

Supplementary Material

This document contains Supplementary Material associated with the paper “**dPotFit**: A Computer Program to Fit Diatomic Molecule Spectral Data to Potential Energy Functions”, submitted to the *Journal of Quantitative Spectroscopy and Radiative Transfer* in February 2016. It consists of the five Appendices enumerated below. Note that Equation and Reference numbering appearing herein refer to the equation and reference numbering in the Journal Article.

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Appendix A: Experimental Data File Structure and Control Parameters

The experimental data are read from a file whose name is specified in the regular Channel-5 input data file *via* READ #2. The data must be arranged as separate vibrational bands (or fluorescence series, or sets of photo-association spectroscopy (PAS) binding energies, tunneling predissociation level widths, or potential function values), each characterized by the upper- and lower-state vibrational quantum numbers $v' = \text{VP}$ and $v'' = \text{VPP}$, respectively, by the three-alphanumeric-character labels LABELP and LABELPP (enclosed between single quotes; e.g. 'X1S') that have been chosen to label the particular upper and lower electronic states, by the (integer) mass numbers MN1 and MN2 of the atoms forming that particular isotopologue, and by a label indicating the source of the data in this band/group, consisting of up to 30 alphanumeric characters (e.g., 'Linton, JMS 151, 159 (1992)'). Note that the electronic state labels must correspond to names used to identify the different electronic states in READ #6 of the Channel-5 input (see below).

For each such band, the data are read, one per line, with each datum consisting of the upper and lower rotational quantum numbers, $J' = \text{JP}$ and $J'' = \text{JPP}$, respectively, the integer +1 (for e -parity levels) or -1 (for f -parity levels) defining the e/f parity of the upper ($p' = \text{EFP}$) and lower ($p'' = \text{EFPP}$) levels, the experimental datum $y_i^{\text{obs}} = \text{FREQ}(i)$ and its uncertainty $u_i = \text{UFREQ}(i)$. A datum line with $\text{JP} < 0$ signals the end of the data set for this band or group, and asks the program to start the input for a new band. The overall data input is assumed to be complete either at the end of the data file, or when a negative value of the band-label quantum number $v' = \text{VP}$ is encountered.

```

      IBAND= 0
      COUNT= 1
    10  IBAND= IBAND+ 1
    #1  READ(4,*,END=20)  VP(IBAND), VPP(IBAND), LABELP, LABELPP, MN1, MN2, BANDNAME(IBAND)
        IF(VP(IBAND).LT.0) GOTO 20
    #2  5  READ(4,*)  JP(COUNT), EFP(COUNT), JPP(COUNT), EFPP(COUNT),FREQ(COUNT), UFREQ(COUNT)
        IF(JP(COUNT).GE.0) THEN
            COUNT= COUNT+1

```

```

      GOTO 5
    ELSE
      COUNT= COUNT-1
      GOTO 10
    ENDIF
  20 CONTINUE

```

For a fluorescence series, this band-type data structure is retained, but the definitions of the ‘band’ and individual datum labels differ. In particular, setting the upper-state input parameter `LABLP = 'FLS'` identifies the data group as a fluorescence series and causes the ‘band’ parameters `VP` and `VPP` (see `READ #1` above) to be defined as the vibration-rotation quantum numbers v' and J' , respectively, for the emitting level, and the transition labels `JP` and `JPP` (`READ #2` above) as the corresponding final (lower) state vibration-rotation quantum numbers v'' and J'' , respectively. The parity label parameters `EFP` and `EFPP` retain their usual meaning, so the former has the same value for all lines in a given fluorescence series ‘band’ or data-group. Note that for a fluorescence series, the quantities v' , J' and `EFP` are merely used to label the various series, and they have no physical significance as far as the analysis is concerned. Indeed, program operation is not affected if the same values of these quantities are used for several different series; it just means that the distinct fitted origins of those several fluorescence series will have the same label in the Channel-6 output file.

A third distinct data type that can be input using this same band-type data structure is a set of individual-level binding energies, such as those yielded by photoassociation spectroscopy (PAS). In this case the nature of the data-group is identified by setting the input upper-electronic-state band label as `LABLP = 'PAS'`. As with fluorescence series, the data parameters `JP`, `JPP` and `EFPP` are defined as the final-state level parameters v'' , J'' , and parity p'' , respectively, while the ‘band parameters’ `VP` and `VPP`, and the data parameter `EFP` are all dummy variables that are ignored by the analysis. This same input data file structure may also be used to input the energies (relative to the associated asymptote) of tunneling-predissociation levels, as measured by ‘translational spectroscopy’ [103–105], except that in this case, the “binding energies” are input as negative numbers [37].

`PAS`-type data are expressed as (positive) binding energies, relative to the dissociation asymptote of the given electronic state. They have special significance in the data analysis only if the vibrational energies are represented by an expression in which the dissociation limit is an explicit parameter, i.e., only for `PSEL = 1 – 5` potential energy functions. If this is not the case, `dPotFit` simply treats a `PAS`-type data-group as an ordinary fluorescence series whose upper level is a free fitting parameter.

A fourth type of experimental data that uses this same band-type input structure is a set of tunneling predissociation level widths. In this case the input parameter value `LABLP = 'WID'` identifies this data-group as a set of FWHM level widths $\Gamma(v, J)$ for levels of electronic state `LABLPP`, and signals that the band parameters `VP` & `VPP` and the parity label `EFP` are dummy variables. The input parameter `JP` is then the vibrational quantum number v , `JPP` is the rotational quantum number J , and `EFPP` is the parity label of the predissociating level, while `FREQ` is its full width at half maximum $\Gamma(v, J)$ and `UFREQ` the estimated uncertainty in that value (both in mcm^{-1}).

A different type of ‘experimental’ data that can be used in a fit is a set of assumed-known potential function values. This allows one to incorporate into an analysis, for example, *ab initio* potential energy values in the very short-range region that is inaccessible to normal spectroscopic data. This type of input data is identified by setting the input parameter value `LABLP = 'VVV'`.

The other band labels VP, VPP, MN1 and MN2 are then all dummy parameters, and the ‘band’ input commands shown above are replaced by

```

COUNT= 1
10 IBAND= IBAND+ 1
#1 READ(4,*,END=20) VP(IBAND), VPP(IBAND), LABLP, LABLPP, MN1, MN2, BANDNAME(IBAND)
IF(VP(IBAND).LT.0) GOTO 20
IF(LABLPP.EQ.'VV') THEN
#2 12 READ(4,*) R(COUNT), VV(COUNT), uVV(COUNT)
IF(R(COUNT).GE.0) THEN
COUNT= COUNT+1
GOTO 12
ELSE
COUNT= COUNT-1
GOTO 10
ENDIF
ENDIF
20 CONTINUE

```

in which $VV(COUNT)$ and $uVV(COUNT)$ are the value and estimated uncertainty (in units cm^{-1}) of the potential energy function at the distance $R(COUNT)$ Å. This type of data should normally be associated with the reference isotopologue, or with $MN1 = MN2 = 0$, if it is an allowed ‘species’.

The final types of experimental data that can be used in a fit are sets of measured second ‘pressure virial’ coefficients [80] or ‘acoustic virial’ coefficients. In this case, one of the isotopologues specified in READ #4 of Appendices B and C should correspond to mass numbers $MN(1, IISTP) = MN(2, IISTP) = 0$ in order to specify that the abundance-averaged isotopic atomic masses to be used to define the reduced mass in the virial coefficient calculation. This type of input data is identified by setting the input parameter value $LABLP = 'VIR'$ for ordinary ‘pressure virial’ coefficients, of $LABLP = 'VAC'$ for ‘acoustic’ virial coefficients. The vibrational band labels VP and VPP are then dummy parameters, while the isotope labels should be set as $MN1 = MN2 = 0$. The ‘band’ input instructions for this case then have the same structure as those for the preceding case of potential-function-value data, except that the variables have different meanings:

```

COUNT= 1
10 IBAND= IBAND+ 1
#1 READ(4,*,END=20) VP(IBAND), VPP(IBAND), LABLP, LABLPP, MN1, MN2
1 BANDNAME(IBAND)
IF(VP(IBAND).LT.0) GOTO 20
IF(LABLPP.EQ.'VV') THEN
#2 14 READ(4,*) TEMP(COUNT), BVIR(COUNT), uBVIR(COUNT)
IF(TEMP(COUNT).GE.0) THEN
COUNT= COUNT+1
GOTO 14
ELSE
COUNT= COUNT-1
GOTO 10
ENDIF
ENDIF
20 CONTINUE

```

Here, $Bvir(COUNT)$ and $uBvir(COUNT)$ are the value and estimated uncertainty (in units $\text{cm}^3 \text{mol}^{-1}$) of the second virial coefficient of the atomic species to which the molecule dissociates, at temperature $T = TEMP(COUNT)$ K.

As an illustration of this data file structure, the listing below presents portions of an experimental data file used in an analysis to determine the potential energy function for the ground $^1\Sigma_g^+$ state of ArXe [80] from a combination of microwave data [106], high-resolution vacuum laser spectroscopy [80], and virial coefficient data [107–109]. Note that text beginning at the “%” sign on a line of the input data file are comments that are ignored by the program.

```

0 0 'X1S' 'X1S' 40 128 'MW data of Jaeger et al. (1993)'
 3 +1 2 +1 0.19375109 3.3D-08 % J' p' J" p" FREQ UFREQ
 4 +1 3 +1 0.25830956 3.3D-08
 5 +1 4 +1 0.32284639 3.3D-08
 6 +1 5 +1 0.38735613 3.3D-08
-1 -1 -1 -1 -1.d0 -1.d0

0 0 'X1S' 'X1S' 40 129 'MW data of Jaeger et al. (1993)'
 3 +1 2 +1 0.19339688 3.3D-08 % J' p' J" p" FREQ UFREQ8
 4 +1 3 +1 0.25783738 3.3D-08
 5 +1 4 +1 0.32225632 3.3D-08
 6 +1 5 +1 0.38664857 3.3D-08
 7 +1 6 +1 0.45100778 3.3D-08
 8 +1 7 +1 0.51532937 3.3D-08
 9 +1 8 +1 0.57960754 3.3D-08
-1 -1 -1 -1 -1.d0 -1.d0

0 0 'X1S' 'X1S' 40 130 'MW data of Jaeger et al. (1993)'
 3 +1 2 +1 0.19304902 3.3D-08 % J' p' J" p" FREQ UFREQ8
 4 +1 3 +1 0.25737363 3.3D-08 % MW data of Jaeger et al. (1993)
 5 +1 4 +1 0.32167676 3.3D-08
 6 +1 5 +1 0.38595299 3.3D-08
 7 +1 6 +1 0.45019693 3.3D-08
-1 -1 -1 -1 -1.d0 -1.d0

2 0 'D0' 'X1S' 40 132 'Piticco [JMS 264, 83 (2010)]'
 1 +1 0 +1 77239.1655 0.0012 % J' p' J" p" FREQ UFREQ
 2 +1 1 +1 77239.2240 0.0012
 3 +1 2 +1 77239.2817 0.0010
 4 +1 3 +1 77239.3348 0.0011
 5 +1 4 +1 77239.3867 0.0008
 6 +1 5 +1 77239.4358 0.0011
..... omit 18 intermediate data to save space .....
13 +1 14 +1 77237.9631 0.0020
16 +1 17 +1 77237.6269 0.0010
-1 -1 -1 -1 -1.d0 -1.d0

0 0 'VIR' 'X1S' 0 0 'Press virials, various sources'
173.2 -141.2 2.d0 % Virial coefft. from Landbolt & Boernstein (2003)
198.2 -108.0 2.d0 % Virial coefft. from Landbolt & Boernstein (2003)
223.2 -86.5 2.d0 % Virial coefft. from Landbolt & Boernstein (2003)
273.2 -56.2 2.d0 % Virial coefft. from Landbolt & Boernstein (2003)
323.2 -36.7 2.d0 % Virial coefft. from Landbolt & Boernstein (2003)
203.0 -95.0 6.d0 % Virial coefft. from Schramm et al. (1977)
213.0 -84.5 6.d0 % Virial coefft. from Schramm et al. (1977)
..... omit 15 intermediate data to save space .....
482.0 -5.1 6.d0 % Virial coefft. from Rentschler & Schramm (1977)
555.0 2.4 6.d0 % Virial coefft. from Rentschler & Schramm (1977)
626.0 4.9 6.d0 % Virial coefft. from Rentschler & Schramm (1977)
695.0 9.5 6.d0 % Virial coefft. from Rentschler & Schramm (1977)
-1 -1.0 -1.d0

