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**A Computer Program for Fitting**  
**Diatomic Molecule Spectral Data**  
**to Potential Energy Functions**

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Chemical Physics Research Report



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**A Computer Program for Fitting Diatomic Molecule  
Spectral Data to Potential Energy Functions**

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This manual describes program DPOTFIT, which performs least-squares fits of diatomic molecule spectroscopic data consisting of any combination of microwave, infrared or electronic vibrational bands, fluorescence series, and tunneling predissociation level widths, involving one or more electronic states and one or more isotopologues, to determine analytic potential energy functions defining the observed levels of each state. Five main families of analytical potential functions are available in the current version of DPOTFIT: the Expanded Morse Oscillator (EMO), the Morse/Lennard-Jones (MLJ) potential, the Morse/Long-Range (MLR) potential, the Double Exponential/Long-Range (DELR) potential, and Šurkus' Generalized Potential Energy Function (GPEF), which incorporates a variety of polynomial potential forms. In addition, DPOTFIT allows the fit to determine atomic-mass-dependent Born-Oppenheimer breakdown functions, and singlet state  $\Lambda$ -doubling or  $^2\Sigma$  splitting radial strength functions for one or more of the electronic states.

DPOTFIT always reports both the 95% confidence limit uncertainty and the "sensitivity" of each fitted parameter; the latter indicates the number of significant digits which must be retained when rounding, in order to ensure predictions remain in full agreement with experiment. It will also, if requested, apply a "sequential rounding and refitting" procedure to yield a final parameter set defined by a minimum number of significant digits, while ensuring no significant loss of accuracy in the predictions yielded by those parameters. The program can also use a set of read-in constants to make predictions and calculate deviations  $[y_i^{\text{calc}} - y_i^{\text{obs}}]$  for any chosen input data set.

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# 1 General

In recent years, it has become increasingly common to analyze diatomic molecule spectroscopic data by performing “direct potential fits”, in which observed transition energies are compared with eigenvalue differences calculated from an effective radial Schrödinger equation based on some parameterized analytic potential energy function. This effective radial Hamiltonian may also include radial strength functions which characterize atomic-mass-dependent adiabatic and non-adiabatic Born-Oppenheimer breakdown (BOB) functions, and (if appropriate) also radial strength functions which account for  $\Lambda$ -doubling in singlet states or doublet splittings in  $^2\Sigma$  states. Partial derivatives of those calculated eigenvalue differences with respect to the parameters defining the potential energy and other radial functions are then used in least-squares fits to determine an optimized radial Hamiltonian for the system. The object of this report is to describe a robust and flexible computer program for performing this type of analysis, which can be downloaded freely, with a PDF file of this manual, from the www site <http://leroy.uwaterloo.ca/programs/>.

As in most direct-potential-fit (DPF) data analyses reported to date, the present code is based on the effective radial Schrödinger equation derived by Watson [1, 2], in which atomic-mass-dependent nonadiabatic contributions to the kinetic energy operator are incorporated into an effective “adiabatic” contribution to the electronic potential energy function and into the non-adiabatic BOB contribution to the effective centrifugal potential of the rotating molecule. Following the conventions of Refs. [3, 4, 5], the resulting effective radial Schrödinger equation for isotopologue  $\alpha$  of molecule  $A-B$  in a singlet electronic state with electronic angular momentum projection quantum number  $\Lambda$ , may be written as

$$\left\{ -\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dr^2} + \left[ V_{\text{ad}}^{(1)}(r) + \Delta V_{\text{ad}}^{(\alpha)}(r) \right] + \frac{[J(J+1) - \Lambda^2]\hbar^2}{2\mu_\alpha r^2} \left[ 1 + g^{(\alpha)}(r) \right] \right\} \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r) \quad (1)$$

Here,  $V_{\text{ad}}^{(1)}(r)$  is the total electronic internuclear potential for the selected reference isotopologue (labeled  $\alpha = 1$ ),  $\Delta V_{\text{ad}}^{(\alpha)}(r)$  is the *difference* between the effective adiabatic potentials for isotopologue- $\alpha$  and for the reference species ( $\alpha = 1$ ),  $g^{(\alpha)}(r)$  is the non-adiabatic centrifugal potential correction function for isotopologue- $\alpha$ , and  $\mu_\alpha$  is Watson’s [1] “charge-modified reduced mass”

$$\mu_\alpha = M_A^{(\alpha)} M_B^{(\alpha)} / \left( M_A^{(\alpha)} + M_B^{(\alpha)} - \text{CHARGE} \times m_e \right) \quad (2)$$

which takes account of the loss or gain of electrons on forming a molecular ion from neutral atoms of mass  $M_A^{(\alpha)}$  and  $M_B^{(\alpha)}$ , respectively, where  $m_e$  is the electron mass, and **CHARGE** is the net  $\pm$  (integer) charge on the molecule. Both  $\Delta V_{\text{ad}}^{(\alpha)}(r)$  and  $g^{(\alpha)}(r)$  are written as a sum of two terms, one for each component atom, whose magnitudes are inversely proportional to the mass of the particular atomic isotope [1, 2, 6, 3],

$$\Delta V_{\text{ad}}^{(\alpha)}(r) = \frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}} \tilde{S}_{\text{ad}}^A(r) + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}} \tilde{S}_{\text{ad}}^B(r) \quad (3)$$

$$g^{(\alpha)}(r) = \frac{M_A^{(1)}}{M_A^{(\alpha)}} \tilde{R}_{\text{na}}^A(r) + \frac{M_B^{(1)}}{M_B^{(\alpha)}} \tilde{R}_{\text{na}}^B(r) \quad (4)$$

where  $\Delta M_A^{(\alpha)} = M_A^{(\alpha)} - M_A^{(1)}$ , the difference between the atomic mass of atom  $A$  in isotopologue  $\alpha$  and in the reference isotopologue ( $\alpha = 1$ ), and the expressions used to represent the mass-independent  $\tilde{S}_{\text{ad}}^{A/B}(r)$  and  $\tilde{R}_{\text{na}}^{A/B}(r)$  radial functions are presented in §2.3. Straightforward extensions of Eq. (1) to take account of the  $e/f$   $\Lambda$ -doubling splittings, which occur for singlet states with  $\Lambda \neq 0$  [5], or doublet splittings for  $^2\Sigma$  states, are presented in §2.4 and 2.5.

## 2 The Parameterized Radial Hamiltonian

### 2.1 The Radial Expansion Variable

The program currently allows the potential energy function for a given electronic state to be represented by one of four families of analytic model potentials. Most of these functions are expressed in terms of a radial expansion variable of the form

$$y_p = y_p(r, r_{\text{ref}}) = \frac{r^p - r_{\text{ref}}^p}{r^p + r_{\text{ref}}^p} \quad (5)$$

in which  $p$  is a small positive integer ( $p = 1, 2, 3, \dots$ ) and  $r_{\text{ref}}$  is a reference distance chosen as the expansion centre for this variable. Most published work using this type of variable have defined  $r_{\text{ref}} = r_e$ , the equilibrium internuclear distance of the potential function  $V_{\text{ad}}^{(1)}(r)$ . However, that is not an essential constraint, and in some cases it may be useful to fix it at some point between  $r_e$  and the outer end of the data-sensitive region (unpublished work). The essential advantage associated with using this type of quantity as the expansion variable rather than, say,  $r$  itself or the traditional Dunham variable  $(r - r_e)/r_e$ , is that while  $y_p(r, r_{\text{ref}}) \propto (r - r_{\text{ref}})$  at distances near the expansion centre  $r_{\text{ref}}$ , it approaches  $-1$  and  $+1$  as  $r \rightarrow 0$  and  $r \rightarrow \infty$ , respectively. This means that a function defined as a finite power series in this variable will not have unphysical singularities, and for larger values of  $p$  will be increasingly strongly inhibited from having implausible spurious extrema at small or very large values of  $r$ .

The expansion variable of Eq. (5) is a special case of a more general expansion variable introduced by Šurkus *et al.* [7]. Those authors use it to represent the overall potential function as a power series in  $y_p(r)$ , and in that work the recommended value of  $p$  was based on the asymptotically dominant inverse-power term in the intermolecular potential for the state of interest. However, the present introduction of this variable is based on our finding [8, 4, 5, 9, 10, 11] that an expansion in powers of  $y_p(r)$  using some small integer power of  $p$  which is  $> 1$  (say,  $p = 2 - 4$ ) greatly reduces the propensity for the resulting expansion to “extrapolate badly” outside the radial interval to which the data are most sensitive. It is this same concern with attaining physically reasonable extrapolation behaviour which motivated the introduction of the option of setting  $r_{\text{ref}}$  at a (fixed) value other than the normal molecular expansion centre of  $r_e$ .

