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Users Guide for SROSOL

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A computer code called SROSOL that calculates wave functions and matrix elements for diatomic molecules is briefly described. The objective of this report is to serve as a users guide to SROSOL; hence, the primary focus is on the input to the code and how it is used. Some results in the form of Franck-Condon factors for nitrogen are displayed; these factors are then used to examine a molecular emission spectrum.

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Users guide to SROSOL

Introduction

This report briefly describes a computer code called SROSOL written by one of the authors, Paul S. Julienne, that calculates wave functions and matrix elements for diatomic molecules. These matrix elements, for example Franck-Condon factors, can then be used to investigate phenonema such as molecular radiative emission and absorption.

The focus of this report is to serve as a users manual for SROSOL; hence the primary emphasis is on the input to the code and how it is used. The input parameters are discussed in some detail, especially for a Morse potential. Then comparisons of results from this code for Franck-Condon factors for the First Positive Band of N_2 are given with two similar calculations.

Finally, an example of the use of SROSOL results is presented in the form of a calculated molecular emission spectrum.

The program SROSOL calculates eigenvalues and normalized bound or continuum solutions to the one-dimensional Schrodinger equation

$$d^2\psi/dR^2 + (4\pi^2/h^2)2\mu(E - U(R))\psi = 0$$

where μ is the reduced mass, and h is Planck's constant. These wave functions can be used to calculate matrix elements of the type

$$< \psi_{1i}|\theta_{12}|\psi_{2k} >$$

where ψ_{1i} is the wave function of level i in potential 1, and ψ_{2k} is the wave function of level k in potential 2: θ_{12} is the operator being evaluated. The numerical algorithm is adapted from Gordon[1].

The first wave function is calculated on a self-determined point grid which optimizes the propagation intervals both for the self-propagation and, by virtue of a comparison with the second potential, for the calculation of the matrix element later. The second wave function is calculated on the fixed point grid established by the propagation of the first wave function.

The actual equation solved by the code is

$$d^2\psi/dx^2 + ((E - U(R))/E_0)\psi = 0$$

where

$$E_0 = (h^2/4\pi^2)/2\mu x_0^2$$

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gives the working energy unit, and x_0 gives the working length unit, e.g., if E_0 is in cm^{-1} , x_0 is in Bohr(Bohr radii), and μ is in atomic mass units(amu), then

$$E_0 = 60.19974/\mu$$

in units of cm^{-1}. The energies and potentials E and U must be given in the same units as E_0 and x_0. The choices available to the user are determined by the parameters IE, IX, and IM defined on Line 3 of the input file; these are discussed in the next section.

Although SROSOL can treat potentials U(R) which are Morse type, exponential repulsive type, and numerical splines, this report is limited primarily to Morse potentials.

Input File

This section is a line-by-line discussion and description of the input file FT05.

The line numbers appear in italics followed by the input parameters on that line. A description of these parameters follows each line number.

Line 1: PRBLBL (This is a label describing the problem being treated.)

Line 2: IPROB, NPOT (see table below)

- -

(value of IPROB: wave functions conditions)

0: calculate eigenvalues only (no matrix elements)

1: ψ_{1i} and ψ_{2k} are both bound states

2: ψ_{1i} is bound and ψ_{2k} is continuum (any energy)

3: ψ_{1i} is bound and ψ_{2k} is a continuum state of the same energy (i.e., predissocation)

4: ψ_{1i} and ψ_{2k} are both continuum states

5: unused

6: only tabulate and graph potentials - no eigenvalues or matrix elements

7: ψ_{1i} and ψ_{2k} are both continuum states; all i,k pairs calculated

8: ψ_{1i} and ψ_{2k} are both bound states; only i=k pairs calculated

- -

NPOT= the number of potentials. The range is from 2 to 5 when IPROB is greater than zero.