```

Appendix B. Structure of The Channel-5 'Instruction' Data File

The logical structure and read statements of the Channel-5 data input that describes the system to be treated, specifies the type of fit to be carried out, and inputs any necessary system parameters, is shown below. The following subsection then provides a detailed description of the nature and options associated with each of the input variables.

```

#1  READ(5,*)  AN(1), AN(2), CHARGE, NISTP, NSTATES, LPRINT, PRINP
#2  READ(5,*)  DATAFILE
#3  READ(5,*)  WRITFILE
#4  IF(CHARGE.ne.0) READ(5,*)  CHARGE1,CHARGE2
*****
*    Loop over isotopologues to read isotope masses
*****
      DO  IISTP= 1,NISTP
#5    READ(5,*) MN(1,IISTP), MN(2,IISTP)
      ENDDO
*****
*    End loop over isotopologues
*****
#6  READ(5,*)  UCUTOFF, NOWIDTHS, IROUND, ROBUST, CYCMAX, uBv
*****
*    Begin loop over electronic states
*****
      DO 20 ISTATE=1,NSTATES
#7    READ(5,*) SLABL(ISTATE), IOMEG(ISTATE), VMIN(ISTATE), VMAX(ISTATE),
          1                                JTRUNC(ISTATE), EFSEL(ISTATE)
#8    IF(VMAX(ISTATE.1).LT.0) READ(5,*) (VMAX(ISTATE,ISOT), ISOT= 1, NISTP)
#9    READ(5,*) PSEL(ISTATE), VLIM(ISTATE), MAXMIN(ISTATE). BOBCN(ISTATE),
          1                                OSEL(ISTATE)
          IF(PSEL(ISTATE).EQ.-2) GOTO 20
          IF(PSEL(ISTATE).EQ.-1) THEN
*****
*    If fitting to band constants, must specify no. for each v and isotop.
*****
              DO  I= VMIN(ISTATE,1),VMAX(ISTATE,1)
#10     READ(5,*) VTST,(NBC(I,IISTP,ISTATE),IISTP= 1,NISTP)
              ENDDO
          ENDIF
#11     READ(5,*) RMIN(ISTATE), RMAX(ISTATE), RH(ISTATE)
          IF(PSEL(ISTATE).EQ.0) THEN
#12     READ(5,*) NPT, NUSE, IR2, ILR, NCN, CNN
#13     READ(5,*) RFACT, EFACT, VSHIFT
#14     READ(5,*) (XI(I), YI(I), I= 1,NTP)
          EXIT
          ENDIF
          IF((PSEL(ISTATE).GE.2).AND.(PSEL(ISTATE).LE.6)) THEN
c** For an MLR or DELR or HPP or TT-type potential ...
#15     READ(5,*) NCMM(ISTATE), rhoAB(ISTATE), IVSR(ISTATE), IDSTT(ISTATE)
          DO  m= 1,NCMM(ISTATE)
#16     READ(5,*) MMLR(m,ISTATE), CmVAL(m,ISTATE), IFXCm(m,ISTATE)
          ENDDO
          ENDIF

```

```

c** For a GPEF potential ...
#17     IF(PSEL(ISTATE).EQ.6) READ(5,*) AGPEF(ISTATE), BGPEF(ISTATE)
c** For all PSEL > 0 cases ...
#18     READ(5,*) DE(ISTATE), IFXDE(ISTATE)
#19     READ(5,*) RE(ISTATE), IFXRE(ISTATE)
#20     READ(5,*) Nbeta(ISTATE), APSE(ISTATE), nPB(ISTATE), nQB(ISTATE), RREF(ISTATE)
        IF((PSEL(ISTATE).EQ.2).AND.(APSE(ISTATE).GE.0) THEN
            DO I= 1,Nbeta(ISTATE)
#21         READ(5,*) ypBETA(I,ISTATE), BETA(I,ISTATE), IFXBETA(I,ISTATE)
            ENDDO
        ELSE
            I1=0
            IF(PSEL(ISTATE).GE.6) I1=1
            DO I= I1, Nbeta(ISTATE))
#22         READ(5,*) BETA(I,ISTATE), IFXBETA(I,ISTATE)
            ENDDO

#23     READ(5,*) NUA(ISTATE), NUB(ISTATE), qAD(ISTATE), pAD(ISTATE), LRad(ISTATE)
c** if appropriate, read isotope shift coeffs as part of BOB correction
#24     IF(LRad(ISTATE)).GT.0) READ(5,*) (dCMVALA(m,ISTATE),m=1, NCMM(ISTATE))
#25     IF(LRad(ISTATE)).GT.0) READ(5,*) (dCMVALB(m,ISTATE),m=1, NCMM(ISTATE))
c** Adiabatic potential energy BOB function parameters for atom-A
        IF(NUA(ISTATE).GE.0) THEN
            DO I= 0, NUA(ISTATE)
#26         READ(5,*) UA(I,ISTATE), IFXUA(I,ISTATE)
            ENDDO
#27         READ(5,*) UAinf, IFXUAinf
            ENDIF
c** Adiabatic potential energy BOB function parameters for atom-B
        IF(NUB(ISTATE).GE.0) THEN
            DO I= 0, NUB(ISTATE)
#28         READ(5,*) UB(I,ISTATE), IFXUB(I,ISTATE)
            ENDDO
#29         READ(5,*) UBinf, IFXUBinf
            ENDIF
#30     READ(5,*) NTA(ISTATE), NTB(ISTATE), qNA(ISTATE) pNA(ISTATE)
c** Centrifugal BOB function parameters for atom-A
        IF(NTA(ISTATE).GE.0) THEN
            DO I= 0, NTA(ISTATE)
#31         READ(5,*) TA(I,ISTATE), IFXTA(I,ISTATE)
            ENDDO
#32         READ(5,*) TAinf, IFXTAinf
            ENDIF
c** Centrifugal BOB function parameters for atom-B
        IF(NTB(ISTATE).GE.0) THEN
            DO I= 0, NTB(ISTATE)
#33         READ(5,*) TB(I,ISTATE), IFXTB(I,ISTATE)
            ENDDO
#32         READ(5,*) TBinf, IFXTBinf
            ENDIF
        IF(IOMEG(ISTATE).NE.0) THEN
c** Lambda-doubling or 2\Sigma splitting expansion parameters
#35     READ(5,*) NwCFT(ISTATE), Pqw(ISTATE), efREF(ISTATE)
            IF(NwCFT(ISTATE).GE.0) THEN

```

```
DO I= 0, NwCFT(ISTATE)
#36   READ(5,*) wCft(I,ISTATE), IFXwCft(I,ISTATE)
      ENDDO
    ENDIF
  ENDIF
ENDDO
c*****
c      End of loop over electronic states
c*****
      IF(DATAFILE.EQ.MAKEPRED) THEN
c** To generate a predicted spectrum, loop over bands & read specifications
70   CONTINUE
#37   READ(5,*,end=99) VP(IBAND), VPP(IBAND), LABLP, LABLPP, MN1, MN2,
      1      PP, PPP, JMAXX, J2DL, J2DU, J2DD
      IBAND= IBAND+ 1
      IF(VP(IBAND).GE.0) GO TO 70
    ENDIF
c*****
c      End of Channel-5 input data file
c*****
```

Appendix C: Definitions of the Parameters in the 'Instruction' Data File

Read integers identifying the molecule and system.

#1. READ(5,*) AN(1), AN(2), CHARGE, NISTP, NSTATES, LPRINT, PRINP

AN(1) & AN(2) are integer atomic numbers of the atoms 1 & 2 forming the molecule.

CHARGE is a (\pm) integer for the total charge on the molecule. It is used to generate Watson's charge-modified reduced mass for molecular ions; see Eq. (2).

NISTP is the number of isotopologues to be considered in the particular analysis (their identifying mass numbers are read below).

NSTATES is the number of different electronic states associated with the data to be input and analyzed.

LPRINT is an integer specifying the level of output to be generated by the least-squares subroutine package NLLSSRR.

- If LPRINT = 0 no internal printout except for convergence-failure warning messages;
- If LPRINT \neq 0, also print convergence test on each fitting cycle and indicate nature of convergence; LPRINT \leq 0 is recommended when there are no problems with the fits.
- If LPRINT \geq 1, also print the change and uncertainty for each parameter in each fitting cycle;
- If LPRINT \geq 2, also print parameter changes on each rounding step.

PRINP is an integer parameter that controls whether (PRINP > 0) or not (PRINP \leq 0) a summary of the experimental data is printed immediately following its input. This option is useful only for helping to identify problems in the input data; in most cases one should set PRINP \leq 0, since an analogous summary is always printed at the end of every (successful) run.

Read the name of the file containing the experimental data to be fitted in the analysis.

#2. READ(5,*) DATAFILE

DATAFILE is the name for the file containing the experimental data to be fitted; it may consist of up to 40 alphanumeric characters and must be enclosed in single quotes with no leading blanks (e.g., 'Li2B(A-X).4'). If the file does not reside in the current directory, this name must include the absolute or relative path. Note that if this file contains data for more states and/or isotopologues than one wishes to consider in a particular analysis, they are simply ignored, so it is not necessary to construct a separate data file if one wishes to consider only a subset of the data (e.g., only the microwave transitions, or only the data for one particular isotopologue).