In any case, as described in §3, values of  $p$  and  $r_{\text{ref}}$  must be chosen by the program user, and specified in the main input data file.

### 2.2 The Potential Energy Function

#### 2.2.1 The Expanded Morse Oscillator (EMO) Potential Function

The first type of potential function form considered here is what we call the *Expanded Morse Oscillator* or EMO function [12], which has the form of a Morse potential [13] in which the exponent coefficient varies with distance. Two other functions of this type were introduced by Coxon and Hajigeorgiou (the “GMO” potential) [14] and by Dulick and co-workers (the “MMO” potential) [15], but because of its simpler form and better extrapolation behaviour, only the EMO form is considered here. An EMO (or EMO <sub>$p$</sub> ) potential has the form

$$V_{\text{EMO}}(r) = \mathfrak{D}_e \left[ 1 - e^{-\phi(r) \cdot (r - r_e)} \right]^2 \quad (6)$$

in which  $\mathfrak{D}_e$  is the well depth,  $r_e$  the equilibrium internuclear distance, and

$$\phi(r) = \phi_{\text{EMO}}(y_p(r, r_{\text{ref}})) = \sum_{i=0}^N \phi_i y_p(r, r_{\text{ref}})^i \quad (7)$$

As discussed in Refs. [8, 5, 9], for cases in which  $r_{\text{ref}} = r_e$ , setting  $p > 1$  in the definition of  $y_p(r, r_{\text{ref}})$  does not always resolve extrapolation problems at small  $r$ . However, such residual extrapolation problems

can usually be resolved by allowing the power series in Eq. (7) to have different orders for  $r > r_e$  and  $r \leq r_e$ :

$$\phi_{\text{EMO}}(y_p(r, r_{\text{ref}})) = \sum_{i=0}^{N_S} \phi_i y_p(r, r_{\text{ref}})^i \quad \text{for} \quad r \leq r_e \quad (8)$$

$$\phi_{\text{EMO}}(y_p(r, r_{\text{ref}})) = \sum_{i=0}^{N_L} \phi_i y_p(r, r_{\text{ref}})^i \quad \text{for} \quad r > r_e \quad (9)$$

Thus, use of different polynomial orders for  $\phi(r)$  at short ( $N_S$ ) and long range ( $N_L$ ) is another option of the program (normally  $N_S \leq N_L$ ). Note, however, that for powers  $i \leq \min\{N_S, N_L\}$ , the coefficients  $\phi_i$  of the ‘inner’ and ‘outer’ exponent expansions of Eqs. (8) and (9), are identical. A dramatic illustration of the utility of using mixed exponent polynomial orders ( $N_S \neq N_L$ ) is seen in Fig. 2 of Ref. [5].

The EMO (or EMO<sub>p</sub>) potential is a very flexible form which has been used successfully in a number of demanding data analyses involving both ‘normal’ single well potentials [12, 16, 10] and states whose potential functions have an additional ‘ripple’ [9]. However, the fact that  $[\mathfrak{D}_e - V_{\text{EMO}}(r)]$  dies off exponentially at large  $r$  makes it a less than ideal function for representing states for which the data extend fairly close to the dissociation limit. This problem stimulated the development of the next two potential forms discussed below.

### 2.2.2 The Morse/Lennard-Jones (MLJ) and Morse/Long-Range (MLR) Potentials

At long range, all intermolecular potential functions may be described as a sum of inverse-power terms, with the limiting long-range behaviour being

$$V(r) \simeq \mathfrak{D} - C_n/r^n - C_m/r^m - \dots \quad (10)$$

where the powers  $n$  and  $m$  are determined by the nature of the atoms to which the given molecular state dissociates [17, 18], and the coefficients  $C_n$  and  $C_m$  may often be calculated from theory. For molecular states for which the observed vibrational levels extend fairly close to the dissociation limit  $\mathfrak{D}$ , it is therefore desirable to use a potential form with the limiting behaviour of Eq. (10). This consideration led to the development of the *Morse/Lennard-Jones* potential function form [19, 20]:<sup>1</sup>

$$V_{\text{MLJ}}(r) = \mathfrak{D}_e \left[ 1 - \left( \frac{r_e}{r} \right)^n e^{-\phi(r) \cdot y_p(r, r_e)} \right]^2 \quad (11)$$

and more recently to the Morse/Long-Range (MLR) potential form [11, 57]

$$V_{\text{MLR}}(r) = \mathfrak{D}_e \left\{ 1 - \left( \frac{r_e}{r} \right)^n \left[ \frac{1 + R_{m,n}/r^{m-n}}{1 + R_{m,n}/r_e^{m-n}} \right] e^{-\phi(r) \cdot y_p(r, r_e)} \right\}^2 \quad (12)$$

in both of which  $\mathfrak{D}_e$  is the well depth,  $r_e$  the equilibrium internuclear distance, and the exponent coefficient  $\phi(r) = \phi_{\text{MLJ}}(r)$  or  $\phi_{\text{MLR}}(r)$  is a (fairly) slowly varying function of  $r$ . The MLJ form of Eq. (11) was introduced over a decade ago [19, 20] and has been used in a number of demanding data analyses [21, 22, 23, 24, 25, 26, 27, 28], while the MLR form of Eq. (12) is introduced for the first time here. However, it is clear that the latter collapses to the former if  $R_{m,n} = 0$ , so further details regarding both forms are presented below as properties of the MLR form. On the other hand, we retain the two distinct names to simplify the labeling when distinguishing between cases in which two versus one long-range inverse-power terms are incorporated into the potential form.

<sup>1</sup> In the early work this was called a *Modified Lennard-Jones oscillator*, but its algebraic form suggests that *Morse/Lennard-Jones* is probably a more appropriate title.

Since  $y_p(r) \rightarrow +1$  as  $r \rightarrow \infty$ , at long range the MLR function of Eq. (12) becomes

$$\begin{aligned} V_{\text{MLR}}(r) &\simeq \mathfrak{D}_e - \left\{ \frac{2\mathfrak{D}_e(r_e)^n e^{-\phi_\infty}}{1 + R_{m,n}/r_e^{m-n}} \right\} \left[ 1 + \frac{R_{m,n}}{r^{m-n}} \right] \frac{1}{r^n} \\ &\simeq \mathfrak{D}_e - \frac{C_n}{r^n} - \frac{C_m}{r^m} \end{aligned} \quad (13)$$

where  $\phi_\infty \equiv \lim_{r \rightarrow \infty} \phi_{\text{MLR}}(r) = \ln\{2\mathfrak{D}_e(r_e)^n / (C_n[1 + R_{m,n}/r_e^{m-n}])\}$ ,  $R_{m,n} \equiv C_m/C_n$ , and  $C_n = 2\mathfrak{D}_e(r_e)^n e^{-\phi_\infty} / [1 + R_{m,n}/r_e^{m-n}]$ . Thus, the values of the asymptotically dominant long-range potential coefficients  $C_n$  and  $C_m$ , and of  $\mathfrak{D}_e$  and  $r_e$ , define the limiting asymptotic value ( $\phi_\infty$ ) of the exponent coefficient  $\phi_{\text{MLR}}(r)$ . In order to use the MLR potential form, it is clearly necessary to know appropriate values for  $n$ ,  $m$ ,  $C_n$  and  $R_{m,n} = C_m/C_n$  for the species being investigated. However, if a realistic estimate of  $C_m$  is not available, one should use the MLJ (rather than the MLR) form, while if no realistic estimate of  $C_n$  is available, the MLJ form has no significant advantages over the simpler EMO function, and the latter will probably be more ‘robust’.