Line 3: IE,IX,IM,μ (see table below)

- -

value	IE	IX	IM
1	au(Hartrees)	Bohr	electron masses
2	1/cm	Angstrom	amu
3	eV	reduced	reduced
4	reduced		

μ is the reduced mass of the molecule. For reduced units, $E_0 = 1/2\mu$

Line 4: DELH,H0,HMIN,DELNOR (see table below)

DELH: basic numerical accuracy (0.001 generally).

H0: initial propagation step (normally set equal to DELH).

HMIN: minimum propagation step size (normally set equal to DELH).

DELNOR: convergence criterion for phase of continuum wave function (generally .001 radian).

Lines 5-8 define the first potential, and are illustrated for the case of a Morse potential. The potential is read by subroutine RDPOT, and evaluated by function UII.

Line 5: LABEL1 (Label for the first state.)

Line 6: 4,JROT, where JROT = rotational quantum number.

Line 7: 1,ITYPE,4, (ITYPE is described in the following table.)

Line 8: A1,A2,A3,A4 (see table below.)

ITYPE	A1	A2	A3	A4
1	ω_e	D_e	R_e	T_e
2	ω_e	$\omega_e x_e$	R_e	T_e
3	$\omega_e x_e$	D_e	R_e	T_e
4	β_e	D_e	R_e	T_e

For the Morse[2] potential,

$$U(R - R_e) = D_e(1 - e^{-\beta(R-R_e)})^2 + T_e,$$

where

$$D_e = \omega_e^2/\omega_e x_e,$$

and

$$\beta_e = 1.2177X10^7\omega_e\sqrt{\mu/D_e}.$$

Here D_e, ω_e, and β_e are in cm^{-1}.

For the exponential repulsive potential, *Line 6* becomes '5,JROT', and ITYPE =0 on *Line 7*. The form of the potential is then

$$U(x) = A2e^{-A3(x-A1)/A2} + A4$$

Lines 9 through 12 describe the second state and are similar to Lines 5 through 8.

Line 13: ITAB(1-5),IPLOT(1-5),XI,XF,XINC,EMIN,EMAX

ITAB(I): (=0, do not tabulate potential I; =1, tabulate potential I.)

IPLOT(I): (=0, do not plot potential I; =1, plot potential I.)

Tabulation and plotting begin at R = XI and run to R = XF in increments of XINC.

EMIN and EMAX are the mininum and maximum energies for the plots.

Line 14: ITYPE

Line 15: FAC(I)

ITYPE	Function	
0	FAC	Constant
1	B*FAC	E_0/R^2, rotational function
2	FAC(1)+FAC(2)	Linear
3	FAC(1)*EXP(-FAC(2)*R)	Exponential
4	Spline f*FAC	Spline function
5	Spline f*FAC*B	Spline function X rotational function
6	Spline f*FAC2	Spline function squared

For example, for ITYPE=2, FAC(1)=1.0, FAC(2)=0 calculates Franck-Condon factors.

For ITYPE=2, FAC(1)=0, FAC(2)=1.0 calculates matrix elements of R.

Line 16: IREAD

IREAD=1: read eigenvalue list for bound eigenvalues.

IREAD=2: read energy list for continuum energies.

IREAD=3: search for eigenvalues.

Line 17: TXL,X0,TXR

X0 is approximately equal to R_e for bound wave functions. TXL and TXR are left and right guesses for classical turning points. For continuum functions when IPROB=4 or 7, X0 is the distance up to which the wavefunction is stored (outer range of integration). When IPROB=2 or 3, X0 is the distance beyond which convergence of the phase is checked (also true for IPROB=4 or 7).

Line 18: NE,EI,EF,DELE

NE = number of equal intervals between EI and EF to be used in the eigenvalue search. the interval should be less than the smallest difference between adjacent eigenvalues. Subroutine EIGEN determines if there is an eigenvalue in each interval and, if so, converges to it.

EI = lowest energy in eigenvalue search. It should be larger than the potential minimum to prevent convergence failure; the point (X0,EI) should be in the classical region of the potential. Beware when changing rotational quantum number J.

EF = highest energy in eigenvalue search. It should be less than the asymptotic energy to prevent convergence failure.