- If the program is being asked to predict data from a set of known input parameters (see §5.3), the filename read here *must* be MAKEPRED (i.e., the data file entry must be 'MAKEPRED').

#3. READ(5,*) WRITFILE

WRITFILE is the root of the names used for the output files written to Channels 6–16 & 20, that will have the names WRITFILE.6, WRITFILE.7, WRITFILE.8, ... , WRITFILE.20, respectively. WRITFILE may consist of up to 20 alphanumeric characters, and should be enclosed in single quotes with no leading blanks (e.g., 'EMO4(6,8)u3t1'). A distinct name should be chosen to identify the results of each particular run; if the same name is used for subsequent runs, previous files with those names will be over-written.

If CHARGE \neq 0, read integers specifying how the mass(es) of the added/subtracted e^- are to be taken into account in the definition of the molecular ion reduced masses.

#4 If (CHARGE \neq 0) READ(5,*) CHARGE1, CHARGE2

CHARGE1 & CHARGE2: the integer number of $m_e/2$ masses to be added to or subtracted from the normal masses of atoms #1 and #2 before calculating a conventional 2-body reduced mass for each isotopologue. If **CHARGE1 = CHARGE2 = 0** use Watson’s charged-modified reduced mass for all species. Otherwise, necessarily, $1/2(\text{CHARGE1} + \text{CHARGE2}) = \text{CHARGE}$.

Loop over the NISTP isotopologues, and for each, read the integer mass numbers of the two atoms. The first isotopologue is defined as the reference species ($\text{ISOT} = \alpha = 1$) for the mass scaling of BOB radial strength functions. The mass numbers for each isotopologue must be on a separate line.

```
#5 READ(5,*) MN(1,ISOT), MN(2,ISOT)
```

MN(1,ISOT) & MN(2,ISOT): integer mass numbers of the atoms/particles 1 & 2 forming the isotopologue $\alpha = \text{ISOT}$. The mass of a normal stable atomic isotope is taken from the tabulation in subroutine **MASSES**; if **MN** is outside the range for the normal stable isotopes for the atom, then the abundance-averaged atomic mass is used.

Read parameters allowing one to set global restrictions on the data set to be used without editing the actual input **DATAFILE**, and to specify general features of the fit and output.

```
#6 READ(5,*) UCUTOFF, NOWIDTHS, IROUND, ROBUST, CYCMAX, uBv
```

UCUTOFF: causes any input spectroscopic data with uncertainties $u_i > \text{UCUTOFF}$ (a real number) to be neglected. It does not apply to virial coefficient data or read-in potential function values and their uncertainties.

NOWIDTHS: if **NOWIDTHS** > 0 , omit calculation of the partial derivatives of tunneling-predissociation level widths of quasibound levels, and ignore any tunneling-level-width data (defined by **SLABLPP= 'WID'**) in the data file; otherwise, set **NOWIDTHS** = 0.

IROUND: Setting (integer) **IROUND** $\neq 0$ causes the “sequential rounding and refitting” procedure of Ref. [93] to be implemented, with each parameter being rounded at the $|\text{IROUND}|$ ’th significant digit of its uncertainty. If **IROUND** > 0 the rounding is applied sequentially to the remaining free parameter having the largest relative uncertainty; if **IROUND** < 0 the rounding proceeds systematically from the last free parameter to the first. If **IROUND** = 0 the fit simply stops after full convergence and performs no parameter rounding; this last option saves considerable computation time, and would normally be chosen except for a “final” fit to obtain parameters for publication and/or distribution.

ROBUST is an integer that is set greater than 0 to cause the *robust* fitting procedure described at the end of § 8.1 to be applied; otherwise (the normal case), it should be set equal to 0 (or negative).

CYCMAX is an integer that sets an upper bound on the number of least-squares cycles allowed in **NLLSSRR**. Normally **MAXCYC** ~ 30 suffices. If larger values are required, there may be something wrong either with the model or with the precision of the calculations.

uBv Setting the integer **uBv** > 0 causes the program to calculate and write to Channel-7 the uncertainties in the final B_v values due to the correlated-parameter uncertainties determined in the fit. Otherwise, set **uBv** ≤ 0 .

Now begin the loop over the NSTATES electronic states to be considered in the analysis. This loop from $s \equiv \text{ISTATE} = 1$ to **NSTATES** includes almost all of the rest of the Channel-5 input data.

First, read integer parameters characterizing the state, and (if desired) set limits on the ranges of the rotational and vibrational levels to be considered for this fit.

```
#7. READ(5,*) SLABL(s), IOMEG(s), VMIN(s), VMAX(s), JTRUNC(s), EFSEL(s)
```

SLABL is a three-alphanumeric-character label for this electronic state, enclosed in single quotes (e.g., ‘X1S’, ‘a1P’, ...), to identify it in the output and in the experimental data input file.

IOMEG: If $IOMEG \geq 0$ the electronic state is treated as a spin singlet with integer electronic angular momentum projection quantum number $IOMEG$. For a state with ${}^2\Sigma$ symmetry, set $IOMEG = -2$.

VMIN & VMAX are data-range selection parameters. All data for this state associated with vibrational levels outside the range **VMIN** to **VMAX** are ignored and are omitted from the analysis.

JTRUNC is an integer data-selection parameter. If $JTRUNC > 0$, all data for this electronic state for which $J > JTRUNC$ are omitted from the analysis; if $JTRUNC < 0$ all data with $J < |JTRUNC|$ are omitted.

EFSEL is an integer that allows a user to consider:

- a) only transitions involving e -parity levels of this state, if $EFSEL > 0$,
- b) only transitions involving f -parity levels of this state if $EFSEL < 0$,
- c) all transitions if $EFSEL = 0$ (the normal case).

The code normally sets **VMAX** for minor isotopologues using first-order semiclassical scaling from the value for isotopologue-1, but if $(VMAX(ISTATE,1).LT.0)$, we override that approach and read in a ‘specified **VMAX** value for each isotopologue. This is sometimes needed when a level search for a small- μ minor isotopologue causes the code to stop because the highest level(s) cannot be found.

#8. `IF(VMAX(ISTATE,1).LT.0) READ(5,*) (VMAX(ISTATE,ISOT), ISOT= 1, NISTP)`

Read parameters to select the analytical potential function model, to specify the potential asymptote, to select the representation to be used for BOB corrections, and to control the size of output print arrays.

#9. `READ(5,*) PSEL(s), VLIM(s), MAXMIN(s), BOBCN(s), OSEL(s)`

PSEL is an integer which specifies the type of analytic function used for the potential.

If $PSEL = 0$ use a fixed potential defined by interpolating over and extrapolating beyond a set of input turning points using the program **LEVEL** subroutine package **PREPOT** [4, 78].

If $PSEL = 1$ use the Expanded Morse Oscillator (EMO) form of §3.1.

If $PSEL = 2$ use the Morse/Long-Range (MLR) potential form of §3.2.

If $PSEL = 3$ use the Double-Exponential/Long-Range (DELR) form of §3.3.

If $PSEL = 4$ use Seto’s modification [14] of Šurkus’ Generalized Potential Energy Function (GPEF) [52], as described in §3.4. Its parameters a_S , b_S and p , are input via **READS** #17 and 20.

- Dunham expansions are generated by setting $p = 1$, $a_S = 0$ & $b_S = 1$.
- SPF expansions are generated by setting $p = 1$, $a_S = 1$ & $b_S = 0$.
- Ogilvie–Tipping expansions are generated by setting $p = 1$, $a_S = b_S = 0.5$.
- These polynomial-type potentials usually have an undefined (or at best, indirectly-defined) asymptote, so in these cases parameter **VLIM** defines the energy at the potential minimum.

If $PSEL = 5$ use the Tiemann/Hannover polynomial of §4.1.

If $PSEL = 6$ use the Tang-Toennies type potential of Eq. (32) in §4.2. In this case **Nbeta** = 9 and the the values of the well depth \mathfrak{D}_e and equilibrium distance r_e are determined internally as properties of the potential.

If $PSEL = 7$ use the Scoles-Aziz HFD-type potential of Eq. (33) in §4.3. In this case $Nbeta = N_\beta = 5$ or 2 (see below), and the values of β_1 and A_{HFD} are determined internally from the other parameters.

If $PSEL = -2$ the energy levels of the state are represented by independent terms values which are labelled by vibrational quantum number v , rotational quantum number J and e/f parity quantum number p . In this case, $VLIM$, $BOBCN$ and $OSEL$ are dummy parameters, and the remainder of the $READS$ for this state, #10–36, are ignored.

If $PSEL = -1$ the energy levels of the state are represented by a set of band constants $\{G_v, B_v, -D_v, H_v, \dots\}$ for each vibrational level of each isotopologue. In this case, $VLIM$, $BOBCN$ and $OSEL$ are dummy parameters, $READ$ #10 is used to input the number of such constants for each state, and the remainder of the $READS$ for this state, #11–36, are ignored.

VLIM: Parameter $VLIM$ specifies the fixed absolute energy (in cm^{-1}) at the potential asymptote for this state. The set of values of $VLIM(ISTATE)$ define the absolute energy scale for this system.

MAXMIN: specifies the maximum number of potential function minima allowed for a given state. If this number is exceeded (e.g., in the midst of a multi-cycle many-parameter fit), the code prints a warning message and **STOPS**. Normally set $MAXMIN = 1$.

BOBCN specifies the manner in which the **BOB** mass-scaling is to be done.

If $BOBCN = 0$, use the mass scaling of Eqs. (3) and (4) with isotopologue #1 as the reference isotopologue.

If $BOBCN = 1$, combine use of the clamped-nuclei reference potential with mass scaling factors $m_e/M_A^{(\alpha)}$, of Eqs. (45) and (46).

OSEL: if (integer) $OSEL > 0$, write every $OSEL$ 'th point of the final potential energy to channel-10. If $OSEL < 0$ also write any **BOB** radial function arrays to Channels 12–16; if $OSEL = 0$, omit all such output. Note that smaller values of $|OSEL|$ yield larger output files written on a finer radial mesh.

If $PSEL = -1$, loop over vibrational levels $VMIN$ to $VMAX$, reading in the vibrational quantum number $VTST = v$ and the number of Band Constants $\{G_v, B_v, -D_v, H_v, \dots\}$ to be used for that level, for each isotopologue, $NBC(I, IISTP, ISTATE)$. If $PSEL \neq -1$, ignore $READ$ #10.

```
DO i= VMIN(ISTATE,1),VMAX(ISTATE,1)
#10.   READ(5,*) VTST,(NBC(I,IISTP,ISTATE),IISTP= 1, NISTP)
      ENDDO
```

For all cases for which $PSEL \geq 0$, read $READ$ #11.

```
#11. READ(5,*) RMIN(s), RMAX(s), RH(s)
```

RMIN & RMAX: are the inner and outer limits, respectively, of the range of numerical integration (in \AA). As zeroth order estimates, one may set $RMIN \approx 0.6 \times (\text{potential inner wall position})$ and $RMAX$ very large (say $= 99 \text{\AA}$); see §6.1.