The algebraic form of Eq. (11) means that at sufficiently long range  $V_{\text{MLR}}(r)$  will always eventually collapse to Eq. (10), and the functional form of the exponent ‘coefficient’  $\phi(r)$  is designed to prevent the potential from having unphysical behaviour in the extrapolation interval between the data region and the asymptotic limit. Two possible forms of this exponent coefficient are allowed by DPOTFIT. One is a generalization of the original form proposed in Ref. [19, 20]

$$\phi(r) = \phi_{\text{MLJ}}^{\text{sw}}(y_p(r, r_{\text{ref}})) = f_{\text{sw}}(r) \sum_{i=0}^N \phi_i y_p(r, r_{\text{ref}})^i + [1 - f_{\text{sw}}(r)] \phi_\infty \quad (14)$$

in which the switching function  $f_{\text{sw}}(r) = [e^{(r-r_{\text{sw}})A_{\text{sw}}} + 1]^{-1}$  is defined by fixed parameters  $r_{\text{sw}}$  and  $A_{\text{sw}}$  which are selected manually to ensure that outside the data region,  $\phi_{\text{MLJ}}^{\text{sw}}(y_p(r, r_e)) \rightarrow \phi_\infty$  as smoothly as possible. For the case  $p=1$ , this model has been applied in a number of detailed data analyses [22–29]. This choice for  $\phi_{\text{MLR}}(r)$  is selected by using some appropriate *positive* value for parameter **Asw**, which is input through **READ #10**. Note, however, that for reasons discussed below, this switching-function based form for the exponent coefficient may only be used for an MLJ potential, which has one constrained long-range term, and not for the two-term MLR form.

An alternate approach (preferred by the authors) is to simply exploit the fact that for larger values of the power  $p$  ( $> 1$ ), the expansion variable  $y_p(r, r_{\text{ref}})$  approach its limiting value (of +1) ever more rapidly [8, 4, 5, 11, 57], so the expansion variable itself may effectively act as a switching function:

$$\phi(r) = \phi_{\text{MLR}}(y_p(r, r_e)) = [1 - y_p(r, r_{\text{ref}})] \sum_{i=0}^N \phi_i y_p(r, r_{\text{ref}})^i + y_p(r, r_{\text{ref}}) \phi_\infty \quad (15)$$

This approach obviates the need to select values for the parameters  $A_{\text{sw}}$  and  $r_{\text{sw}}$ , and an appropriate choice of the power  $p$  may be guided by the constraint discussed below and by consideration of the manner in which the potential function approaches its limiting long-range behaviour (see, e.g., Figs. 3 and 4 of Ref. [11]). This choice of exponent function is selected by setting the input data parameter **Asw**  $\leq 0$ .

One additional restriction associated with the use of the MLR form is a limitation on the value of  $p$  allowed for a given combination of  $n$  and  $m$ . The polynomial exponent expansion form of Eq. (15) means that at large  $r$ , the leading deviation from the limiting value ( $e^{-\phi_\infty}$ ) of the exponent term in the potential energy function expression is proportional to  $1/r^p$ . As a result, the limiting long-range behaviour of  $V_{\text{MLR}}(r)$  will only be defined by Eq. (13) if the power  $p$  defining the exponent variable satisfies the constraint  $p > (m - n)$ , where the values of  $n$  and  $m$  are defined by the nature of the particular physical system [17, 18]. This consideration is the reason that Eq. (14) cannot be used as the exponent function for

an MLR potential, since the leading deviation of  $\{\phi_{\text{MLJ}}^{\text{sw}}(r) y_p(r)\}$  from the limiting value  $\phi_\infty$  would not be well defined.

For an MLJ or MLR potential, DPOTFIT can treat the long-range potential coefficient  $C_n$ , and even the coefficient ratio  $R_{m,n} = C_m/C_n$ , as a free parameter to be determined by the fit. However, this option should only be used for the very rare cases in which data for a substantial number of levels lying very close to dissociation are present in the data set. In most cases this will not be true, and those parameters should be held fixed at the best available theoretical values. This more common case is illustrated by the analysis for ground-state  $\text{N}_2$  reported in Ref. [11], while an example of a case in which  $C_n$ , but not  $R_{m,n}$ , may be defined by the fit is seen in Ref. [57].

As was the case for the EMO potential, for either of  $\phi_{\text{MLJ}}^{\text{sw}}(r)$  or  $\phi_{\text{MLR}}(r)$ , the power series  $\sum_{i=1}^N \phi_i y_p(r, r_{\text{ref}})^i$  in Eq. (14) or (15) may have different upper bounds of  $N = N_S$  and  $N_L$ , respectively, for  $r \leq r_e$  and  $r > r_e$ .

### 2.2.3 The Double-Exponential/Long-Range (DELR) Model Potential

While the MLJ or MLR functions of Eqs. (11) and (12) can impose a desired attractive long-range inverse-power form on a potential, neither it nor the EMO form of Eq. (6) can describe a potential function with a barrier which protrudes above the potential asymptote at distances  $r > r_e$ . This shortcoming led to the introduction of the *double-exponential/long-range* (DELR) potential function form [8, 5]

$$V_{\text{DELR}}(r) = \left\{ A e^{-2\phi(r)\cdot(r-r_e)} - B e^{-\phi(r)\cdot(r-r_e)} + \mathfrak{D}_e \right\} + V_{\text{LR}}(r) \quad (16)$$

in which the exponent coefficient  $\phi(r)$  is defined as the same type of simple power series in  $y_p(r, r_{\text{ref}})$  used for the EMO<sub>p</sub> potential, Eqs. (7-9), with the same flexibility in allowing different power-series orders to be used for  $r \leq r_e$  and  $r > r_e$ .  $V_{\text{LR}}(r)$ , which may be attractive or repulsive, is a function chosen to represent the potential at larger values of  $r > r_e$ . The pre-exponential coefficients  $A$  and  $B$  are then defined in terms of the well depth  $\mathfrak{D}_e$  (relative to the potential asymptote) and the equilibrium distance  $r_e$  by the expressions

$$A = \mathfrak{D}_e + V_{\text{LR}}(r_e) + V'_{\text{LR}}(r_e)/\phi_0 \quad (17)$$

$$B = 2\mathfrak{D}_e + 2V_{\text{LR}}(r_e) + V'_{\text{LR}}(r_e)/\phi_0 \quad (18)$$

in which  $V'_{\text{LR}}(r_e) \equiv [dV_{\text{LR}}(r)/dr]_{r=r_e}$ . If  $V_{\text{LR}}(r) = 0$  the DELR potential becomes the EMO function of Eq. (6). However, other choices of  $V_{\text{LR}}(r)$  allow it to represent the outer wall of a potential function with a barrier [5], a multi-term attractive inverse-power long-range potential, or even the outer well of a double-minimum or shelf-state potential.

In the present version of DPOTFIT,  $V_{\text{LR}}(r)$  is assumed to be a sum of damped inverse-power terms

$$V_{\text{LR}}(r) = \sum_{m \geq n} D_m(r) C_m/r^m \quad (19)$$

in which  $C_m/r^m$  are the assumed-known leading terms defining the long-range potential for the state in question, and  $D_m(r)$  are ‘‘damping functions’’ which cut off those inverse-power terms at smaller distances. In the present version of the code there are two choices for the form of the damping functions:

$$D_m^{\text{TT}} = 1 - e^{-3.16 \rho_d r} \sum_{k=0}^m (3.16 \rho_d r)^k / k! \quad (20)$$

$$D_m^{\text{D}}(r) = [1 - \exp\{-3.97(\rho_d r)/m - 0.39(\rho_d r)^2/\sqrt{m}\}]^m \quad (21)$$

in which  $r$  has units Å and the dimensionless parameter  $\rho_d$  is a system-dependent scaling factor. The first of these functions is a form proposed by Tang and Toennies [29], and the second is one suggested by Douketis *et al.* [30]. The scaling parameter  $\rho_d$  was defined by Douketis *et al.* [30] in terms of ratios of the ionization potentials of the atoms forming the molecule relative to that of an H atom, but other values can be used too. Indeed, other damping function expressions [31] or entirely different types of expressions for  $V_{\text{LR}}(r)$  could equally well be used in the DELR type of potential form.