DELE = convergence parameter in eigenvalue search. The eigenvalue is located to within DELE of its actual value (more correctly, the zero of the mixed Wronskian of the left and right numerically propagated wave-functions is located to within DELE of the actual zero for the given propagation parameter). An extra linear interpolation usually locates the eigenvalue to within approximately 0.1DELE. Thus, DELE = 1 cm^{-1} usually results in eigenvalues to a few hundredths of one cm^{-1}.

Lines 19 through 21 describe the second state and are similar to Lines 16 through 18.

Applications

Examples of the use of SROSOL are given in the following pages. In Table 1, a sample input file is shown to illustrate the descriptions in the preceding section. In Table 2, a calculation of Franck-Condon factors for the First Positive band of N_2 is displayed, along with two similar results from the literature; agreement is good.

An estimated emission spectrum for this same N_2 band is plotted in Figure 1. For this calculation, the electronic, vibrational, and rotational temperatures were set at 5000^o Kelvin. Populations for the various vibrational and rotational levels were obtained from an LTE calculation[5] . A pressure of 100 atmospheres was assumed. A Voigt profile was assumed for each line with collisional broadening of 10 MHz/Torr of gas pressure as suggested by Steinfeld[6] (see also Wang and Xia[7]).

Figure 2 shows an emission spectrum of the First Positive band of N_2 obtained from a discharge tube as given by Keck, et. al[8]. Virtually no information about this spectrum is given in Ref. 8; however, it was used as a model for generating the calculated spectrum shown in Figure 1. Parameters were adjusted in this calculation to try to obtain essentially the same spectral shape given in Figure 2. It is not known if the assumed pressure and temperatures are correct, or if LTE applies in this case.

For a comprehensive treatment of N_2 molecular emission and absorption, several bands must be included in the spectra. It would be necessary to apply SROSOL to each band to obtain Franck-Condon factors and matrix elements in order to be able to calculate the contribution of each band. Such calculations have been attempted for N_2 and S_2.

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Table 1: Sample SROSOL input file

Line 1 : N2 1st Positive
Line 2 : 1 2
Line 3 : 2 2 2 7.00335
Line 4 : 0.001 0.001 0.001 0.0000001
Line 5 : N2 B 3 Pi g State
Line 6 : 4 0
Line 7 : 1 2 4
Line 8 : 1733.39 14.122 1.212600 59619.4
Line 9 : N2 A 3 Sigma+u State
Line 10: 4 0
Line 11: 1 2 4
Line 12: 1460.64 13.872 1.286600 50203.6
Line 13: 1100000000 0.5 3 .1 0 10000
Line 14: 2
Line 15: 1.0 0.0
Line 16: 3
Line 17: 0.8 1.212 2.0
Line 18: 5 60000 90000 0.000001
Line 19: 3
Line 20: 0.8 1.293 2.0
Line 21: 5 50300 75000 0.000001

This input file is constructed to calculate Franck-Condon factors for the First Positive band of Nitrogen. On Line 14, ITYPE = 2; on Line 15, FAC(1) = 1.0, and FAC(2) = 0.0. NPOT = 2 (Line 2). On Line 3, IE = IX = IM = 2, which gives energy in 1/cm, length in Angstroms, and mass in amu. On Lines 7 and 11, ITYPE = 2; on Lines 8 and 12, A1, A2, A3, and A4 are defined by the following equations:

$$A1 = \omega_e,$$
$$A2 = \omega_e x_e,$$
$$A3 = R_e,$$
$$A4 = T_e.$$

On Line 16, IREAD = 3, which tells SROSOL to search for eigenvalues. The parameters on Lines 17 and 18, and Lines 20 and 21, are obtained from potential plots U(R) of the states involved in the calculation.