RH: the numerical integration mesh size; see Eq. (55) in §6.1.

If $PSEL = 0$, define a fixed potential for this state by reading, interpolating over and extrapolating beyond a given set of turning points, in the manner specified here. For $PSEL \neq 0$, skip $READS$ #12 – 14.

```
#12. READ(5,*) NTP, NUSE, IR2, ILR, NCN, CNN
```

NTP: gives the number of turning point pairs to be input via $READ$ #14 to define the potential.

NUSE: Specifies how the interpolation is to be done. If $\text{NUSE} > 0$, use NUSE -point piecewise polynomials; if $\text{NUSE} \leq 0$, perform cubic spline interpolation. For highly precise and smooth input points, such as those generated from an RKR calculation, $\text{NUSE} = 8, 10$ or 12 is usually most appropriate; for less precise or less dense points, such as those from *ab initio* calculations, low-order piecewise polynomials ($\text{NUSE} = 4$) or splines ($\text{NUSE} \leq 0$) are usually best [4, 78].

IR2: For very steep repulsive potential walls, better interpolation is often attained by interpolating over $r^2 \times V(r)$ rather than over $V(r)$ itself; setting the integer $\text{IR2} > 0$ causes this to be done (normally recommended). A comparison between results obtained with this option turned on *vs.* off (setting $\text{IR2} \leq 0$ causes interpolation to be performed over $V(r)$ itself) provides an indication of the magnitude of “interpolation noise” uncertainties in the final results.

ILR: Specifies how to extrapolate from the outermost read-in turning points to the asymptote. For a long energy extrapolation, a choice of $\text{ILR} = -1, 0$, or 1 is often most appropriate; however, if the outer turning points extend moderately close to the dissociation limit (at VLIM), one should set $\text{ILR} \geq 2$ and specify the theoretically appropriate value of NCN (≥ 1), and if it is available, also input an estimate of CNN (see below).

For $\text{ILR} < 0$, fit the last 3 points to: $V(r) = \text{VLIM} - A \times \exp[-b(r - r_o)^2]$

For $\text{ILR} = 0$, fit the last 3 points to: $V(r) = \text{VLIM} - A \times r^p \times \exp[-br]$.

For $\text{ILR} = 1$, fit the last 2 points to: $V(r) = \text{VLIM} - A/r^B$.

For $\text{ILR} = 2$ or 3 , respectively, fit the outermost 2 or 3 points to a sum of 2 or 3 inverse-power terms, with powers differing by 2: $V(r) = \text{VLIM} - \sum_{m=0}^{\text{ILR}-1} C_{\text{NCN}+2m}/r^{\text{NCN}+2m}$.

For $\text{ILR} \geq 4$, fit outermost ILR turning points to a sum of ILR inverse-power terms, with powers differing by 1: $V(r) = \text{VLIM} - \sum_{m=0}^{\text{ILR}-1} C_{\text{NCN}+m}/r^{\text{NCN}+m}$.

NCN: For inverse-power potential extrapolation with $\text{ILR} \geq 2$, NCN (> 0) specifies the (inverse) power of the asymptotically dominant long-range term: $V(r) \propto \text{VLIM} - \text{CNN}/r^{\text{NCN}}$. Otherwise (for $\text{ILR} \leq 1$) it is a dummy parameter.

CNN: For inverse-power potential extrapolation with $\text{ILR} \geq 2$, setting $\text{CNN} \neq 0$ causes the leading inverse-power coefficient to be fixed at the read-in value $\text{CNN} = C_{\text{NCN}} [\text{cm}^{-1} \text{\AA}^{\text{NCN}}]$ rather than to be determined from a fit to the outermost turning points.

#13. READ(5,*) RFACT, EFACT, VSHIFT

#14. READ(5,*) (XI(I), YI(I), I=1,NTP)

RFACT & EFACT: are multiplicative factors required to convert units of the NTP input turning point distances $\text{XI}(i)$ and energies $\text{YI}(i)$ to \AA and cm^{-1} , respectively. If no conversion is required, read in factors of 1.0d+00.

VSHIFT: An energy shift (in cm^{-1}) to be added to the input potential point energies to make them consistent with VLIM . It addresses the fact that *ab initio* or RKR turning points may be expressed relative to an energy zero that is inconsistent with the user-specified asymptote energy VLIM .

XI(i) & YI(i): are the (distance, energy) input turning points defining the potential function.

If $\text{PSEL} = 2, 3$, or $5 - 7$ (for an MLR, DELR, HPP, TT or HFD-type potential), specify the long-range potential energy tail function $u_{\text{LR}}(r)$. For other cases, skip READs #15 & 16.

#15. READ(5,*) NCMM(s), rhoAB(s), IDF(s), IDSTT(s)
DO i= 1, NCMM(s)

#16. READ(5,*) MMLR(i,s), CmVAL(i,s), IFXCm(i,s)
ENDDO

NCMM(s) is the number of inverse-power terms included in the definition of $u_{\text{LR}}(r)$ in Eq. (11).

If $\text{rhoAB} \leq 0.0$, the long-range potential is the pure inverse-power sum of Eq. (9); i.e., all $D_{m_i}(r) = 1.0$.

If $\text{rhoAB} > 0.0$, include damping functions in the definition of $u_{\text{LR}}(r)$ by Eq. (11), in which and $\text{rhoAB} = \rho \equiv \rho_{\text{AB}}$ is the system-dependent scaling factor of Eq. (15). In this case:

- $\text{IVSR} \equiv 2s$ selects the damping function from the family specified by parameter IDSTT that has the limiting short-range behaviour $D_m(r)/r^m \propto r^s = r^{\text{IVSR}/2}$.
- If $\text{IDSTT} > 0$, use the generalized Douketis-type damping functions of Eq. (12) (recommended). Allows any integer $-4 \leq \text{IVSR} \leq 0$, +2 or +4 ($\text{IVSR} = -2, -1$, or 0 recommended for an MLR).
- If $\text{IDSTT} \leq 0$, use the generalized Tang-Toennies-type damping functions of Eq. (13). Allows even integers $-4 \leq \text{IVSR} \leq 4$.

MMLR(i,s) is the power and CmVAL(i,s) the coefficient of the i 'th contribution to $u_{\text{LR}}(r)$ in Eq. (11), C_{m_i}/r^{m_i} . Positive CmVAL values yield attractive potential energy terms.

IFXCm(i,s) controls whether $C_{m_i} = \text{CmVAL}(i,s)$ is to be fitted ($\text{IFXCm} \leq 0$) or held fixed ($\text{IFXCm} = 1$) in the fit. Fitting to one or more C_{m_i} values should only be considered if a substantial amount of data is available for levels lying very near dissociation [19]. Setting $\text{IFXCm} > 1$ causes this C_m coefficient to be constrained to equal the value of parameter #IFXCm, which has a smaller parameter # index than its own. E.g. to fix C_m for state ISTATE equal to the leading C_m value for the first electronic state (ISTATE = 1), set $\text{IFXCm}(s) = 3$ (since r_e and \mathcal{D}_e are parameters #1 and 2, respectively). This allows one to fit simultaneously to potentials for two states with this C_m coefficient allowed to vary subject to the constraint that the values for the two states always remain the same.

For the special case of states of a homonuclear alkali dimer dissociating to the $(nS) + (nP)$ asymptote, to use the Aubert-Frécon 2×2 diagonalization long-range form [19, 36, 110], set $\text{NCMM} = 7$ with $\text{MMLR}(i) = x, 3, 3, 6, 6, 8, \& 8$, for which the input values of CmVAL(i) are $A_{\text{so}}, C_3^\Sigma, C_3^\Pi, C_6^\Sigma, C_6^\Pi, C_8^\Sigma$ and C_8^Π , for $i = 1 \dots 7$, respectively, and

- For the 2×2 tail of the $A^1\Sigma_u^+$ state, set $x = \text{MMLR}(1) = 0$.
- For the 2×2 tail of the $b^3\Pi_u$ state, set $x = \text{MMLR}(1) = -1$.

Similarly, to use the Aubert-Frécon 3×3 diagonalization long-range form [21, 36, 111], set $\text{NCMM} = 10$ with $\text{MMLR}(i) = x, 3, 3, 3, 6, 6, 6, 8, 8, \& 8$, for which the input values of CmVAL(i) are $A_{\text{so}}, C_3^\Sigma, C_3^{\Pi}, C_3^{\Pi}, C_6^\Sigma, C_6^{\Pi}, C_6^{\Pi}, C_8^\Sigma, C_8^{\Pi}, C_8^{\Pi}$, and C_8^{Π} , for $i = 1 \dots 10$, respectively, and

- For the 3×3 tail of the $1^3\Sigma_g$ state, set $x = \text{MMLR}(1) = -2$.
- For the 3×3 (mainly repulsive) tail of the $B^1\Pi_u$ state, set $x = \text{MMLR}(1) = -3$.

If $\text{PSEL} = 7$, read in parameters defining the expansion variable in the GPEF potential of Eq. (25); otherwise, skip READ #17.

#17. READ(5,*) AGPEF(s), BGPEF(s)

In the GPEF radial expansion variable of Eq. (25): $a_S = \text{AGPEF}$ and $b_S = \text{BGPEF}$, while $p = \text{nPB}$ is input via READ #20.

Read the dissociation energy and equilibrium distance of the potential function for this state.

#18. READ(5,*) DE(s), IFXDE(s)

#19. READ(5,*) RE(s), IFXRE(s)

DE $\equiv \mathfrak{D}_e$ is the well depth. It is a dummy variable for the case of a GPEF potential. For a TT potential (PSEL = 5) the reported values of \mathfrak{D}_e and r_e should be read in, but the code will report more accurate values. variable for the ca

IFXDE controls whether \mathfrak{D}_e is to be fitted (IFXDE ≤ 0) or held fixed (IFXDE > 0) in the fit.

RE is the equilibrium radial distance r_e for this state, and IFXRE controls whether it is to be fitted (IFXRE ≤ 0) or held fixed (IFXRE > 0) in the fit.

Read integers specifying the form used for the exponent-coefficient function $\beta(r)$, the order of the polynomial defining the potential function $V_{\text{ad}}^{(1)}(r)$ (or $V_{\text{CN}}(r)$), and the nature of the radial variables of Eqs. (5) and (6).

#20. READ(5,*) Nbeta(s), APSE(s), nQB(s), nPB(s), RREF(s)

For PSEL = 1 (an EMO potential), Nbeta is the order of the potential function exponent-coefficient polynomial expansion of Eq. (8) while APSE(ISTATE) is a dummy parameter.