### 2.2.4 Šurkus' Generalized Potential Energy Function (GPEF)

The fourth family of potential functions is a generalization of the familiar Dunham polynomial potential [32] which Šurkus *et al.* [7] introduced and called the *Generalized Potential Energy Function* (GPEF). Using a modified (but exactly equivalent) expression for his expansion variable devised by Seto [33], the GPEF potential form is

$$V_{\text{GPEF}}(r) = c_0 z_p^2 \left[ 1 + \sum_{m=1}^N c_m z_p^m \right] \quad \text{where} \quad z_p = \frac{(r^p - r_e^p)}{(a_S r^p + b_S r_e^p)} \quad (22)$$

For appropriate choices of the (fixed) parameters  $a_S$  and  $b_S$ , this expansion takes on a number of familiar forms:

- Setting  $p=1$ ,  $a_S=0$  and  $b_S=1$  yields Dunham expansions [32].
- Setting  $p=1$ ,  $a_S=1$  and  $b_S=0$  yields Simons-Parr-Finlan (SPF) expansions [34].
- Setting  $p=1$ ,  $a_S=b_S=0.5$  yields the Ogilvie-Tipping (OT) potential expansion [35].
- Setting  $a_S=b_S=1$  yields the expansion variable of Eq. (5).
- Setting  $p=1$  and  $a_S=1$  yields the expansion variable used by Tiemann and coworkers [36, 37].
- When  $a_S \neq 0$  this function always asymptotically approaches a finite limit with a  $1/r^p$  functional behaviour. Thus, if appropriate constraints are applied to the coefficients, it can in principle be required to have the theoretically predicted limiting long-range behaviour of Eq. (10).

## 2.3 Born-Oppenheimer Breakdown Radial Functions

Following the discussion of Ref. [4], the radial strength functions characterizing the atom-dependent potential-energy and centrifugal BOB corrections of Eqs. (3) and (4) are expanded in the forms

$$\tilde{S}_{\text{ad}}^A(r) = [1 - y_\ell(r, r_e)] \sum_{i=0} u_i^A y_p(r, r_e)^i + u_\infty^A y_\ell(r, r_e) \quad (23)$$

$$\tilde{R}_{\text{na}}^A(r) = [1 - y_p(r, r_e)] \sum_{i=0} t_i^A y_p(r, r_e)^i + t_\infty^A y_p(r, r_e) \quad (24)$$

As for the various potential function definitions presented in §2.2, the integer  $p$  which defines the variable  $y_p(r, r_e)$  in the power series expansions of Eqs. (23) and (24) is selected by the user ( $p = 2 - 4$  are reasonable trial values) to ensure that these functions approach their asymptotic values without having spurious oscillations in the interval beyond the data-sensitive region (see Fig.3 of Ref. [4]). It may be convenient to use a common value of  $p$  for the potential energy and BOB radial function expansions, but DPOTFIT also allows a user to use independent values of  $p$  to define a different expansion variable for each type of radial function.

At long range, the factor  $[1 - y_\ell(r)] \simeq 2(r_e/r)^\ell$ . Thus, if the potential is represented by an MLJ, MLR, or DELR function, the power  $\ell$  in our expression for  $\tilde{S}_{\text{ad}}^N(r)$ , Eq. (23), should be set equal to the power  $n$  characterizing the limiting long-range behavior of the potential function itself; this is necessary to ensure that the potential functions for all isotopologues have the same inverse-power limiting long-range

functional behavior. This question is in principle independent of the choice of the power  $p$  used to define the expansion variable of the power series in Eq. (23). However, when an MLJ, MLR, or DELR function is used for the potential, it may be convenient also to set the power  $p$  used in Eq. (23) equal to  $\ell = n$  in order to yield an expression for  $\tilde{S}_{\text{ad}}^N(r)$  that involves only a single type of expansion variable [11]. Of course, since EMO functions do not have *any* inverse-power limiting long-range behavior, DPOTFIT sets  $\ell = p$  in Eq. (23) when an EMO function is used for the potential energy.

The structure of Eqs. (23) and (24) was designed to allow the asymptotic behaviour and equilibrium properties of these functions to be explicitly specified by the user or determined in a fit. In particular, the limiting asymptotic value of  $\tilde{S}_{\text{ad}}^A(r)$  is  $u_\infty^A$ . Hence, if the zero of energy is defined as ground-state atoms separated at  $r \sim \infty$ ,  $u_\infty^A \equiv 0$  for all electronic states which dissociate to yield a ground-state  $A$  atom, while for a state which dissociates to yield atom  $A$  in an excited electronic state,  $u_\infty^A$  is defined by the associated atomic isotope shifts [4]. In this case  $u_0^A(X)$  defines the difference between the well depths of the ground electronic state for different atom- $A$  isotopologues,  $\delta\mathfrak{D}_e^A(X) = (\Delta M_A^{(\alpha)}/M_A^{(\alpha)})u_0^A$ , while for excited electronic states this parameter defines the electronic isotope shift. Alternatively, if one wished to define the potential minimum of the ground state as the absolute zero of energy, one would fix  $u_0^A(X) = u_0^B(X) = 0$  and the values of  $u_\infty^A$  and  $u_\infty^B$  would define the isotopologue dependence of the ground state dissociation energy. A user of DPOTFIT may select one of these conventions by making an appropriate choice for fixing parameters in the input data file. For excited electronic states,  $u_0^A$  and  $u_0^B$  would of course determine the electronic isotope shift.

As discussed in Ref. [4], the limiting asymptotic value of the centrifugal BOB correction function  $\tilde{R}_{\text{na}}^A(r)$  should be  $t_\infty^A = 0$ , unless the species in question is a molecule ion which yields  $A^+$  or  $A^-$  upon dissociation, in which case  $q_\infty^A$  would have a small non-zero value. A convention commonly associated with use of the Watson radial Hamiltonian of Eq. (1) is to fix the leading power-series coefficient of Eq. (24) as  $t_0^A = 0$ . However, it has been pointed out [38, 39, 40] that the value of  $g^{(\alpha)}(r = r_e)$  is related to observable electronic properties of the molecule, so in some cases it may be desirable to fix  $t_0^A$  at some specific non-zero value, or even allow it to be varied in the fit. DPOTFIT allows a user to select any one of these options.

Although the BOB parameterization of Eqs. (1), (3) and (4) is preferred for a number of reasons [3], the formally equivalent alternate parameterization of Watson’s original paper [1] has sometimes been used by other research groups, and DPOTFIT allows a user to use either formulation. In the latter approach, the effective adiabatic potential for the reference isotopologue  $V_{\text{ad}}^{(1)}(r)$  is replaced by the “clamped nuclei” potential  $V_{\text{CN}}(r)$ ,

$$\left\{ -\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dr^2} + \left[ V_{\text{CN}}(r) + \Delta V_{\text{ad,W}}^{(\alpha)}(r) \right] + \frac{[J(J+1) - \Lambda^2]\hbar^2}{2\mu_\alpha r^2} \left[ 1 + g_{\text{W}}^{(\alpha)}(r) \right] \right\} \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r) \quad (25)$$

while the mass-independent radial functions in the BOB terms are scaled by the factors  $m_e/M_A^{(\alpha)}$  and  $m_e/M_B^{(\alpha)}$ , where  $m_e$  is the electron mass:

$$\Delta V_{\text{ad,W}}^{(\alpha)}(r) = \frac{m_e}{M_A^{(\alpha)}} \tilde{S}_{\text{ad,W}}^A(r) + \frac{m_e}{M_B^{(\alpha)}} \tilde{S}_{\text{ad,W}}^B(r) \quad (26)$$

$$g_{\text{W}}^{(\alpha)}(r) = \frac{m_e}{M_A^{(\alpha)}} \tilde{R}_{\text{na,W}}^A(r) + \frac{m_e}{M_B^{(\alpha)}} \tilde{R}_{\text{na,W}}^B(r) \quad (27)$$

Program DPOTFIT requires a user to select either this parameterization or that of Eqs. (3) and (4) by specifying an appropriate value of the parameter BOBCN in the input data file (see §6.2). In either case, the radial strength functions  $\tilde{S}_{\text{ad}}^{A/B}(r)$  and  $\tilde{R}_{\text{ad}}^{A/B}(r)$  are expanded as in Eqs. (23) and (24), but the magnitudes of the expansion parameters will differ by the factor  $M_A^{(\alpha)}/m_e$  for atom  $A$  and  $M_B^{(\alpha)}/m_e$  for atom  $B$ .

