A PROGRAM FOR THE CALCULATION OF LANDAU–ZENER CROSS SECTIONS AND RATE COEFFICIENTS

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PROGRAM SUMMARY

Title of program: LZRATE

Catalogue number: AACJ

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Computer 1: VAX 11/780; *Installation:* Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA

Computer 2: IBM 3033: *Installation:* Argonne National Laboratory, Argonne, Illinois, USA

Operating systems: VMS and MVS, respectively

Programming language used: FORTRAN IV

High speed storage required: approximately 40 Kbytes

No. of bits in a byte: 8

Peripherals used: video or hard-copy terminal and disk store, or card reader and line printer

No. of cards in source program: 651

Card punching code: EBCDIC

Keywords: charge exchange, charge transfer, cross sections, exponential integrals, ionic-covalent interactions, ionic recombination, Landau–Zener, mutual neutralization, scattering

Nature of the problem
The Landau–Zener (LZ) approximation is a widely used procedure for estimating the cross sections and rate coefficients for a number of collision processes which are describable in terms of potential curve crossings. Among them are charge transfer [1]

and mutual neutralization [2,3]. The LZ method has the advantage of requiring only a minimum of information about the physical system under consideration; furthermore calculations are very inexpensive.

Method of solution
The main equations in refs. [1–3] have been programmed. Accurate and efficient procedures have been implemented for the calculation of exponential integrals, and of Maxwellian averages of the same. Much of the information required was available in the numerical analysis literature but had not been applied to this problem. The present computer code will calculate LZ cross sections or rates in a few milliseconds of processor time and should run on almost any computer which has a FORTRAN compiler. It was written for atomic physicists or astrophysicists wishing to calculate cross sections or rates at the planning stage of an experiment, or to carry out a survey of a particular class of atomic processes in order to identify which of those would warrant calculation by more elaborate techniques.

Restrictions on the complexity of the problem
No more than 20 cross sections or rate coefficients can be calculated by the current version in a single run.

Typical running time
About 5 ms per cross section on the VAX 11/780 (0.4 ms on the IBM 3033). About twelve times as long for a rate coefficient.

References
[1] D.R. Bates and T.J.M. Boyd, Proc. Phys. Soc. London A69 (1956) 910.
[2] D.R. Bates and B.L. Moiseiwitsch, Proc. Phys. Soc. London A67 (1955) 805.
[3] S.E. Butler and A. Dalgarno, Astrophys. J. 241 (1980) 838.

LONG WRITE-UP

1. Introduction

Adiabatic potential energy curves of the same molecular symmetry cannot cross. If they approach closely, an avoided crossing occurs at some distance $R = R_x$, at which a rapid change occurs in the nature of the adiabatic eigenfunctions. In a diabatic description of a reactive collision the corresponding diabatic potential energy curves cross near R_x and are coupled by the off-diagonal elements $H_{12}(R)$ of a symmetric potential matrix. In 1932, Landau [1], Zener [2] and Stueckelberg [3] independently found the transition probability to be given by $\mathcal{P} = 2P(1 - P)$, where P is the probability that a crossing occurs during a single pass through R_x. The Landau–Zener (LZ) approximation asserts that $P = \exp(-w)$, where

$$w = \frac{2\pi[H_{12}(R_x)]^2}{\hbar v(R_x)\left|\dfrac{d}{dR}(H_{11} - H_{22})\right|_{R_x}}, \tag{1}$$

v is the radial component of the relative velocity and $H_{11}(R)$ and $H_{22}(R)$ are the diagonal elements of the diabatic potential energy matrix. The energy separation of the adiabatic curves at R_x is $\Delta U(R_x) = 2H_{12}(R_x)$.

The LZ formula for the probability of a transition has been used to calculate cross sections and rate coefficients for mutual neutralization (cf. Bates and Lewis [4], Bates and Boyd [5]) and for charge transfer (cf. Bates and Moiseiwitsch [6], Dalgarno [7]). Other publications [7–13] have concentrated on the calculation and the systematics of the energy separation $\Delta U(R_x)$ for different classes of processes of physical or astrophysical interest. LZ results have been compared with classical trajectory calculations [14], and with quantal calculations for mutual neutralization [15,16] and for charge transfer [13]. The sensitivity with respect to the 'size' of the transition region, as measured by $\delta R_x/R_x = R_x \Delta U$ [17] and the effect of additional crossings [18] have been explored.