For PSEL = 2 (an MLR potential),

- Setting APSE(s) $>< 0$ invokes use of the ‘Pashov-Spline’ expression for the MLR exponent coefficient $\beta_{\text{SE-MLR}}(r)$, Eq. (20), in which Nbeta(ISTATE) is the total number of spline points to be considered [5, 48]
- Setting APSE(s) ≤ 0 invokes use of the constrained-polynomial expansion of Eq. (18) for the exponent-coefficient function $\beta(r) = \beta_{\text{PE-MLR}}(r)$ of the MLR potential with $N_\beta = \text{Nbeta(ISTATE)}$, while the numerical value of APSE(ISTATE) is immaterial.

For PSEL = 3 (a DELR potential),

- For Nbeta(ISTATE), is the order of the DELR exponent polynomial, while APSE(s) is a dummy parameter.

For PSEL = 4, Nbeta is the order of the GPEF polynomial expansion of Eq. (25) and APSE(ISTATE) is a dummy variable.

For PSEL = 5, (an HPP potential)

Nbeta is the order of the “X-representation” polynomial expansion of Eq. (30) and APSE(ISTATE) is a dummy variable.

For PSEL = 6 (a Tang-Toennies potential)

set Nbeta = 9; APSE(ISTATE) is a dummy variable, and omit READS #23-36.

For PSEL = 7 (an HFD potential), set Nbeta = 5 for the HFD-ABC potentials of Eqs. (33)–(35), while Nbeta = 4 for the HFD-D potentials of Eqs. (33), (36) and (37). In both cases APSE, nPB, nQB and RREF are dummy variables, and we omit READS #23-36.

nPB = p , nQB = q and RREF = r_{ref} define the radial variables of Eqs. (5), (6), (18) and (25).

For PSEL = 2 and APSE(ISTATE) > 0 , loop over the range $i = 1$ to $N_\beta = \text{Nbeta}(s)$, and for the fixed values of the reduced distance yqBETA(I,s), read initial trial values of the exponent function values $\beta_i = \text{BETA}(i)$ of Eqs. (20), while IFXBETA(I,s) controls whether β_i is to be fitted (IFXBETA ≤ 0) or held fixed (IFXBETA > 0).

#21. READ(5,*) ypbETA(I,s), BETA(I,s), IFXBETA(I,s)

For other PSEL > 0 cases, loop over the range $i = 0$ to $N_\beta = \text{Nbeta}(s)$ ($i = 1$ to $N_\beta = \text{Nbeta}(s)$ PSEL = 6 or 7) and read initial trial values of the expansion parameters $\beta_i = \text{BETA}(i)$ of Eqs. (8), (18), (25), (31) or (32).

For PSEL = 7 with Nbeta = 5 (an HFD-ABC potential), BETA(i, s) for $i = 0 - 2$ are the α_i parameters of Eq. (35), while BETA(4, s) = β_2 and BETA(5, s) = γ from Eq. (33).

For PSEL = 7 with Nbeta = 2 (an HFD-D potential), BETA(1, s) = β_2 and BETA(2, s) = γ from Eq. (33)

Skip this loop and READ statement if PSEL \leq 0.

#22. READ(5,*) (BETA(I, s), IFXBETA(I, s), I=0, Nbeta(s))

BETA(I, s) is the initial trial value of the potential exponent expansion coefficients β_i or (if PSEL=6) of the GPEF expansion coefficients $c_i = \beta_i$.

IFXBETA(I, s) controls whether β_i is to be fitted (IFXBETA \leq 0) or held fixed (IFXBETA $>$ 0).

Now, read in parameters specifying the Born-Oppenheimer breakdown radial functions. First, for the effective adiabatic functions \tilde{S}_{ad}^A and \tilde{S}_{ad}^B of Eqs. (3) and (38).

#23. READ(5,*) NUA(ISTATE), NUB(ISTATE), qAD(ISTATE), pAD(ISTATE), LRad(ISTATE)

NUA = N_{ad}^A and NUB = N_{ad}^B are the (integer) orders of the polynomial in $y_{q_{\text{ad}}}(r)$ used to define the effective adiabatic BOB radial function of Eq. (38) for atoms A and B, respectively. If NUA $<$ 0 or NUB $<$ 0, omit reading the adiabatic BOB terms for that atom; i.e., skip READs #24, #26 and #27, or READs #25, #28 and #29, respectively.

- *Note:* for a chemically homonuclear molecule (AN(1) = AN(2)), set NUB = -1, as the parameters for atom A are used for both atoms.

QAD(s) = q_{ad} and PAD(s) = p_{ad} define the nature of the radial variables $y_{q_{\text{ad}}}(r)$ and $y_{p_{\text{ad}}}(r)$ appearing in Eq. (38). In cases for which NCMM(s) $>$ 0 normally set pAD(s) \geq MMLR(NCMM(s), s).

LRad(s) = 0 for cases in which the function \tilde{S}_{ad} is defined by the simple constrained polynomial of Eq. (38) with u_{∞} being a constant.

LRad(s) = 1 for cases in which the factor u_{∞} in Eq. (38) is to be represented by the expansion of Eq. (41). In this case, values of $\overline{\delta C}_{m_i}^{A/B}$ must be read in for $i = 1$, NCMM(s), for both atoms.

If NLad(s) \geq 0 read in, one per line, values of the isotopologue-*independent* parameters $\overline{\delta C}_m(A/B)$ that define how the long-range coefficients $C_m^{A/B, \alpha}$ for atoms ‘A’ and ‘B’ differ from one isotopologue to another. For cases in which no values are known, read in values of 0.0.

#24. IF(NLad(ISTATE) $>$ 0) READ(5,*) dCmVALA((m), m=1, NCMM(ISTATE))

#25. IF(NLad(ISTATE) $>$ 0) READ(5,*) dCmVALB((m), m=1, NCMM(ISTATE))

If NUA(s) \geq 0, loop over $i = 0$ to NUA(s) while reading in initial trial values of parameters UA(i, s) = u_i^A of Eq. (38) and integer parameter IFXUA(i, s) to control whether u_i^A is to be fitted (IFXUA(i, s) \leq 0) or held fixed (IFXUA(i, s) $>$ 0). Also read UAinf = u_{∞}^A , the limiting asymptotic value of the atom-A radial BOB function $\tilde{S}_{\text{ad}}^A(R)$, and integer parameter IFXUAinf that controls whether UAinf is to be fitted (IFXUAinf \leq 0) or held fixed (IFXUAinf $>$ 0).

#26. READ(5,*) UA(I, s), IFXUA(I, s), I=0, NUA(s)

#27. READ(5,*) UAinf, IFXUAinf

If NUB(s) \geq 0, loop over $i = 0$ to NUB(s) while reading in initial trial values of parameters UB(i, s) = u_i^B of Eq. (38) and integer parameter IFXUB(i, s) to control whether u_i^B is to be fitted (IFXUB(i, s) \leq 0) or held fixed (IFXUB(i, s) $>$ 0). Also, read UBinf = u_{∞}^B , the limiting asymptotic

value of the atom- B radial BOB function $\tilde{S}_{\text{ad}}^{\text{B}}(R)$, and integer parameter IFXUBinf that controls whether UBinf is to be fitted ($\text{IFXUBinf} \leq 0$) or held fixed ($\text{IFXUBinf} > 0$).

#28. READ(5,*) (UB(I,s), IFXUB(I,s), I=0, NUB(s))

#29. READ(5,*) UBinf, IFXUBinf

Now, read in parameters defining the centrifugal BOB radial functions $\tilde{R}_{\text{na}}^{\text{A}}$ and $\tilde{R}_{\text{na}}^{\text{B}}$ of Eqs. (4) and (39).

#30. READ(5,*) NTA(ISTATE), NTB(ISTATE), qNA(ISTATE), pNA(ISTATE)

$\text{NTA} = N_{\text{na}}^{\text{A}}$ and $\text{NTB} = N_{\text{na}}^{\text{B}}$ are the (integer) orders of the polynomial in $y_{q_{\text{na}}}(r)$ used to define the centrifugal BOB radial function of Eq. (39) for atoms A and B, respectively. If $\text{NTA} < 0$ or $\text{NTB} < 0$, omit the centrifugal BOB terms for that atom; i.e., skip READs #31 and #32, or READs #33 and #34, respectively.

• *Note:* for a chemically homonuclear molecule ($\text{AN}(1) = \text{AN}(2)$), set $\text{NTB} = -1$, as the parameters for atom A are automatically used for both atoms.

$\text{pNA}(s) = p_{\text{na}}$ and $\text{qNA}(s) = q_{\text{na}}$ define the nature of the radial variables $y_{p_{\text{na}}}(r)$ and $y_{q_{\text{na}}}(r)$ appearing in Eq. (39).

If $\text{NTA}(s) \geq 0$, loop over $i = 0$ to $\text{NTA}(s)$ while reading in initial trial values of parameters $\text{TA}(i, s) = t_i^{\text{A}}$ of Eq. (38), and integer parameter $\text{IFXTA}(i, s)$ to control whether t_i^{A} is to be fitted ($\text{IFXTA}(i, s) \leq 0$) or held fixed ($\text{IFXTA}(i, s) > 0$). Also, read $\text{TAinf} = t_{\infty}^{\text{A}}$, the limiting asymptotic value of the atom-A radial BOB function $\tilde{R}_{\text{na}}^{\text{A}}(R)$, and the integer parameter IFXTAinf that controls whether TAinf is to be fitted ($\text{IFXTAinf} \leq 0$) or held fixed ($\text{IFXTAinf} > 0$).

#31. READ(5,*) TA(I,s), IFXTA(I,s)a

#32. READ(5,*) TAinf, IFXTAinf

If $\text{NTB}(s) \geq 0$, loop over $i = 0$ to $\text{NTB}(s)$ while reading in initial trial values of parameters $\text{TB}(i, s) = t_i^{\text{B}}$ of Eq. (39), and integer parameter $\text{IFXTB}(i, s)$ to control whether t_i^{B} is to be fitted ($\text{IFXTB}(i, s) \leq 0$) or held fixed ($\text{IFXTB}(i, s) > 0$). Also read $\text{TBinf} = t_{\infty}^{\text{B}}$, the limiting asymptotic value of the atom-B radial BOB function $\tilde{R}_{\text{na}}^{\text{B}}(R)$, and the integer parameter IFXTBinf which controls whether TBinf is to be fitted ($\text{IFXTBinf} \leq 0$) or held fixed ($\text{IFXTBinf} > 0$).

#33. READ(5,*) (TB(I,s), IFXTB(I,s), I=0, NTB(s))

#34. READ(5,*) TBinf, IFXTBinf

Finally, if the electronic angular momentum quantum number $\text{IOMEG}(s)$ is not zero, read in parameters defining the radial Λ -doubling or ${}^2\Sigma$ spin-splitting radial strength function of Eqs. (49) or (53), respectively.

#35. READ(5,*) NwCFT(s), Pqw(s), efREF(s)

NwCFT is the order of the polynomial defining the radial strength function $f_{\Lambda}(r)$ or $f_{\Sigma}(r)$.
If $\text{NwCFT}(s) < 0$, omit READ #36.

