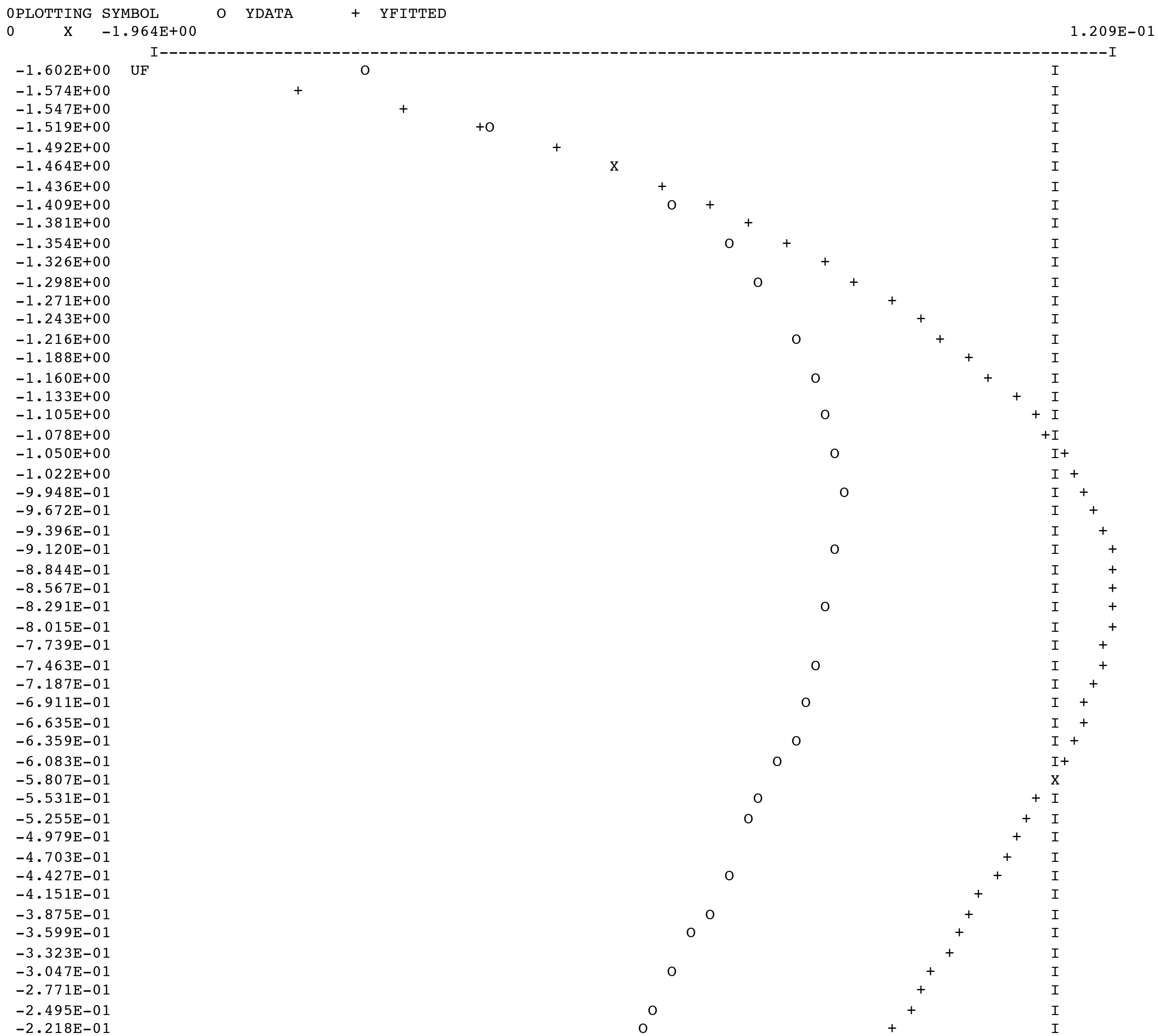


Figure adapted from: T. Shirai et al., to be published.

Optimization of Adjustable Parameters (5)

- Rough plot with initial values: $\delta_{rms} = 2.4$



Optimization of Adjustable Parameters (6)

- Check the result obtained
  - Look at the plot

```
0PLOTTING SYMBOL      O  YDATA      +  YFITTED
0     X   -1.588E+00                                                                                          -4.701E-01
               I----------------------------------------------------------------------------------------------------I
 -1.602E+00    +      O
 -1.574E+00                      +
 -1.547E+00                                  +
 -1.519E+00                                   O         +
 -1.492E+00                                                    +
 -1.464E+00                                                          + O
 -1.436E+00                                                                +
 -1.409E+00                                                                     + O
 -1.381E+00                                                                          +
 -1.354E+00                                                                              +   O
 -1.326E+00                                                                                  +
 -1.298E+00                                                                                     + O
 -1.271E+00                                                                                         +
 -1.243E+00                                                                                           +
 -1.216E+00                                                                                              +O
 -1.188E+00                                                                                                +
 -1.160E+00                                                                                                  +O
 -1.133E+00                                                                                                   +
 -1.105E+00                                                                                                     +O
 -1.078E+00                                                                                                      +
 -1.050E+00                                                                                                       X
 -1.022E+00                                                                                                       +
 -9.948E-01                                                                                                        X
 -9.672E-01                                                                                                        +
 -9.396E-01                                                                                                        +
 -9.120E-01                                                                                                       O+
 -8.844E-01                                                                                                       +
 -8.567E-01                                                                                                       +
 -8.291E-01                                                                                                     O+
 -8.015E-01                                                                                                     +
 -7.739E-01                                                                                                    +
 -7.463E-01                                                                                                   X
 -7.187E-01                                                                                                  +
 -6.911E-01                                                                                                O+
 -6.635E-01                                                                                               +
 -6.359E-01                                                                                              X
 -6.083E-01                                                                                            X
 -5.807E-01                                                                                          +
 -5.531E-01                                                                                        O+
 -5.255E-01                                                                                       X
 -4.979E-01                                                                                     +
 -4.703E-01                                                                                   +
 -4.427E-01                                                                                 +O
 -4.151E-01                                                                               +
 -3.875E-01                                                                             +O
 -3.599E-01                                                                          O+
 -3.323E-01                                                                         +
 -3.047E-01                                                                       X
 -2.771E-01                                                                     +
 -2.495E-01                                                                   +O
 -2.218E-01                                                                 +O
```