2. Theory

2.1. Mutual neutralization

The LZ cross section for mutual neutralization,

$$A^+ + B^- \rightarrow A + B,$$
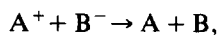
for an energy E of relative motion in the initial channel is given by [5]

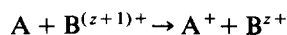$$\sigma(E) = 4\pi p R_x^2\left(1 + \frac{\Delta E}{E}\right)F_3(\eta), \tag{2}$$

where

$$\eta = \pi^2 e^2 \mu^{1/2}[\Delta U(R_x)]^2$$
$$/2^{1/2}\hbar(E + \Delta E)^{1/2}(\Delta E)^2 \tag{3}$$

and $\Delta E = e^2/R_x$, μ being the reduced mass and p the probability that the collision proceeds initially along the potential energy surface $H_{11}(R)$, and

$$F_3(\eta) = \int_1^\infty e^{-\eta x}(1 - e^{-\eta x})x^{-3}dx. \tag{4}$$

2.2. Charge transfer

The LZ cross section for charge transfer from metal atoms to doubly or multiply charged ions

$$A + B^{(z+1)+} \rightarrow A^+ + B^{z+}$$

is given by [5,13]

$$\sigma(E) = 4\pi p R_x^2(1 + \lambda)F_3(\eta), \tag{5}$$

where

$$\eta = 2\pi^3 \mu[\Delta U(R_x)]^2$$
$$/kh^2(1 + \lambda)^{1/2}\left|\frac{d}{dR}(H_{11} - H_{22})\right|_{R_x}, \tag{6}$$

$$\lambda = [H_{11}(\infty) - H_{11}(R_x)]/E,$$

and $k = \mu v/\hbar$ is the momentum in the initial channel 1. The parameter λ represents a correction resulting from the deviation of $H_{11}(R)$ from a constant potential, due to attractive polarization effects. In order to estimate λ reliably quantal calculations of the shape of $H_{11}(R)$ would be needed. Fortunately, except at low temperatures, $\lambda = 0$ is a reasonable approximation. Polarization

effects are normally ignored for the ionic potential $H_{22}(R)$, hence $dH_{22}/dR = -ze^2/R_x^2$.

3. Numerical considerations

3.1. Calculations of rate coefficients from cross sections

Rate coefficients at thermal equilibrium are obtained by averaging the cross sections σ over the Maxwellian distribution of relative velocities. Thus

$$\langle v\sigma \rangle_E = \sqrt{\frac{8k_BT}{\pi\mu}} \frac{1}{(k_BT)^2}$$

$$\times \int_0^\infty \sigma(E) E \, e^{-E/k_BT} dE$$

$$= \langle v \rangle \langle \sigma \rangle, \tag{7}$$

where

$$\langle v \rangle = \sqrt{8k_BT/\pi\mu}$$

and

$$\langle \sigma \rangle = \int_0^\infty \sigma(E) \frac{E}{k_BT} e^{-E/k_BT} d\left(\frac{E}{k_BT}\right). \tag{8}$$

The evaluation of $\langle \sigma \rangle$ in eq. (8) is facilitated by converting the integral over the infinite range to one over a finite range. Let $\epsilon = E/(k_BT)$. It is convenient to regard $\langle \sigma \rangle$ as the integral of σ over a weight function $U(\epsilon)$ [19] defined by

$$dU = \rho(E)dE = \epsilon e^{-\epsilon} d\epsilon,$$

with normalization $U(\infty) = 1$.
This gives

$$U(\epsilon) = 1 - (1 + \epsilon) e^{-\epsilon}.$$

Hence,

$$\langle \sigma \rangle = \int_0^\infty \sigma\epsilon \, e^{-\epsilon} d\epsilon \equiv \int_0^1 \sigma dU$$

$$\doteq \sum_{i=1}^n w_i \sigma(U_i),$$

where the points and weight are chosen according to some quadrature scheme, e.g. Gauss–Legendre. In order to evaluate $\sigma(U_i)$ one must find the value of $\epsilon = \epsilon_i$ corresponding to each quadrature point

Table 1
Points U_i and modified points $\epsilon(U_i)$ for six-point and twelve-point Gauss–Legendre quadratures

i	U_i	$\epsilon(U_i)$
1	0.033765243	0.285482901
2	0.169395307	0.738791803
3	0.380690407	1.32126022
4	0.619309593	2.09582241
5	0.830604693	3.21391152
6	0.966234757	5.21534447
1	0.009219683	0.142349933
2	0.047941372	0.347033224
3	0.115048663	0.579039152
4	0.206341023	0.841897938
5	0.316084251	1.14136316
6	0.437383296	1.48571841
7	0.562616704	1.88724978
8	0.683915749	2.36524821
9	0.793658977	2.95259815
10	0.884951337	3.71265059
11	0.952058628	4.79472434
12	0.990780317	6.73174985

$U = U_i$. This is easily accomplished by solving the equation

$$1 - (1 + \epsilon) e^{-\epsilon} - U_i = 0 \quad (i = 1, 2, \ldots, n)$$

by a Newton-like method. Table 1 gives the usual and the transformed Gauss-Legendre points for a six-point and for a twelve-point quadrature. We have found the twelve-point rate coefficients to be accurate to better than 1%. Six-point results are usually accurate to a few percent.