Pqw is the integer q_{Λ} or q_{Σ} defining the radial expansion variable $y_{q_{\Lambda}}^r(r)$ in Eq. (49) or $y_{q_{\Sigma}}^r(r)$ in Eq. (53).

efREF : specifies the choice of reference (or zero-shift) parity levels for Λ -doubling splittings. Select them as the f -parity sublevels when $\text{efREF} = -1$, the e -parity sublevels when $\text{efREF} = +1$, or their mid-point when $\text{efREF} = 0$; e.g., for a ${}^1\Pi$ state, if $\text{efREF} = -1$ the f -levels are treated as unperturbed and the e -levels shifted by $+q_B(v)[J(J+1)]$, ... etc. For ${}^2\Sigma$ splitting, efREF is a dummy parameter.

If $\text{NwCFT}(s) \geq 0$, loop over $i = 1$ to $\text{NwCFT}(s)$ while reading in initial trial values of parameters $\text{wCFT}(i, s) = w_i$ of Eq. (49) or (53), and integer parameter $\text{IFXwCFT}(i, s)$ to control whether this w_i is to be fitted ($\text{IFXwCFT}(i, s) \leq 0$) or held fixed ($\text{IFXwCFT}(i, s) > 0$).

#36. READ(5,*) wCFT(I,s), IFXwCFT(I,s)

To Generate predictions from a set of fixed system parameters.

Loop over READ #37 for all bands for which predictions are desired, and for each one read the following. Input stops at the end of the data file or if the read-in value of VP for a band is negative.

#37. READ(5,*) VP(IBAND),VPP(IBAND), LABLP,LABLP, MN1, MN2, PP, PPP,
1 JMAXX,J2DL,J2DU,J2DD

VP(IBAND) & VPP(IBAND): are the vibrational indices v' and v'' , respectively, labeling that band. Set $v' = \text{VP}(\text{IBAND}) < 0$ to indicate the end of the prediction data set,

LABLP & LABLPP: are the three-alphanumeric-character names (enclosed in single quotes, as in 'X1S') identifying the upper and lower electronic state for which the predicted band is to be generated. Set LABLP = LABLPP to generate IR or MW transitions for that state.

MN1 & MN2: are the integer mass numbers identifying the isotopologue for which the predictions are to be generated.

PP & PPP: are integers with values +1, 0 or -1 to indicate the e/f parity of the upper ($p' = \text{PP}$) and lower ($p'' = \text{PPP}$) levels in the band.

JMAXX, J2DL, J2DU & J2DD: generate predicted transition energies for $J'' = 0$ to JMAXX, subject to the selection rule that $\Delta J = J' - J''$ runs from J2DL to J2DU in steps of J2DD.

Appendix D: Illustrative Application: Determine an MLR Potential for $X^1\Sigma_g^+$ -State Ca_2

This program has been successfully applied to a wide variety of problems [9, 10, 12, 13, 15–21, 23, 24, 39, 41, 80, 97, 112]. The present subsection briefly describes one of these cases and presents the associated Channel-5 ‘instruction’ input data file and portions of the Channel-6 main output file.

Appendix D.1 Input Instruction Data File for the Ground $X^1\Sigma_g^+$ State of Ca_2

This is the case described in Refs. [16] and [20], in which 3553 fluorescence series transitions from 180 levels of the $B^1\Sigma_u^+$ state of Ca_2 into 924 levels of the $X^1\Sigma_g^+$ state spanning 99.97% of its well [100, 101] are fitted to an MLR potential whose long-range tail is defined by accurate fixed theoretical C_8 , and C_{10} values, but with the C_6 coefficient treated as a free parameter. The following input ‘instruction file’ is for the fit to the updated version of the model described in Ref. [20]. The Channel-4 file containing the 3553 experimental data used in this analysis may be obtained from the author on request.

```

20 20 0 1 1 0 0          % AN(1) AN(2) CHARGE NISTP NSTATES LPRINT PRINP
'./Ca2_X_FS.4'          % Name of dPotFit input data file
'N7q4C6rr6_85'         % Writefile
40 40                   % MN1(1) MN2(1)
1.d0 1 -0 0 30 0        % UCUTOFF NOWIDTHS IROUND ROBUST CYCMAX uBv
'X1S' 0 0 38 300 0      % (1) SLABL IOMEG VMIN VMAX JTRUNC EFSEL
2 0.d0 1 0 20           % PSEL VLIM MAXMIN BOBCN OSEL
3.00 99.0 0.0005d0      % RMIN RMAX RH

3 0.5870d0 -2 1         % NCMM rhoAB IVSR IDSTT
6 1.04600000D+07 0      % MMLR(1) CMVAL(1) IFXCm(1)
8 3.06080000D+08 1      % MMLR(2) CMVAL(2) IFXCm(2)
10 8.34400000D+09 1     % MMLR(3) CMVAL(3) IFXCm(3)

1.102080000000D+03 0
4.277820000000D+00 0

7 0 3 5 5.55D+00       % NSpow NLpow nPB nQB RREF
-1.4672501 0
-0.20012 0
-0.72633 0
0.1229 0
-0.2763 0
0.506 0
0.357 0
1.022 0

-6 -6 3 3 0           % NUA NUB qAD pAD LRad
-6 -6 3 3             % NTA NTB qNA pNA

```

Appendix D.2 Main Output File for an MLR Fit to Ground($X^1\Sigma_g^+$)-State Ca_2

Note that the value of $DRMSD = \overline{dd}$ reported at the end of the first cycle of fit is very large ($\sim 10^6$), while those for the next two cycles are small and identical to one another. This behaviour arises because the reported value for each cycle is calculated using the trial parameters available at the *beginning* of the cycle, and at the beginning of the very first cycle the trial values of all fluorescence series origins were zero. In this initial phase of a fit, the code fits only those parameters w.r.t. which the data are strictly linearly dependent, while holding all PEF parameters fixed. As for any truly linear least-squares fit, one cycle gives the final result, but in our case an additional (third) cycle is then run because the convergence criterion requires the \overline{dd} values in two consecutive cycles to agree to 1 part in 10^7 ,

The above behaviour of occurs for all fits involving fluorescence series data, or in which the energy levels for one or more states are represented by term values or band constants. Following that initial 3-cycle convergence, the full fit in which *all* parameters are free commences, and it then continues until it too converges fully.

A prominent feature of the output shown below is the nest of 48 lines of warning messages immediately preceding the “After Cycle # 1 DRMSD=” message. These indicate that 18 of the reported transitions involve five lower-state levels that the code was unable to locate, and hence that those 48 lines were omitted from the analysis. In the present case those five lower levels in are very high- J quasibound levels lying near the centrifugal barrier maximum for which the procedure for generating initial trial values seems to have failed. Such problems are not encountered often, but when they do, the omission of the associated handful of lines (here 18 out of 3553) has little effect on the fit. While these warnings occur on every cycle of the current fit, they are only show once below in order to make the structure of the rest of the results easier to see.

```

Input data for 1 isotopologues(s)
*****
  Isotopologues      Mass of atom-1      Mass of atom-2      Reduced mass
-----
Ca( 40) - Ca( 40)      39.962590864      39.962590864      19.981295432

Use experimental data input file: Ca2_Robbie.4
Uncertainties for transitions involving quasibound levels modified to:
      Sqrt{(u(i;exp)**2 + ( 0.20*width)**2)}
For electrically homonuclear molecules, B0 correction functions are the same
for both atoms, so only the first sets of correction coefficients
UA(s) and TA(s) are used, and the mass scaling factors are sums over
the two individual atoms.
Fit uses standard 1/[uncertainty(i)]**2 data weighting
Non-linear fits are allowed a maximum of CYCMAX= 25 cycles

For state X0
  integrate from RMIN= 3.00 to RMAX= 48.00 with mesh RH= 0.00050
=====

State X0 represented by an MLR(q= 3, p= 5) potential defined in terms of
===== exponent coefficient: beta(R)= betaINF*y5 +(1-y5)*Sum{beta_i*y3^i}
                                for i= 0 to 7
      with radial variable: y_{p,q} = (R^q - 5.550000^q)/(R^q + 5.550000^q)
uLR inverse-power terms incorporate NO damping functions
                                C6= 1.0460000D+07 [cm-1 Ang^6]
                                C8= 3.0608000D+08 [cm-1 Ang^8]
                                C10= 8.3440000D+09 [cm-1 Ang^{10}]
                                betaINF= -1.3499558834
      These constants yield:
Parameter  Initial Value  Uncertainty  Sensitivity
VLIM      0.00000000000D+00  --          --
De        1.102080000000D+03  0.0D+00    0.0D+00

```

Re	4.277820000000D+00	0.0D+00	0.0D+00
C 6	1.046000000000D+07	0.0D+00	0.0D+00
C 8	3.060800000000D+08	--	--
C10	8.344000000000D+09	--	--
beta(0)	-1.467250100000D+00	0.0D+00	0.0D+00
beta(1)	-2.001200000000D-01	0.0D+00	0.0D+00
beta(2)	-7.263300000000D-01	0.0D+00	0.0D+00
beta(3)	1.229000000000D-01	0.0D+00	0.0D+00
beta(4)	-2.763000000000D-01	0.0D+00	0.0D+00
beta(5)	5.060000000000D-01	0.0D+00	0.0D+00
beta(6)	3.570000000000D-01	0.0D+00	0.0D+00
beta(7)	1.022000000000D+00	0.0D+00	0.0D+00
beta_INF	-1.349955883434D+00	--	--
C11{exp}	-6.107145366294D+10	--	--