## 2.4 $\Lambda$ -Doubling Splittings for Singlet States

It was shown in Ref. [5] that for singlet states with  $\Lambda > 0$ , the effect of  $\Lambda$ -doubling splittings may be taken into account by inclusion of an additional term in the effective radial Hamiltonian, yielding

$$\left\{ -\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dr^2} + \left[ V_{\text{ad}}^{(1)}(r) + \Delta V_{\text{ad}}^{(\alpha)}(r) \right] + \frac{[J(J+1) - \Lambda^2]\hbar^2}{2\mu_\alpha r^2} \left[ 1 + g^{(\alpha)}(r) \right] + \text{sg}_\Lambda(e/f) \Delta V_\Lambda^{(\alpha)}(r) [J(J+1)]^\Lambda \right\} \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r) \quad (28)$$

in which  $\text{sg}_\Lambda(e/f)$  is a dimensionless numerical factor defined by the  $e/f$  parity of the level of interest (see below), and the  $\Lambda$ -doubling radial strength function is defined as<sup>2</sup>

$$\Delta V_\Lambda^{(\alpha)} = \left( \frac{\hbar^2}{2\mu_\alpha r^2} \right)^{2\Lambda} f_\Lambda(r) \quad (29)$$

Although we know of no rigorous arguments for specifying any particular limiting value for  $f_\Lambda(r)$  as  $r \rightarrow \infty$ , perturbation theory arguments suggest that  $f_\Lambda(r)$  should not change algebraic sign as a function of distance [5], and the ability to impose a specified asymptotic value of  $w_\infty^\Lambda = 0$  will sometimes be useful. It is therefore convenient to write it in the same form used for the BOB radial functions discussed above. The mass-independent radial function  $f_\Lambda(r)$  is therefore written as

$$f_\Lambda(r) = [1 - y_p(r, r_e)] \sum_{i=0} w_i^\Lambda y_p(r, r_e)^i + w_\infty^\Lambda y_p(r, r_e) \quad (30)$$

in which the expansion coefficients  $w_i^\Lambda$  have units  $1/(\text{cm}^{-1})^{2\Lambda-1}$ .<sup>3</sup> If  $w_\infty^\Lambda$  is treated as a free parameter,  $f_\Lambda(r)$  is effectively an unconstrained polynomial. In any case, the fact that  $y_p(r, r_e) \rightarrow 1$  as  $r \rightarrow \infty$  means that  $f_\Lambda(r)$  will necessarily approach a finite value in this limit, and hence that at long range  $\Delta V_\Lambda^{(\alpha)}(r) \rightarrow 0$  as  $1/r^{2\Lambda}$ .

If the dominant perturbing state giving rise to the  $\Lambda$ -doubling has  $^1\Sigma^+$  symmetry, then  $\text{sg}_\Lambda(e/f) = +1$  for  $e$ -parity levels and  $=0$  for  $f$ -parity levels. Similarly, if that perturbing state has  $^1\Sigma^-$  symmetry, then  $\text{sg}_\Lambda(e) = 0$  and  $\text{sg}_\Lambda(f) = -1$ . Alternately, if the identity of the dominant perturbing state is not known or one does not wish to make any *a priori* assumption about its symmetry,  $\text{sg}_\Lambda(e/f)$  is normally set to  $+\frac{1}{2}$  for  $e$ -parity levels and  $-\frac{1}{2}$  for  $f$  levels. DPOTFIT requires a user to select one of these conventions for  $\text{sg}_\Lambda(e/f)$  when fitting to or predicting  $\Lambda$ -doubling splittings for a given electronic state.

## 2.5 Doublet Splittings for $^2\Sigma$ States

In  $^2\Sigma$  state molecules, the quantum-number label  $J$  is normally used for the total angular momentum, which is the vector sum of the spin ( $\vec{S}$ ) and nuclear rotation ( $\vec{N}$ ) angular momenta,  $\vec{J} = \vec{N} + \vec{S}$ . The interaction of  $\vec{N}$  with the total electron spin angular momentum  $\vec{S}$  gives rise to a term in the Hamiltonian with the form  $\gamma \vec{N} \cdot \vec{S}$ , which causes shifts of the  $e$  and  $f$  parity components of a given rotational level which increase linearly with  $N$ . A derivation analogous to that used for  $\Lambda$ -doubling yields the following effective radial Hamiltonian for an electronic state with  $^2\Sigma$  symmetry:

$$\left\{ -\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dr^2} + \left[ V_{\text{ad}}^{(1)}(r) + \Delta V_{\text{ad}}^{(\alpha)}(r) \right] + \frac{N(N+1)\hbar^2}{2\mu_\alpha r^2} \left[ 1 + g^{(\alpha)}(r) \right] + \text{sg}_\Sigma(e/f; N) \Delta V_\Sigma^{(\alpha)}(r) \right\} \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r) \quad (31)$$

in which  $\text{sg}_\Sigma(e; N) = +N/2$ ,  $\text{sg}_\Sigma(f; N) = -(N+1)/2$  and

<sup>2</sup> Note that while the derivation of Ref. [5] addressed the case of  $\Lambda$ -doubling in  $\Pi$  states, the present implementation has been extended to the case of states for which  $\Lambda > 1$ .

<sup>3</sup> This assumes, of course, that the factor  $\hbar^2/(2\mu_\alpha r^2)$  has units  $\text{cm}^{-1}$ .

$$\Delta V_{\Sigma}^{(\alpha)} = \left( \frac{\hbar^2}{2\mu_{\alpha} r^2} \right) f_{\Sigma}(r) \quad (32)$$

and as for the case of  $\Lambda$  doubling, the radial function is expanded as

$$f_{\Sigma}(r) = [1 - y_p(r, r_e)] \sum_{i=0}^{\Sigma} w_i^{\Sigma} y_p(r, r_e)^i + w_{\infty}^{\Sigma} y_p(r, r_e) \quad (33)$$

in which the expansion coefficients  $w_i^{\Sigma}$  are dimensionless.

In spite of their different mass dependence, the formal structure of the treatments of  $\Lambda$ -doubling  $\{e/f\}$  splittings and  ${}^2\Sigma$  state  $\{e/f\}$  splittings are quite similar. As a result, the control parameters governing this treatment are input to DPOTFIT through a common set of **READ** statements, and an integer formally associated with the definition of the value of  $\Lambda$  is used to distinguish between the two cases (see §4).

### 3 Solving the Radial Schrödinger Equation

The central computational activity of program DPOTFIT is solving the effective radial Schrödinger equation of Eq. (1), (25), (28) or (31) many hundreds or thousands or tens of thousands of times. In particular, in each cycle of the iterative non-linear fit, it must solve one of these equations to determine the upper- and lower-state eigenvalue of every transition in the data set with a numerical accuracy at least an order of magnitude better than the experimental uncertainty of that datum. In each case, it must also accurately determine the associated eigenfunctions, and use them to generate the partial derivatives of those eigenvalues with respect to each of the parameters in the model Hamiltonian for that electronic state

$$\frac{\partial E_{v,J}}{\partial p_j} = \left\langle \psi_{v,J} \left| \frac{\partial \hat{H}}{\partial p_j} \right| \psi_{v,J}(r) \right\rangle \quad (34)$$

These quantities are required to provide the partial derivatives of each datum with respect to all parameters of the model required by the least-squares fitting procedure.

DPOTFIT performs these eigenvalue/eigenfunction calculations using a numerical propagation algorithm based on the famous Cooley-Cashion-Zare subroutines **SCHR** [41, 42, 43, 44, 45]. The present version of those routines incorporates several unique features, such as the ability to automatically locate and calculate both the widths of quasibound (or tunneling-predissociation) levels and the partial derivatives of those widths with respect to potential function parameters [46, 47, 5, 48]. This last capability is required for cases in which measured tunneling predissociation level widths are included in the experimental data set being analyzed [5]. Most details and features of the Schrödinger-solver routine **SCHRQ** used by DPOTFIT are described in the manual for program **LEVEL** [48], and need not be discussed here. However, it is important to point out the role and significance of three parameters which control the numerical propagation procedure, and must be specified in the input data file.