3.2. Evaluation of the integral $F_3(\eta)$

The calculation of LZ cross sections reduces, from a computational viewpoint, to the evaluation of the function $F_3(\eta)$ in eqs. (2), (4) and (5). This function is related to the exponential integral $E_3(\eta)$ [5] and hence to the incomplete gamma function $\Gamma(-2, \eta)$ [20] according to

$$F_N(\eta) = E_N(\eta) - E_N(2\eta), \tag{9}$$

where

$$E_N(\eta) = \int_1^\infty e^{-\eta x} x^{-N} dx$$

$$= \eta^{N-1} \Gamma(1 - N, \eta)$$

and

$$\Gamma(1 - N, \eta) = \int_\eta^\infty e^{-x} x^{-N} dx.$$

Bates and Boyd [5] have given plots of the mutual neutralization rate coefficients as a function of $\log(\eta)$ obtained from a tabulation of the function $E_3(\eta)$. Subsequent papers, including recent ones, either reference these graphs [18,21] or use rather crude approximations valid for small η [11], or have integrated eq. (4) numerically [13]. We now suggest a more convenient approach. The recurrence relation [20]

$$E_{N+1}(\eta) = \frac{1}{N}[e^{-\eta} - \eta E_N(\eta)] \quad (N = 1, 2, \ldots)$$

(10)

together with eq. (9) allows one to express the function $F_3(\eta)$ in terms of the canonical exponential integral $E_1(\eta)$, for which accurate and efficient Chebyshev approximations have been available since 1969 [22]. Routines based on these minimax approximations, e.g. our function EIONE or those found in widely distributed software libraries [23–25], make possible the accurate calculation of LZ cross sections in milliseconds on a minicomputer.

4. Program description

4.1. Main program

The main program controls input and output operations and, if appropriate, calculates rate coefficients by twelve-point Gauss–Legendre quadrature, from the cross sections calculated in the rest of the code.

The first card reads in a title used to identify each run. The second card read is a control card defining whether cross sections (IOPTN = 0), rate coefficients for the direct process (IOPTN = 1), or rate coefficients for both the direct and the reverse processes (IOPTN = 2) are to be calculated; whether the reaction under consideration is mutual neutralization (ITYPE = 0) or charge transfer (ITYPE > 0), and whether the energy separation at the crossing $\Delta U(R_x)$ is to be used as read in

(ITYPE = 0 or 5) or calculated from the formulae in ref. [13] (ITYPE = 1–4). Other parameters inputted are the reduced mass μ, crossing point R_x, product of charges in the ionic channel z, statistical factor p, energy separation at the crossing ΔU, potential energy $H_{11}(R_x)$ for the initial channel and its radial derivative at the crossing. For a cross section calculation, the number and list of energies are read in the third card. For a rate coefficient calculation, the number and list of temperatures are read instead in the third card and, if applicable, a fourth card is read containing the threshold energy and the statistical weight of the reverse process.

4.2. Subroutine LZS0

Called by the main program, this subroutine evaluates LZ cross sections for mutual neutralization (entry point LZS1) and for charge transfer (entry point LZS2).

4.3. Function EXPINT

Called by LZS0, EXPINT calculates the exponential integral $E_N(\eta)$ in terms of $E_1(\eta)$ by the recurrence relation, eq. (10).

4.4. Function EIONE

Called by EXPINT, EIONE calculates Chebyshev approximations to the function $E_1(\eta)$; it makes use of the coefficients of Cody and Thacher [22]. Other exponential integrals may also be evaluated with this routine. Further details are given in the program comment cards.

5. Test cases

Three examples are included with the code, which test some of its options. The first two runs are mutual neutralization calculations with LZ parameters from ref. [11]; the last case is a charge exchange calculation.