=====
Neglect data with: Uncertainties > UCUTOFF= 1.00D+00 (cm-1)
and State X0 data with J > JTRUNC= 300
or v outside range 0 to 38 for ISOT= 1
State X0 Energy Convergence criterion EPS is 1.0D-06 cm-1

```

Search for v= 8 J=162 starting from E= 299.89 finds E(v= -1)= 308.57
*** SCECOR failed 1 times, Currently Seeking v= 8, J=162; Found v= -1
*** FAIL to find level(X0 ) v= 8 J=162 so ignore YOBS( 85)= 19370.3320
Search for v= 9 J=160 starting from E= 298.10 finds E(v= -1)= 295.27
*** SCECOR failed 2 times, Currently Seeking v= 9, J=160; Found v= -1
*** FAIL to find level(X0 ) v= 9 J=160 so ignore YOBS( 86)= 19373.9930
Search for v= 8 J=162 starting from E= 299.89 finds E(v= -1)= 308.57
*** SCECOR failed 3 times, Currently Seeking v= 8, J=162; Found v= -1
*** FAIL to find level(X0 ) v= 8 J=162 so ignore YOBS( 154)= 19406.1530
Search for v= 9 J=158 starting from E= 280.50 finds E(v= -1)= 288.24
*** SCECOR failed 4 times, Currently Seeking v= 9, J=158; Found v= -1
*** FAIL to find level(X0 ) v= 9 J=158 so ignore YOBS( 165)= 19354.4750
Search for v= 17 J=120 starting from E= 124.90 finds E(v= -1)= 131.05
*** SCECOR failed 5 times, Currently Seeking v= 17, J=120; Found v= -1
*** FAIL to find level(X0 ) v= 17 J=120 so ignore YOBS( 474)= 20531.1610
Search for v= 21 J=102 starting from E= 81.01 finds E(v= -1)= 80.83
*** SCECOR failed 6 times, Currently Seeking v= 21, J=102; Found v= -1
*** FAIL to find level(X0 ) v= 21 J=102 so ignore YOBS( 904)= 18444.0030
Search for v= 21 J=102 starting from E= 81.01 finds E(v= -1)= 80.83
*** SCECOR failed 7 times, Currently Seeking v= 21, J=102; Found v= -1
*** FAIL to find level(X0 ) v= 21 J=102 so ignore YOBS( 1253)= 18444.0000
Search for v= 8 J=162 starting from E= 299.89 finds E(v= -1)= 308.57
*** SCECOR failed 8 times, Currently Seeking v= 8, J=162; Found v= -1
*** FAIL to find level(X0 ) v= 8 J=162 so ignore YOBS( 1962)= 19370.3340
Search for v= 9 J=160 starting from E= 298.10 finds E(v= -1)= 295.27
*** SCECOR failed 9 times, Currently Seeking v= 9, J=160; Found v= -1
*** FAIL to find level(X0 ) v= 9 J=160 so ignore YOBS( 1963)= 19373.9660
Search for v= 8 J=162 starting from E= 299.89 finds E(v= -1)= 308.57
*** SCECOR failed 10 times, Currently Seeking v= 8, J=162; Found v= -1
*** FAIL to find level(X0 ) v= 8 J=162 so ignore YOBS( 2030)= 19406.1440
Search for v= 21 J=102 starting from E= 81.01 finds E(v= -1)= 80.83
*** SCECOR failed 11 times, Currently Seeking v= 21, J=102; Found v= -1
*** FAIL to find level(X0 ) v= 21 J=102 so ignore YOBS( 2142)= 18444.0430
Search for v= 21 J=102 starting from E= 81.01 finds E(v= -1)= 80.83
*** SCECOR failed 12 times, Currently Seeking v= 21, J=102; Found v= -1
*** FAIL to find level(X0 ) v= 21 J=102 so ignore YOBS( 2438)= 18444.0500
Search for v= 18 J=116 starting from E= 115.09 finds E(v= -1)= 119.39
*** SCECOR failed 13 times, Currently Seeking v= 18, J=116; Found v= -1
*** FAIL to find level(X0 ) v= 18 J=116 so ignore YOBS( 2939)= 19345.3040
Search for v= 18 J=116 starting from E= 115.09 finds E(v= -1)= 119.39
*** SCECOR failed 14 times, Currently Seeking v= 18, J=116; Found v= -1
*** FAIL to find level(X0 ) v= 18 J=116 so ignore YOBS( 3138)= 19345.3200
Search for v= 18 J=116 starting from E= 115.09 finds E(v= -1)= 119.39
*** SCECOR failed 15 times, Currently Seeking v= 18, J=116; Found v= -1
*** FAIL to find level(X0 ) v= 18 J=116 so ignore YOBS( 3249)= 19345.3200
Search for v= 18 J=116 starting from E= 115.09 finds E(v= -1)= 119.39
*** SCECOR failed 16 times, Currently Seeking v= 18, J=116; Found v= -1
*** FAIL to find level(X0 ) v= 18 J=116 so ignore YOBS( 3383)= 19345.3030

```

After Cycle # 1: DRMSD= 2.6142116D+06 test(PS)= 2.6D+02 test(PU)= 4.3D+00
 After Cycle # 2: DRMSD= 6.1891004D-01 test(PS)= 5.0D-07 test(PU)= 8.5D-09
 After Cycle # 3: DRMSD= 6.1891004D-01 test(PS)= 9.3D-08 test(PU)= 1.6D-09

Full 3-cycle convergence: {ABS(RMSR/RMSRB)-1}= 5.73D-13 TSTPS= 9.3D-08

After Cycle # 1: DRMSD= 6.1891004D-01 test(PS)= 1.1D+04 test(PU)= 2.7D-01
 After Cycle # 2: DRMSD= 6.2197176D-01 test(PS)= 3.0D+02 test(PU)= 4.1D-02
 After Cycle # 3: DRMSD= 6.1900333D-01 test(PS)= 5.9D+01 test(PU)= 9.1D-03
 After Cycle # 4: DRMSD= 6.1886942D-01 test(PS)= 1.3D+01 test(PU)= 2.0D-03
 After Cycle # 5: DRMSD= 6.1886276D-01 test(PS)= 2.9D+00 test(PU)= 4.5D-04
 After Cycle # 6: DRMSD= 6.1886243D-01 test(PS)= 6.5D-01 test(PU)= 1.0D-04
 After Cycle # 7: DRMSD= 6.1886241D-01 test(PS)= 1.4D-01 test(PU)= 2.3D-05

Full 7-cycle convergence: {ABS(RMSR/RMSRB)-1}= 2.65D-08 TSTPS= 1.4D-01

3553 data fit to 191 param. yields DRMS(devn)= 6.1886241D-01 tst(PS)= 1.4D-01
 PV(1) = 1.10207930826358D+03 (+/- 4.0D-03) PS= 3.6D-06 PC= 1.3D-10
 PV(2) = 4.27781557316645D+00 (+/- 1.9D-05) PS= 1.4D-08 PC= -4.2D-10

..... omit 189 lines to save space

PV(192) = 2.01725642628215D+04 (+/- 8.7D-03) PS= 7.1D-05 PC= -2.2D-10
 PV(193) = 1.96650081930497D+04 (+/- 4.4D-03) PS= 2.1D-05 PC= -1.8D-10

=====
 Fitting 191 free parameters to 3553 transitions yields DSE= 0.63619882
 =====

=====
 The following 180 Fluorescence Series Origins were determined
 =====

(v', J', p'; ISTEP)	T(value)	Uncertainty	Sensitivity
(5, 67, +1; 1)	18847.271302	4.6D-03	2.6D-05
(6, 97, +1; 1)	19247.654565	5.7D-03	2.2D-05
(2,161, +1; 1)	19666.758095	1.0D-02	3.2D-05

..... omit 174 lines to save space

(12, 91, +1; 1)	19895.675096	6.1D-03	5.0D-05
(11,125, +1; 1)	20172.564263	8.7D-03	7.1D-05
(12, 63, +1; 1)	19665.008193	4.4D-03	2.1D-05

=====
 State X0 represented by an MLR(q= 3, p= 5) potential defined in terms of

=====
 exponent coefficient: $\beta(R) = \beta_{INF} y^5 + (1-y^5) \sum_{i=0}^7 \beta_i y^{3i}$
 for $i = 0$ to 7

with radial variable: $y_{\{p,q\}} = (R^q - 5.550000^q) / (R^q + 5.550000^q)$

uLR inverse-power terms incorporate NO damping functions

C6= 1.0454962D+07 [cm-1 Ang⁶]

C8= 3.0608000D+08 [cm-1 Ang⁸]

C10= 8.3440000D+09 [cm-1 Ang¹⁰]

These constants yield: $\beta_{INF} = -1.3498686606$

Parameter	Final Value	Uncertainty	Sensitivity
VLIM	0.00000000000D+00	--	--
De	1.102079308264D+03	4.0D-03	3.6D-06
Re	4.277815573166D+00	1.9D-05	1.4D-08
C 6	1.045496176200D+07	3.2D+04	6.6D-01
C 8	3.06080000000D+08	--	--
C10	8.34400000000D+09	--	--
beta(0)	-1.467382773954D+00	8.4D-04	1.2D-08
beta(1)	-2.005944207706D-01	3.2D-03	5.3D-08
beta(2)	-7.272203056978D-01	6.0D-03	1.1D-07
beta(3)	1.217583441954D-01	8.9D-03	2.4D-07
beta(4)	-2.771089629303D-01	7.0D-03	4.5D-07
beta(5)	5.036641109431D-01	1.5D-02	9.3D-07
beta(6)	3.515368692379D-01	3.6D-02	1.7D-06

```

beta( 7)  1.019354103000D+00    5.2D-02    3.4D-06
beta_INF -1.349868660575D+00    --        --
C11{exp} -6.062033969002D+10    --        --

```

```

*** Discrepancies for 180 bands/series of Ca( 40)-Ca( 40) ***

```

```

3553 Fluorescence transitions into State X0 Ca( 40)-Ca( 40) in 180 series

```

```

===== Avge. =====
v'  j'  p'  #data  v"min  v"max  AvgeUnc  Max.Unc.  Err/Unc  DRMSD
-----
 5  67  e   33     0    22   8.3D-03  1.2D-02  -0.02059  0.650  as per Mol.P. 105,663(2007)
 6  97  e   37     0    21   7.6D-03  1.5D-02   0.03076  0.492  as per Mol.P. 105,663(2007)
 2 161  e   16     1     9   8.8D-03  5.0D-02  -0.00001  0.338  as per Mol.P. 105,663(2007)

```

..... omit 174 lines to save space

```

12  91  e   12     0     9   1.1D-02  1.5D-02  -0.17667  0.753  as per Mol.P. 105,663(2007)
11 125  e    9     0     8   1.2D-02  1.5D-02   0.19259  0.978  as per Mol.P. 105,663(2007)
12  63  e   40     0    21   8.3D-03  1.8D-02   0.00945  0.600  as per Mol.P. 105,663(2007)
----- For these 3553 lines, overall:  -0.00371  0.619

```

```

Fit of 191 total param to 3553 data yields DRMS(devn.)= 0.61886241

```

Appendix E: Application to Determine an MLR PEF and BOB functions for $X^2\Sigma^+$ -State MgH

This case involves the simultaneous analysis of data for six isotopologues, formed by ^1H and ^2H with ^{24}Mg , ^{25}Mg , and ^{26}Mg , in a $^2\Sigma^+$ electronic state. Thus, as well as determining the main ‘mechanical’ potential energy function itself, it was possible to determine potential-energy (‘adiabatic’) and centrifugal BOB radial strength functions, as well as the Λ -doubling radial strength function whose radial expectation values are the conventional v -dependent $^2\Sigma$ splitting parameters.