Optimization of Adjustable Parameters (7)

- Rounding parameters

```
RMS RELATIVE RESIDUAL                          = 5.90643E-02
MAXIMUM IN MAGNITUDE OF RESIDUAL              = 2.214E-01 AT DATA NO.   2

RELATIVE RMS DEVIATION OF DATA FROM EQUATION = 5.81E-02

A( 1) =  1.216085675E-01 +/-  3.5E-03
A( 2) =  9.357022265E-01 +/-  3.6E-02
A( 3) =  8.532963359E-02 +/-  7.3E-03
A( 4) =  8.724773152E-01 +/-  5.5E-02
```

Fitting ↗ (initial values)

$a_1 = 3.0\mathrm{E}{-}02$
$a_2 = 1.5\mathrm{E}{+}00$
$a_3 = 1.0\mathrm{E}{-}01$
$a_4 = 1.0\mathrm{E}{+}00$

Rounding ↘

$a_1 = 1.216\mathrm{E}{-}01$
$a_2 = 9.36\mathrm{E}{-}01$
$a_3 = 8.53\mathrm{E}{-}02$
$a_4 = 8.72\mathrm{E}{-}01$

Checking ⇄

$\delta_{rms} = 5.9\%$
$\delta_{max} = 22\%$

Optimization of Adjustable Parameters (8)

- Notice:
  - Optimization by ALESQE sometimes comes to a dead end for certain combinations of data and function even by the use of considerably good starting values.
  - Then try to fit a partial function to partial set of data, or temporarily fix some parameters in fitting.
  - It is a good idea to use ABS(A(I)) instead of A(I) in the function subprogram to define the fitting function, when A(I) is definitely positive.

Further References

- "Cross sections for charge transfer of helium atoms and ions colliding with gaseous atoms and molecules," T. Tabata, et al., Radiat. Center Osaka Pref. Tech. Rep. 7 (1987).
- "A semiempirical formula for single-electron capture cross sections of multiply charged ions colliding with H, H_2 and He," Y. Nakai et al., Physica Scripta, **T28**, 77 (1989).
- "Partial Cross-sections for single-electron capture of hydrogen ions colliding with gaseous atoms and molecules," T. Tabata, et al., Radiat. Center Osaka Pref. Tech. Rep. 11 (1990).
- "Extended scaling of cross-sections for ionization of H, H_2 and He by multiply charged ions," T. Tabata et al., Plasma-Mater. Interaction Data for Fusion **2**, 91 (1992).
- Recommended cross sections for state-selective electron capture in collisions of C^{6+} and O^{8+} ions with atomic hydrogen," R. K. Janev et al., At. Data & Nucl. Data Tables **55**, 201 (1993).
- "Analytic cross sections for collisions of H^+, H_2^+, H_3^+, H, H_2, and H^- with hydrogen molecules," T. Tabata and T. Shirai, At. Data & Nucl. Data Tables **76**, 1 (2000).

Concluding Remarks

- Modified Green–McNeal formulas have been useful to express various atomic collision cross sections as a function of energy.
- The ALESQ code has helped us to optimize adjustable parameters in analytic expressions for atomic collision cross sections, though some skills are needed for masterly use of it.

Appendix: An Anecdote about This Talk

- At the middle of my talk a foreigner came into the room to participate in our meeting. Seeing the slide “Optimization of Adjustable Parameters (4)” he said, “The process of C^+ production by electron collisions with CO being ionization, the fitting function should include a logarithmic form to express the asymptotic behavior.” Thinking that this guy knows much about this topic, I said, “Sure, you’re right,” or something like that, and continued my talk by changing the language from Japanese to English. That guy also gave many comments during the discussion session after my talk, and Prof. Takako Kato or someone called him Dr. Janev. . . .
- Oh! He was Dr. Ratko Janev famous in the atomic-collision community. Without noticing this, I said about the reference written in blue on the slide “Further References,” “I did not participate in this work, but it was done by Janev’s group at IAEA and Dr. Shirai of JAERI, and our ALESQ code was used,” by mentioning his name without title in spite of attaching “Dr.” to my long-time coworker Toshizo Shirai. I had seen Dr. Janev at IAEA in 1989, but this time he seemed much younger than that time. So I was unable to recognize him.