Table 2: Comparison of Franck-Condon factors from SROSOL with other calculations

N2 1st Positive (B 3 Pi g -> A 3 Sigma+ u) (SROSOL)

v'\v''	0	1	2	3	4	5	6	7	8	9
0	.4006E+00	.3301E+00	.1663E+00	.6710E-01	.2402E-01	.8043E-02	.2595E-02	.8223E-03	.2573E-03	.8207E-04
1	.3993E+00	.2796E-02	.1589E+00	.1965E+00	.1303E+00	.6566E-01	.2850E-01	.1134E-01	.4283E-02	.1570E-02
2	.1614E+00	.2741E+00	.6951E-01	.2178E-01	.1245E+00	.1430E+00	.1012E+00	.5634E-01	.2733E-01	.1218E-01
3	.3428E-01	.2770E+00	.9437E-01	.1525E+00	.5377E-02	.4205E-01	.1079E+00	.1118E+00	.8041E-01	.4746E-01
4	.4152E-02	.9764E-01	.2961E+00	.6894E-02	.1510E+00	.5205E-01	.2090E-02	.5488E-01	.9439E-01	.9029E-01
5	.2909E-03	.1673E-01	.1699E+00	.2399E+00	.1149E-01	.9423E-01	.9572E-01	.9084E-02	.1393E-01	.5996E-01
6	.1140E-04	.1526E-02	.4006E-01	.2302E+00	.1515E+00	.6057E-01	.3396E-01	.1048E+00	.4022E-01	.6745E-07
7	.2311E-06	.7409E-04	.4644E-02	.7376E-01	.2643E+00	.6935E-01	.1084E+00	.2470E-02	.8110E-01	.6867E-01
8	.2111E-08	.1807E-05	.2735E-03	.1071E-01	.1150E+00	.2668E+00	.1659E-01	.1293E+00	.5736E-02	.4360E-01

N2 1st Positive (B 3 Pi g -> A 3 Sigma+ u) (Benesch, et. al., Ref. 3)

v'\v''	0	1	2	3	4	5	6	7	8	9
0	.4011E+00	.3309E+00	.1661E+00	.6692E-01	.2384E-01	.7992E-02	.2570E-02	.8211E-03	.2605E-03	.8249E-04
1	.3976E+00	.2907E-02	.1595E+00	.1973E+00	.1306E+00	.6578E-01	.2833E-01	.1133E-01	.4274E-02	.1566E-02
2	.1617E+00	.2744E+00	.6877E-01	.2208E-01	.1246E+00	.1431E+00	.1004E+00	.5608E-01	.2724E-01	.1213E-01
3	.3423E-01	.2757E+00	.9557E-01	.1514E+00	.5122E-02	.4236E-01	.1073E+00	.1120E+00	.8058E-01	.4750E-01
4	.4063E-02	.9739E-01	.2976E+00	.7468E-02	.1509E+00	.5125E-01	.2223E-02	.5492E-01	.9428E-01	.8989E-01
5	.2680E-03	.1640E-01	.1690E+00	.2425E+00	.1046E-01	.9617E-01	.9428E-01	.8752E-02	.1409E-01	.5993E-01
6	.1338E-04	.1408E-02	.3929E-01	.2311E+00	.1544E+00	.5839E-01	.3521E-01	.1041E+00	.3932E-01	.2021E-05
7	.4460E-06	.6177E-04	.4318E-02	.7188E-01	.2657E+00	.7415E-01	.1057E+00	.3002E-02	.8127E-01	.6737E-01
8	.2788E-06	.8721E-06	.2221E-03	.9946E-02	.1118E+00	.2695E+00	.1991E-01	.1278E+00	.4815E-02	.4441E-01

N2 1st Positive (B 3 Pi g -> A 3 Sigma+ u) (Suchard and Meizer, Ref. 4)