This is the case described in Ref. [112], in which a fit to microwave, infrared and electronic data for the $X^2\Sigma^+$ and $A^1\Sigma^+$ states of the ^{24}Mg , ^{25}Mg and ^{26}Mg isotopologues of MgH and MgD was used to determine an MLR(12) (i.e., $N_\beta = 12$) potential energy function, as well as adiabatic (potential energy) and centrifugal BOB functions, and a radial strength function to characterize the $^2\Sigma$ doublet splittings. The fact that the data span almost the entire potential well while the long-range part of the potential is important only at energies very close to dissociation is the reason for the relatively high orders of the MLR exponent polynomial and the expansions for the BOB functions. The Channel-4 input file of the 20 103 experimental data used in this analysis may be obtained in a link from the HTML version of Ref. [112] on the Journal’s www site, or from the author. In this case, the energy levels of all three excited states are represented by independent term values.

```

12 1 0 6 4 4 0          % AN1 AN2 CHARGE NISTP NSTATES LPRINT PRINP
'./data_MgHD_2012-01-27.4' % Name of input data file
'tst_5412rref2_74'      % WRITEFILE
24 1                    % MN1 MN2
25 1
26 1
24 2                    % MN1 MN2
25 2
26 2
0.5 1 0 0 30 0         % UCUTOFF NOWIDTHS IROUND ROBUST CYCMAX uBv
'X1S' -1 0 -11 99 0    % SLABL IOMEG VMAX JTRUNC EFSEL
11 10 10 15 11 11     % VMAX(istp), ISTEP= 1,6
2 0.000 1 0 20        % PSEL VLIM MAXMIN BOBCN OSEL
0.60 99.50 0.0025     % RMIN RMAX RH
3 0.81 -2 1           % NCMM rhoAB IVSR IDSTT
6 2.77550000D+05      1 % MMLR, CmVAL, IFXCm
8 3.45490000D+06      1 % MMLR, CmVAL, IFXCm
10 4.61400000D+07     1 % MMLR, CmVAL, IFXCm

1.110424552400D+04 0   % De IFXDe
1.729685380255D+00 0   % Re IFXRe

12 -1 4 5 2.74D+00    % Nbeta APSE nQB nPB RREF
1.170476601132D+00 0   % BETA 0 IFXBETA 0
1.080170651332D+00 0   % BETA 1 IFXBETA 1
2.673340658164D+00 0   % BETA 2 IFXBETA 2
2.483625825973D+00 0   % BETA 3 IFXBETA 3
7.400354782870D-01 0   % BETA 4 IFXBETA 4
1.921267534841D-01 0   % BETA 5 IFXBETA 5
6.071160601044D-01 0   % BETA 6 IFXBETA 6
-2.486057829458D+00 0 % BETA 7 IFXBETA 7
-7.676067408675D+00 0 % BETA 8 IFXBETA 8

```

```

-5.742858200526D+00 0      % BETA 9  IFXBETA 9
 2.850001493731D+00 0      % BETA10 IFXBETA10
 6.076990710549D+00 0      % BETA11 IFXBETA11
 2.409626277526D+00 0      % BETA12 IFXBETA12

 3 13  4  6  0              % NUA NUB  qAD pAD  LRad
 1.300728351881D+00 0      % UA 0  IFXUA 0
 4.148196460337D+00 0      % UA 1  IFXUA 1
 2.612257669548D+00 0      % UA 2  IFXUA 2
 4.341067654483D+00 0      % UA 3  IFXUA 3
 0.000000000000D+00 1      % uAinf  IFXuAinf

-1.517859106465D+01 0      % UB 0  IFXUB 0
 3.753517600616D+01 0      % UB 1  IFXUB 1
-1.153600397884D+01 0      % UB 2  IFXUB 2
 3.213195588821D+01 0      % UB 3  IFXUB 3
 5.866458845349D+01 0      % UB 4  IFXUB 4
 2.347347913310D+02 0      % UB 5  IFXUB 5
-1.543302677803D+03 0      % UB 6  IFXUB 6
-2.076874526486D+03 0      % UB 7  IFXUB 7
 1.249385587088D+04 0      % UB 8  IFXUB 8
 5.664228044773D+03 0      % UB 9  IFXUB 9
-4.993237165924D+04 0      % UB10  IFXUB10
 1.007715179054D+04 0      % UB11  IFXUB11
 7.172546964411D+04 0      % UB12  IFXUB12
-4.723470281067D+04 0      % UB13  IFXUB13
 0.000000000000D+00 1      % uBinf  IFXUBinf

-3  7  4  4  0              % NTA NTB  qNA pNA
 0.000000000000D+00 1      % TB 0  IFXTB 0
 7.250023689953D-04 0      % TB 1  IFXTB 1
 2.862180763657D-04 0      % TB 2  IFXTB 2
 9.395028124006D-04 0      % TB 3  IFXTB 3
 2.804097571256D-03 0      % TB 4  IFXTB 4
-1.917529464250D-03 0      % TB 5  IFXTB 5
-6.715122481617D-03 0      % TB 6  IFXTB 6
 2.263936298448D-02 0      % TB 7  IFXTB 7
 0.000000000000D+00 1      % tBinf  IFXTBinf

 3  4  0                      % NwCFT Pqw efREF
 4.619303623412D-03 0      % wCFT 0  IFXwCFT 0
-3.135099829025D-03 0      % wCFT 1  IFXwCFT 1
 2.688086629368D-04 0      % wCFT 2  IFXwCFT 2
-4.537525776361D-03 0      % wCFT 3  IFXwCFT 3

'A1' 0 0 99 99 0           % SLABL IOMEG VMAX JRUNC EFSEL
-2 0.1 1 0 20             % PSEL VLIM MAXMIN BOBCN OSEL
'A2' 0 0 99 99 0           % SLABL IOMEG VMAX JRUNC EFSEL
-2 0.1 1 0 20             % PSEL VLIM MAXMIN BOBCN OSEL
'BO' 0 0 99 99 0           % SLABL IOMEG VMAX JRUNC EFSEL
-2 0.1 1 0 20             % PSEL VLIM MAXMIN BOBCN OSEL

```

Appendix F. Schematic Description of Program Structure

The present section lists the names and outlines the functions of the various subroutines used by **dPotFit**, and indicates their hierarchy. In particular, the level of indentation in this list indicates which subroutines call which others.

DPOTFIT: The main program that reads the input data characterizing the molecular system and the type of fit to be performed, calls the actual fitting routines, and prints descriptions of the system and the results.

MASSES: A data subroutine containing the best current [92] values of the atomic masses (and other properties) of all stable atomic isotopes. Its presence obviates the need for a user to look up and type precise particle masses into the input data file.

READPOT: The subroutine that reads in and organizes the parameters and properties of the potential energy, BOB, and (as appropriate) Λ -doubling or $^2\Sigma$ splitting radial strength functions to be used for a particular electronic state.

WRITEPOT: Writes out a complete listing of the parameters defining the potential energy and other radial strength functions in the Hamiltonian. When called at the end of a run, it also lists the uncertainties and sensitivities of the fitted parameters.

READATA: The data input subroutine for reading in, arranging, and characterizing the experimental data to be used in the fit.

TVSORT: If the vibration-rotation levels of one or more states are to be represented by independent term values, sorts through global data file, and for each isotopomer in state **ISTATE**: (i) finds the number of transitions coupled to each level (v, J, p), (ii) for levels ordered by increasing v, J , and p , add a free parameter for each level involved in one or more transitions, and (iii) label each transition involving one of these levels by the index/counter of the parameter associated with that term value.

PREPOT: A subroutine package, described in detail in the manual for program **LEVEL** [4, 78], that can generate a potential function by interpolating over a set of input points. This allows one to run a ‘forward’ calculation (without performing a fit) to test the ability of a pointwise potential function obtained from some other source to describe a given data set.

MAPPAR: A subroutine to convert the ‘external’ parameters characterizing the potential energy and other radial functions into the ‘internal’ parameter array $\{\text{PV}(\mathbf{i})\}$ used by the fitting subroutine package **NLLSSRR**, and vice versa.

NLLSSRR: A general non-linear (or linear) least-squares fitting subroutine package that can also implement (when input parameter **IROUND** $\neq 0$) the “sequential rounding and refitting” procedure of Ref. [93].

DYIDPJ: The key user-supplied subroutine required by **NLLSSRR**, that for each datum returns the calculated value and partial derivatives with respect to all parameters of the model for the current set of trial parameters.

VGEN: Prior to each cycle of fit, this subroutine updates the arrays of values of the potential energy functions and of their partial derivatives w.r.t. their defining parameters.

Scalc when using the Pashov cubic spline approach to represent the MLR exponent-coefficient function $\beta(r)$, this routine returns values of the $S_n(x)$ partial derivative functions.

Lkcoef When using the Pashov cubic spline approach to represent the MLR exponent-coefficient function, on calling this function subroutine with a list of ‘ n ’ spline ordinate values, it returns the array of ‘rKL’ coefficients used for generating the ‘ n ’ $S_n(x)$ spline coefficient functions.

INITDD: At the beginning of each cycle of fit, this subroutine updates the sets of band constants employed for generating the trial eigenvalues required by the Schrödinger solver subroutine **SCHRQ**.

ALF: This (**A**utomatic **L**evel **F**inder) subroutine automatically determines the eigenvalues of all specified vibrational levels supported by a given potential energy curve.

SCHRQ: This is the core Schrödinger solver subroutine that provides the eigenvalue and radial wavefunctions required for the data simulation and partial derivative calculations. A number of features of this routine are described in the manual for program **LEVEL** [4, 78].

SCECOR: If the normal level-finding method fails, **SCECOR** uses semiclassical dE/dv estimates to attempt to hone in on the correct level energy .

CDJOEL: For a given vibrational level, this subroutine calculates the inertial rotational constant and the first six centrifugal distortion constants. These band constants are used to generate the trial eigenvalues required by **SCHRQ** for each datum.

DEDP: For each level energy associated with each datum, this routine generates and returns the eigenvalue and its partial derivatives with respect to the various parameters required for the least-squares fit.

DWDP: For each tunneling predissociation level width in the data set, this subroutine returns values of its partial derivatives with respect to the parameters of the Hamiltonian.

locateTP: For a predissociation level-width calculation, this routine determines the classical turning points required for the phase-integral calculations (to machine precision!).

PhaseIntegral: Evaluates the phase integrals required for calculating the tunneling predissociation level widths and their partial derivatives with respect to parameters of the Hamiltonian. ‘

DVIRDP: For each virial coefficient value in the data set, this subroutine generates the corresponding value implied by the current potential function, and its partial derivatives w.r.t. the various potential function parameters.

VPENp for virial coefficient calculations, generates and returns values of the potential function and its first two radial derivatives, and of all of their partial derivatives w.r.t. the potential parameters, at 8 quadrature points on each call. Currently only coded for the case of an MLR potential.

FUNUNC: On completion of a fit, this subroutine generates and writes to Channels 10–16

arrays of the values *and* the fully correlated 95% confidence uncertainties in the various radial functions determined from the fit.

DIFFSTATS: On completion of a fit, summarizes dimensionless RMS deviations for the entire data set on a band-by-band basis.

MKPREDICT: If the input parameter (see **READ #2**) **DATAFILE** is equal to 'MAKEPRED', this subroutine reads input to cause the program to prediction transitions for specified bands which are generated from by a complete fixed set of molecular-state parameters.