Acknowledgements

References

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TEST RUN OUTPUT

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             Test 1: Li-F mutual neutralization rate coefficient, data from [11]
   MU =      5.1150 AMU
   RX =     14.0000 BOHR
TYPE =  0
   Z =      -1.0
   P =       1.0000
  DU(RX) =    1.06E-02 eV    H1INF =     1.94E+00 eV


             ENERGY( eV )      SIGMA( 10(-16)cm2 )
             1.0000E+01          3.8133E+00
             1.5000E+01          3.0441E+00
             2.0000E+01          2.6072E+00
             2.5000E+01          2.3171E+00
             3.0000E+01          2.1065E+00
             3.5000E+01          1.9447E+00
             4.0000E+01          1.8155E+00
             4.5000E+01          1.7091E+00
             5.0000E+01          1.6195E+00
             5.5000E+01          1.5427E+00



Test 2: Li-F mutual neutralization rate coefficient, data from [11]
   MU =      5.1150 AMU
   RX =     14.0000 BOHR
TYPE =  0
   Z =      -1.0
   P =       1.0000
  DU(RX) =    1.06E-02 eV    H1INF =     1.94E+00 eV


REDUCED MASS IN ATOMIC MASS UNITS   =     5.1150E+00
TEMPERATURE (K) =    3000.00
ENERGIES (eV):                3.6800E-02    8.9715E-02    1.4969E-01    2.1765E-01    2.9507E-01    3.8409E-01
                              4.8789E-01    6.1147E-01    7.6331E-01    9.5980E-01    1.2395E+00    1.7403E+00
CROSS SECTIONS (10(-16) cm2): 4.0428E+02    1.6818E+02    1.0237E+02    7.1613E+01    5.3822E+01    4.2213E+01
                              3.4011E+01    2.7860E+01    2.3011E+01    1.8991E+01    1.5437E+01    1.1875E+01

RATE COEFFICIENT  (cm3 PER MOLECULE PER SECOND) =     2.0436E-09

STATISTICAL WEIGHTS  WF = 1.0000E+00  WR = 8.3333E-02
THRESHOLD (eV) = 2.0000E+00
REVERSE (ENDOTHERMIC) RATE (cm3 PER MOLECULE PER SECOND) =     7.4363E-14


REDUCED MASS IN ATOMIC MASS UNITS   =     5.1150E+00
TEMPERATURE (K) =    6000.00
ENERGIES (eV):                7.3601E-02    1.7943E-01    2.9939E-01    4.3530E-01    5.9013E-01    7.6818E-01
                              9.7579E-01    1.2229E+00    1.5266E+00    1.9196E+00    2.4791E+00    3.4806E+00
CROSS SECTIONS (10(-16) cm2): 2.0413E+02    8.6045E+01    5.3099E+01    3.7680E+01    2.8739E+01    2.2887E+01
                              1.8735E+01    1.5604E+01    1.3118E+01    1.1038E+01    9.1760E+00    7.2724E+00

RATE COEFFICIENT  (cm3 PER MOLECULE PER SECOND) =     1.5316E-09

STATISTICAL WEIGHTS  WF = 1.0000E+00  WR = 8.3333E-02
THRESHOLD (eV) = 2.0000E+00
REVERSE (ENDOTHERMIC) RATE (cm3 PER MOLECULE PER SECOND) =     2.6672E-12
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```
Test 3: C(3+) + H ---> C(2+) + H(+) triplet sigma+ symmetry
  MU  =        0.9230 AMU
  RX  =       11.1100 BOHR
TYPE =  1
  Z  =        2.0
  P  =        1.0000
       DU(RX)  =      5.03E-02 eV
       H11(RX) =      0.00E+00 eV
  DH11(RX)/DR  =      0.00E+00 eV/BOHR
  DH22(RX)/DR  =     -4.41E-01 eV/BOHR


REDUCED MASS IN ATOMIC MASS UNITS  =      9.2300E-01
TEMPERATURE (K) =   10000.00
ENERGIES (eV):                    1.2267E-01    2.9905E-01    4.9898E-01    7.2549E-01    9.8355E-01    1.2803E+00
                                  1.6263E+00    2.0382E+00    2.5444E+00    3.1993E+00    4.1318E+00    5.8010E+00
CROSS SECTIONS (10(-16) cm2):     3.4769E+01    2.6323E+01    2.1937E+01    1.9042E+01    1.6896E+01    1.5190E+01
                                  1.3763E+01    1.2518E+01    1.1389E+01    1.0315E+01    9.2208E+00    7.9285E+00

RATE COEFFICIENT  (cm3 PER MOLECULE PER SECOND) =      2.3659E-09
```