The accuracy of the eigenfunctions and eigenvalues obtained using subroutine **SCHRQ** is largely determined by the size of the (fixed) radial mesh **RH** (read on line #9 of the data file) used in the numerical integration of Eq. (1), (25), (28) or (31). For potentials that are not too steep or too sharply curved, adequate accuracy is usually obtained using an **RH** value which yields a minimum of 20 to 30 mesh points between adjacent wavefunction nodes in the classically allowed region. An appropriate mesh size (in units Å) may be estimated using the particle-in-a-box expression

$$\text{RH} = \pi / \left( \text{NPN} \times [\mu \times \max\{E - V(r)\} / 16.85762920]^{1/2} \right) \quad (35)$$

in which `NPN` is the selected minimum number of mesh points per wavefunction node (say 30),  $\max\{E - V(r)\}$  is the maximum of the local kinetic energy (in  $\text{cm}^{-1}$ ) for the levels under consideration (in general it is  $\lesssim$  the potential well depth  $\mathfrak{D}_e$ ), the reduced mass  $\mu$  is in amu, and the numerical factor is  $\hbar^2/2$  expressed in “spectroscopists’ units” ( $\text{cm}^{-1}$ ,  $\text{\AA}$  and amu). A value of `NPN` which is too small yields results which are unreliable, while a value which is too large may require excessive computational effort or may require array dimensions to be made inconveniently large. Note that while Eq. (35) is a useful guide, a careful user *should always* try different `RH` values in order to ensure that the calculation yields results of the accuracy desired for their particular application.

The numerical integration is performed on the interval from `RMIN` to `RMAX` (see `READ` statement #9) using the Numerov algorithm [41, 49]. These bounds must lie sufficiently far into the inner and outer classically-forbidden regions (where  $V_{\text{eff}}(r) > E_{v,J}$ ) that the wavefunction has decayed by several orders of magnitude relative to its amplitude in the classically-allowed region. The present version of the code prints warning messages if this decay is not by a factor of at least  $10^{-9}$ ; if such warnings are printed, a smaller `RMIN` or larger `RMAX` value should be used to ensure that the desired accuracy is achieved. On the other hand, if `RMIN` or `RMAX` lie far into the classically-forbidden regions and  $[V_J(R) - E]$  becomes extremely large, the integration algorithm can become numerically unstable for the given mesh size. For realistic diatomic molecule potential curves, this situation is most likely to occur near `RMIN`. If it does, a warning message is printed and the beginning of the integration range is automatically shifted outward until the problem disappears. However, use of a slightly larger value of `RMIN` will cause these warning messages to disappear and (marginally) reduce the computational effort. For most diatomic molecules, a reasonable value of `RMIN` is ca. 0.5 – 0.8 times the smallest inner turning point for the levels involved in the data set, but for hydrides or other species of low reduced mass, even smaller values may be required.

The program internally defines the upper bound on the range of numerical integration `RMAX` as the smaller of the read-in value, or the largest distance consistent with the specified mesh and the internally-defined (see Section 4) potential energy array dimension. As with `RMIN`, the choice of `RMAX` is not critical as long as (for truly bound states) the wave function has decayed to an amplitude much smaller than that in the classically allowed region, and the same amplitude decay test of  $10^{-9}$  is used for it. However, due to the anharmonicity of typical molecular potential curves, the requisite values of `RMAX` are much larger for highly excited vibrational levels than for those lying near the potential minimum. Moreover, for quasibound levels, `RMAX` should lie in the classically-allowed region beyond the outermost potential function turning point for the level in question.

## 4 Fitting Strategies

### 4.1 Initial Trial Parameters

In a DPF treatment of experimental data, the observables – the transition energies or tunneling lifetimes – are not linear functions of the parameters of the radial functions characterizing the effective Hamiltonian. As in any non-linear least-squares procedure, it is essential to have a set of realistic initial trial values of all fitting parameters. For BOB radial functions and  $\Lambda$ -doubling or  $^2\Sigma$ -splitting radial functions, this presents little practical difficulty. All of those functions are relatively weak, and it has been found that if their parameters are initially all set to zero or (for the  $w_0$  coefficient for  $\Lambda$ -doubling or  $^2\Sigma$  splitting) given some plausible small initial trial value, and then let go free, the fits are stable and well-behaved. However, one would not normally try to obtain an accurate final determination of those supplementary radial strength functions until a realistic description of the potential energy function for the reference isotopologue  $V_{\text{ad}}^{(1)}(r)$  is obtained.

For the potential energy function  $V_{\text{ad}}^{(1)}(r)$  (or  $V_{\text{CN}}(r)$ ) itself, the problem of determining initial trial parameters is somewhat more challenging, and a number of strategies have been used. From a conventional preliminary analysis of the data, it is usually fairly straightforward to obtain a good estimate of the potential minimum position  $r_e$ , which is a central parameter in all of our model potentials. It is usually also not difficult to obtain a plausible initial estimate of the well depth  $\mathfrak{D}_e$ , which is a central parameter in the EMO, MLJ, MLR and DELR potential models. However, experience suggests that this initial trial value of  $\mathfrak{D}_e$  should then be held fixed until a good fit to some associated set of exponent expansion coefficients  $\{\phi_i\}$  is obtained.

The most generally useful method of generating a realistic set of initial trial  $\phi_i$  values is to fit a set of approximate potential function points generated in some other manner to the chosen potential form. For example, one might use a conventional “parameter-fit” analysis of the data set of interest to determine analytic level energy expressions such as Dunham expansions or near-dissociation expansions [50], and then use the resulting functions to generate a pointwise RKR potential for that state [51]. Alternately, one may use available *ab initio* predictions to define such a preliminary potential, or (say, for a double minimum potential) a combination of RKR and *ab initio* points. A companion program named PHIFIT has been developed for fitting such input potential arrays to determine realistic estimates of the exponent expansion coefficients  $\{\phi_i\}$  of an EMO, MLR or DELR potential, or of the power-series coefficients  $\{c_i\}$  of a GPEF potential.

It is very important to realize that direct potential fits of the type performed by DPOTFIT are *very* non-linear, and care must be taken to prevent them from diverging. To that end, when initial trial values of each of the fitting parameters are read in, DPOTFIT requires the user to specify, one-by-one, whether each parameter is to be held fixed or varied in that particular fit. This allows a user to initially release a small number of parameters (say,  $r_e$ ,  $\phi_0$  and  $\phi_1$ ) while holding all others fixed, and then when preliminary optimized values of those parameters are determined, they may be used to replace the original trial values in the input data file, and a new fit may be performed which allows additional parameters (say  $\phi_2$  and  $\phi_3$ ) also to be free. This sort of stepwise procedure is often necessary if the fit to determine the main supporting potential is to be stable. However, once a converged value of  $r_e$  and set of  $\{\phi_i\}$  parameters are determined, the basic description of the system is usually sufficiently well defined that all BOB and/or  $\Lambda$ -doubling or  $^2\Sigma$  splitting parameters may be released at the same time.

As an alternative to the use of a code such as PHIFIT to determine a complete set of trial  $\{\phi_i\}$  parameters in a single step, one may also proceed in a stepwise manner by initially considering only a small fraction of the data and a small number of parameters, and then progressively extending the range until the whole data set is included. In particular, DPOTFIT allows a user to limit the range of data to be utilized in a given fit without having to edit the data file. Hence, it would be quite straightforward to restrict the vibrational range of the data to be considered to (say)  $v = 0 - 3$  and fit to a potential model which had only (say)  $r_e$ ,  $\phi_0$  and  $\phi_1$  as free parameters, with all higher-order  $\phi_i$  (for  $i \geq 2$ ) fixed at zero. Once a converged fit to that restricted data set was obtained, the vibrational range of data and number of  $\phi_i$  parameters could be extended, using initial trial values of zero for the added higher-order coefficients  $\phi_i$ , and the process repeated until the whole data set is included.

## 4.2 Multi-State Fits

If one is performing a simultaneous fit to data involving more than one electronic state, it may be necessary to utilize a stepwise procedure – initially optimizing parameters for one state at a time – before proceeding to the final step in which all parameters are simultaneously freed. This tends to be necessary because a relatively poor initial representation of one state can inhibit one’s ability to determine an optimum

representation for another. In some cases, this might be a simple matter of first performing a one-state fit to the pure rotational and vibration-rotation data for one state, then holding those parameters fixed while performing a two-state fit which includes the electronic transition data and varies only the parameters of the second state. When a good model is determined for the second state, the two-state fit would then be repeated while allowing the parameters for both state to be fitted simultaneously. However, the electronic transition data which yields information about the excited state(s) is often also the only source of information about the upper levels of the initial (usually ground) state, so it cannot be ignored when attempting to obtain a good description of that first state.