v'\v''	0	1	2	3	4	5	6	7	8	9
0	.406E+00	.327E+00	.164E+00	.667E-01	.244E-01	.838E-02	.280E-02	.926E-03	.307E-03	.103E-03
1	.401E+00	.371E-02	.159E+00	.193E+00	.129E+00	.657E-01	.272E-01	.120E-01	.473E-02	.183E-02
2	.158E+00	.285E+00	.659E-01	.225E-01	.122E+00	.139E+00	.994E-01	.566E-01	.283E-01	.131E-01
3	.317E-01	.277E+00	.105E+00	.150E+00	.467E-02	.409E-01	.103E+00	.108E+00	.788E-01	.478E-01
4	.347E-02	.918E-01	.306E+00	.111E-01	.153E+00	.494E-01	.204E-02	.513E-01	.885E-01	.858E-01
5	.201E-03	.141E-01	.163E+00	.259E+00	.694E-02	.100E+00	.929E-01	.881E-02	.122E-01	.537E-01
6	.572E-05	.107E-02	.341E-01	.226E-01	.176E+00	.505E-01	.402E-01	.104E+00	.392E-01	.473E-04
7	.881E-07	.370E-04	.324E-02	.436E-01	.268E+00	.930E-01	.970E-01	.500E-02	.829E-01	.671E-01
8	.828E-10	.514E-06	.135E-03	.750E-02	.101E+00	.283E+00	.320E-01	.126E+00	.275E-02	.468E-01

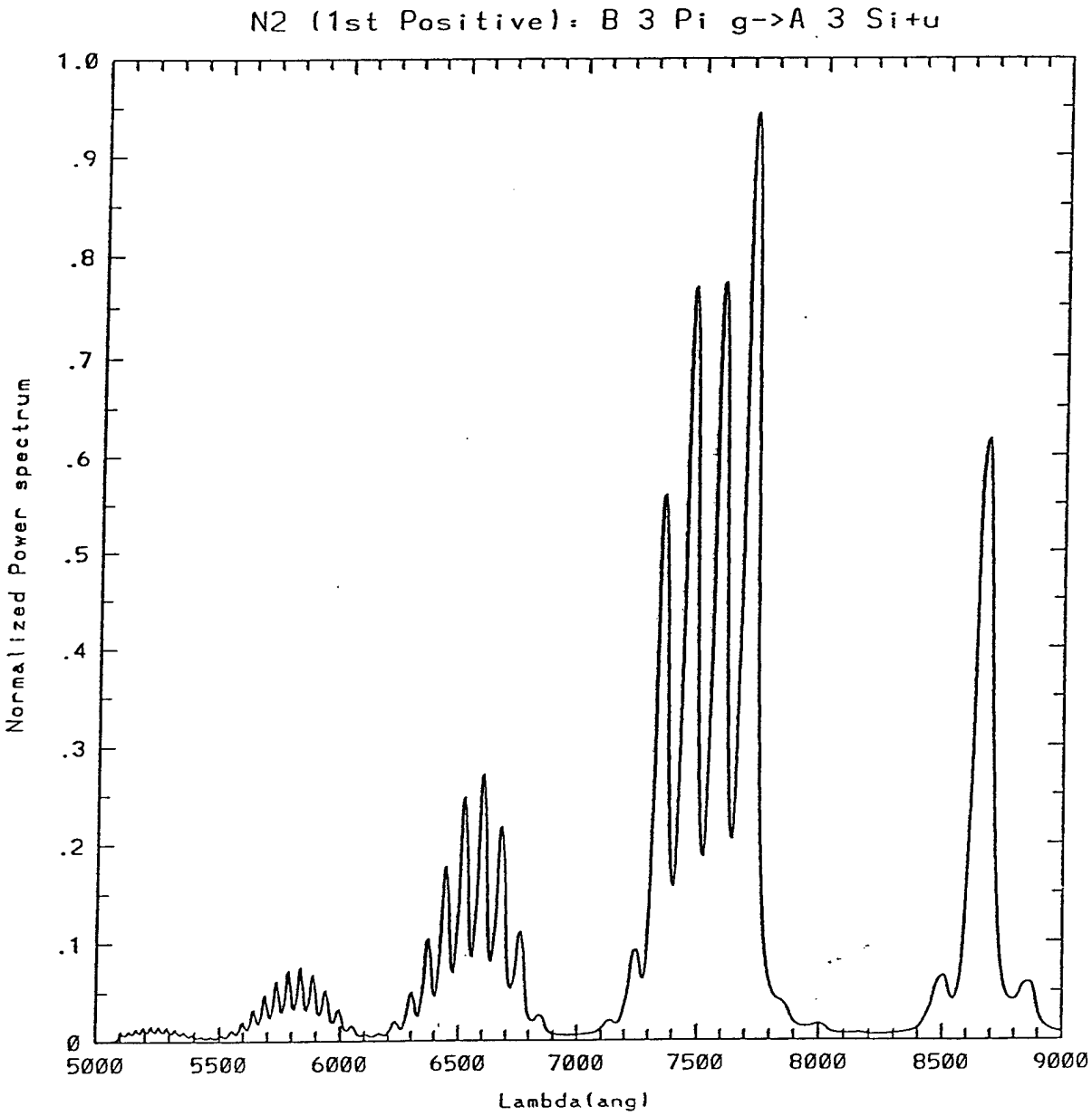

Figure 1. Calculated emission spectrum from the First Positive Band of N_2.

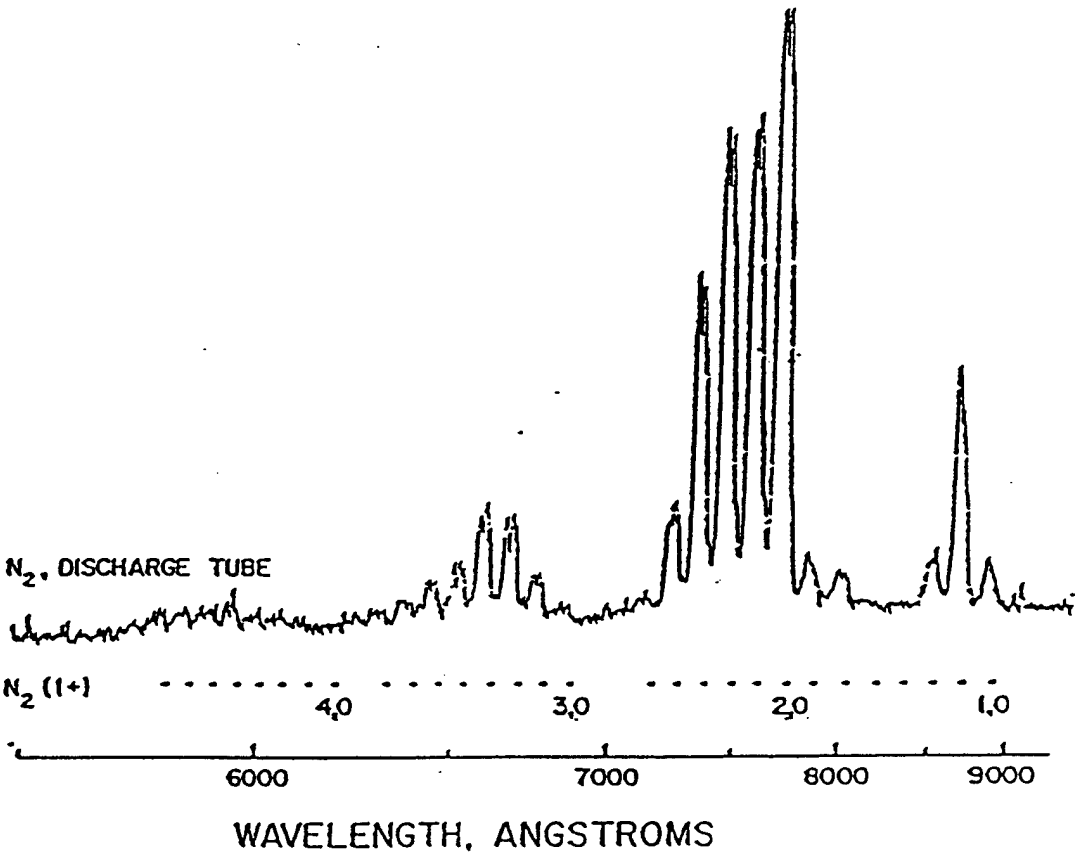

Figure 2. Discharge tube spectrum for N_2 from Keck, et. al[8].

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