The best way to treat this problem is to first fit to *all* of the data (electronic and other) involving the first (usually ground) state, while representing the levels of all other electronic states by individual term values. While a relatively large number of parameters tend to be required for such fits, use of this approach means that the determination of parameters for the first state is not affected by the models chosen to represent the other states. In the companion ‘parameter-fit’ program DPARFIT [50], such term-value fits for selected (usually excited) electronic states can be accomplished directly, simply by setting a parameter in the input data file. However, this has not yet been implemented in DPOTFIT, and a somewhat more circuitous approach must be followed. In particular, the vibrational band data associated with the excited electronic state(s) must be converted into ‘fluorescence series’ format, in which all transitions associated with a particular  $(v, J, p)$  level of each excited state are treated as a fluorescence series. A one-state fit may then be performed in which the fitted fluorescence series origins are the term values of the excited states. A simple FORTRAN program BAND2FS.f for converting vibrational-band formatted electronic transition data into fluorescence-series format may be downloaded from the DPOTFIT link on the www page <http://leroy.uwaterloo.ca/programs/>.

Once a ‘good’ fit is obtained to a model for the potential energy and other radial functions describing the first electronic state, the parameters describing that state may be held fixed in a two-state fit to determine an optimum model for the second electronic state to be considered. When such a model is determined, the parameters of both states should be fitted simultaneously. This stepwise procedure may then continue until all of the data are being fitted simultaneously to models for all of the coupled electronic states involved in the data set.

## 5 Using DPOTFIT

### 5.1 Units, Uncertainties and Parameter Rounding

The units of mass, length and energy used throughout this program, and assumed for all input data, are u (amu), Å and  $\text{cm}^{-1}$ , respectively. The values of the physical constants occur in the program as the single factor  $\hbar^2/(2\mu) = 16.85762920/\mu [\text{cm}^{-1} \text{Å}^2]$  (where  $\mu$  is in amu) in the effective radial Schrödinger equation of Eq. (1), (25), (28) or (31). This numerical constant is based on the 2002 CODATA recommended physical constant values [52], while the atomic isotope masses stored in subroutine MASSES were taken from the compilation of Ref. [53].

Because DPOTFIT performs weighted least-squares fits, each input datum must be accompanied by an estimated uncertainty  $u_i$  in the same units ( $\text{cm}^{-1}$ ) as the observable. The quality of a fit of an  $M$ -parameter model to  $N$  input data which yields the predicted quantities  $\{y_i^{\text{calc}}\}$  is indicated by the value of the dimensionless root mean square deviation

$$\text{DRMSD} \equiv \overline{dd} = \left\{ \frac{1}{N} \sum_{i=1}^N \left[ \frac{y_i^{\text{calc}} - y_i^{\text{obs}}}{u_i} \right]^2 \right\}^{1/2} \quad (36)$$

or by the dimensionless standard deviation  $\text{DSE} \equiv \bar{\sigma}_f = \overline{dd} \sqrt{N/(N-M)}$ . This data weighting allows

observables with very different magnitudes and very different absolute uncertainties (e.g., microwave *vs.* electronic fluorescence data) to be treated concurrently in an appropriate balanced manner. A “good” fit is one which yields DSE and  $\overline{dd}$  values close to unity, since a  $\overline{dd}$  value of (say) 3.7 would mean that on average the predictions of the model disagree with the input data by 3.7 times the estimated experimental uncertainties. However, that converged values larger than unity may also reflect the fact that the experimental uncertainties assigned to the data were too small.

In addition to reporting the 95% confidence limit (approximately ‘two-sigma’) uncertainty in each fitted parameter, DPOTFIT follows the approach of Ref. [54] by always listing also the associated “parameter sensitivity” (identified as PS in the output). This quantity is defined (see Eq. (4) of Ref. [54]) as the magnitude of the largest change in the given parameter whose effect on the predictions of the model could increase  $\bar{\sigma}_f$  by a maximum of  $(0.1/M)\bar{\sigma}_f$ . The parameter sensitivity indicates the degree to which any particular fitted parameter value may be rounded off while having no significant effect (within the data uncertainties) on the ability of the resulting parameter set to accurately predict the input data. For the illustrative cases considered in Ref. [54], to three significant digits, rounding off all parameters at the first significant digit of their sensitivity had no significant effect on the values of  $\bar{\sigma}_f$  or  $\overline{dd}$ .

Another feature of DPOTFIT is its implementation (via subroutine NLLSSRR) of the automated “sequential rounding and refitting” (SRR) procedure of Ref. [54], which minimizes the total number of significant digits required to represent the overall parameter set with no (significant) loss of accuracy. Application of this procedure involves a substantial increase (by up to a factor of  $M/2$ ) in computational effort relative to that required for an ordinary fit, so it is usually not desirable to use it in the many preliminary trial fits involved in any detailed data analysis. Application of this procedure is turned on or off by the value of the flag IROUND which is set by the user in the input data file. One would normally turn this flag off (set IROUND=0) for preliminary analyses, and only turn it on when one wishes to generate a final parameter set to report and distribute. As discussed in Ref. [54], in most cases setting IROUND =  $\pm 1$  yields a maximum degree of rounding without significant loss of precision, but in some cases it may be necessary to set  $|\text{IROUND}| > 1$  (see §6.2).

One final choice regarding the manner in which the least-squares fits are performed is whether or not to perform “robust” fits. As described in Ref. [55] and references therein, *robust* least-squares fits attempt to minimize the effect of data “outliers”, which are defined as observations which yield anomalously large discrepancies with the model. When this choice is invoked, DPOTFIT adopts the approach of Ref. [55] and replaces the normal least-squares data weights  $w_i = 1/(u_i)^2$  by the ‘robust’ weights  $w_i^{\text{rob}} = 1/[(u_i)^2 + (y_i^{\text{calc}} - y_i^{\text{obs}})^2/3]$ . Because the latter depend on the then-current degree of agreement of the data with the model, fits of this type must be repeated iteratively, with the parameter values and the weights being updated in each cycle until self-consistency is achieved. As a result, *robust* fits require substantially more computer time than do normal fits. Moreover, the fact that *robust* weighting reduces the effect of large  $[y_i^{\text{calc}} - y_i^{\text{obs}}]$  values on DSE and  $\overline{dd}$  makes it more difficult to interpret differences in those quantities obtained from fits to different versions of a model, and it may tend to obscure the presence of systematic discrepancies which indicate shortcomings of the model, rather than of the data. The authors’ limited experience with this option indicates that it can also facilitate examining data sets both for local irregularities and for systematic discrepancies from a model, when examining the  $[y_i^{\text{calc}} - y_i^{\text{obs}}]$  results in the channel-8 output file.

## 5.2 Array Dimensions, Input/Output Conventions, and Program Execution

The operation of program DPOTFIT involves the use of a number of moderately large multi-dimensional integer and real-number arrays whose size is specified at the time the program is compiled. If those arrays

are unnecessarily large, it could slow or hinder computations on some computers. The current version of DPOTFIT assumes (but does not require; it works with F'90 compilers too) the use of a Fortran-77 compiler which does not allow run-time array dimensioning. Thus, while one does not wish to have to recompile the code case-by-case, setting those array dimensions at modest (but adequate) values should facilitate computations by minimizing computer memory requirements. Parameters which place upper bounds on the sizes of the large arrays are set by `PARAMETER` statements contained in the utility routine `arrsizes.h`, which is supplied with the program. If this file resides in the same directory as the source code when the program is being compiled, FORTRAN compilers will automatically incorporate it into relevant subroutines at compilation time through FORTRAN 'include' statements in the code. Parameters defined in this way include the maximum number of isotopologues being considered `NISTPMX`, the maximum number of electronic states `NSTATEMX`, the maximum number of fitting parameters `NPARMX`, the maximum number of data `NDATAMX`, the maximum number of observed vibrational levels in any of the electronic states considered `NVIBMX`, and the maximum dimension for the radial arrays used to store the potential energy and related functions `NPNTMX`. A user should edit file `arrsizes.h` before compiling the code, and give these parameters values appropriate for the types of systems they will be considering.

DPOTFIT reads two separate input data files. The first one contains the experimental data being fitted to; its name is read in line #2 of the second data file. This second data file is the 'standard input' file read on channel 5; it contains the input parameters and control variables which characterize the problem and specify what type of fit is to be performed. The structure of these data files, and the definitions of and options for the various input quantities are presented below in § 6.

The program writes standard output to Channel-6 and supplementary output files to a selection of channels 7 – 16. The output to Channel-X is written to the file `WRITFILE.X`, where `WRITFILE` is a user-specified output filename which is specified in line #3 of the input data file.

**Channel-6 output** summarizes the input data, describes the nature of the fit being performed, reports the results of the fit, lists fitted parameters, their sensitivities, and their (95% confidence limit, or 'two-sigma') uncertainties, and presents a summary of the  $[y_i^{\text{calc}} - y_i^{\text{obs}}]$  results.

**Channel-7 output** contains values of the band constants for all levels of all isotopologues of all states involved in the analysis, as generated from the final results of the fit.

**Channel-8 output** consists of a full listing of the  $\{[y_i^{\text{calc}} - y_i^{\text{obs}}]\}$  and  $\{[y_i^{\text{calc}} - y_i^{\text{obs}}]/u_i\}$  values for all data used in the fit.

**Channels 10–16 output** files contain arrays of values of the various radial functions associated with the model Hamiltonian, and the associated 95% confidence limit uncertainties.

**Channel-10** contains the effective radial potential for the reference isotopologue  $V_{\text{ad}}^{(1)}(r)$  (or  $V_{\text{CN}}(r)$ ),

**Channel-11** the radial exponent function  $\phi(r)$  for the EMO, MLJ, MLR or DELR model potentials,

**Channels 12 & 13** the adiabatic BOB radial strength functions  $\tilde{S}_{\text{ad}}^A(r)$  and  $\tilde{S}_{\text{ad}}^B(r)$ ,

**Channels 14 & 15** the non-adiabatic BOB radial strength functions  $\tilde{R}_{\text{na}}^A(r)$  and  $\tilde{R}_{\text{na}}^B(r)$ , and

**Channel 16** the radial strength function associated with  $\Lambda$ -doubling or  ${}^2\Sigma$  level splittings,  $f_\Lambda(r)$  or  $f_\Sigma(r)$ , as appropriate.

Those executing DPOTFIT in a UNIX or LINUX operating system environment may find it convenient to do so using a shell named (say) `rdpot`, such as that shown below, which may be stored in the system 'bin' directory or the user's 'bin' directory:

```

#!/bin/sh
# UNIX shell 'rdpot' to execute the compiled version of program DPotFit named
# dpot.x, which is stored in the user directory /userpath/. The channel-5
# input data file $1.5 and the output files WRITFILE.6, WRITFILE.7, ...
# etc., will be in the same directory.
#
time /userpath/dpar.x < $1.5
if [ -e MAKEPRED ]; then
    rm MAKEPRED
fi

```

in which `userpath` is a path specifying the location of the executable file `dpot.x` on the user's computer, and `MAKEPRED` is defined below. This shell allows the program to be executed with the simple command:

```
rdpot filename
```

in which `filename.5` is the data file containing the instructions regarding the type of fit to be performed; `filename` may be any name chosen by the user, but it is usually convenient if it has a name which identifies the particular case. If this file does not reside in the current directory, this name must, of course, also include the relative path.

### 5.3 Generating Sets of Predicted Transition Energies

DPotFit may also be used to generate a set of data predictions  $\{y_i^{\text{calc}}\}$  from a given fixed set of input parameters. This option is invoked by setting the value of the input variable in `READ #2`, which is normally the name of the file containing the experimental data, to be `MAKEPRED`. In this case the program will use `READ #32` in the channel-5 instruction data file to read specifications and selection rules for bands for which the user wishes to generate predictions. The resulting predictions are written in the normal channel-8 output format to file `filename.8`, and in 'data input' format to file `filename.4`.

## 6 Data File Structure and Input Parameter Definitions

### 6.1 The Experimental Data File

The experimental data are read from a file whose name is specified in the regular channel-5 input data file (see `READ #2`). The data must be collected into separate vibrational bands (or fluorescence series, or sets of photo-association spectroscopy (PAS) binding energies, or tunneling predissociation level widths), each characterized by the upper- and lower-state vibrational quantum numbers  $v' = \text{VP}$  and  $v'' = \text{VPP}$ , respectively, by the two-alphameric-character labels `LALBP` and `LALPP` (enclosed between single quotes; e.g. 'X0') chosen to label those particular upper and lower electronic states, and by the (integer) mass numbers `MN1` and `MN2` of the atoms forming that particular isotopologue. The electronic state labels must correspond to the names used to identify the different electronic states in 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 `JP < 0` signals the end of the data for this band 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), LALBP, LALPP, MN1, MN2

```

```

        IF(VP(IBAND.LT.0) GOTO 20
#2   5 READ(4,*)  JP(COUNT), EFP(COUNT), JPP(COUNT), EFPP(COUNT),
      1          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 input parameter `LABLP = 'FS'` 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 emitting level’s vibration-rotation quantum numbers  $v'$  and  $J'$ , respectively, and the transition labels `JP` and `JPP` (`READ #2` above) as the final (lower) state vibration-rotation quantum numbers  $v''$  and  $J''$ , respectively. The parity label parameters `EFP` and `EFPP` retain their usual significance, 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. Moreover, program operation is not affected if the same values of these quantities are used for several different series; it just means that the different fitted origins for those several fluorescence series will have the same label in the channel-6 output file.

Another distinct data type which can be input using this same band-type data structure is a set of individual-level binding energies, such as those yielded by PAS. In this case the nature of this data-group is identified by making the input upper-electronic-state band label `LABLP = 'PA'`. 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 which are ignored by the analysis.

PA-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 if EMO, MLR, MLJ or DELR functions are used for the potential energy function. If this is not the case, DPOTFIT simply treats a PA-type data-group as an ordinary fluorescence series.

A final additional type of experimental data which the program can use is a set of tunneling predissociation level widths. Again, the band-type input data structure is retained, but in this case the input parameter value `LABLP = 'WI'` identifies this data-group as a set of FWHM level widths  $\Gamma(v, J)$  for levels of electronic state `LABLP`, and signals that the band parameters `VP` & `VPP` and the transition label `EFP` are dummy variables, while the input parameter `JP` is actually the vibrational quantum number  $v$ , `JPP` the rotational quantum number  $J$ , and `EFPP` the parity label of the predissociating level, while `FREQ` is its full width at half maximum  $\Gamma(v, J)$  and `UFREQ` its uncertainty (both in  $\text{cm}^{-1}$ ).

As an illustration of this data file structure, the listing below presents fragments of an experimental data file used for an analysis of the chemiluminescence spectrum of  $^{138}\text{BaO}$ ,  $^{137}\text{BaO}$ ,  $^{136}\text{BaO}$ ,  $^{135}\text{BaO}$ . In addition to the new electronic chemiluminescence spectra reported in that work [56], the analysis used MW and IR data and two older optical-optical double resonance (OODR) fluorescence series taken from the literature. Although the OODR data had uncertainties two orders of magnitude larger than the chemiluminescence data (0.5 *vs.* 0.005  $\text{cm}^{-1}$ ), they were included because of their much greater vibrational range ( $v''=0-34$  *vs.* 0-20). Note that text beginning at the “%” sign on a line of the input data file are comments that

are ignored by the program.

```

 7 7 'A0' 'A0' 137 16 % v' v" LABLP LABLPP MN1 MN2
2 1 1 1 0.998277282 0.000050035 % J' p' J" p" FREQ UFREQ
-1 1 -1 1 -1.1 -1.1 % Microwave data from the literature
 7 7 'A0' 'A0' 137 16 % incorporated into our analysis
3 1 2 1 1.497415922 0.000050035
-1 1 -1 1 -1.1 -1.1

 3 2 'X0' 'X0' 137 16 % v' v" LABLP LABLPP MN1 MN2
 7 1 6 1 661.99806 0.01 % J' p' J" p" FREQ UFREQ
25 1 24 1 672.27464 0.01 % Infrared data from the literature
39 1 38 1 679.59709 0.01 % incorporated into our analysis.
14 1 15 1 648.17157 0.01
19 1 20 1 644.84254 0.01
24 1 25 1 641.44710 0.01
-1 1 -1 1 -1.1 -1.1

 0 6 'A0' 'X0' 135 16 % v' v" LABLP LABLPP MN1 MN2
 47 1 48 1 12653.22414 0.005 % J' p' J" p" FREQ UFREQ
 43 1 44 1 12672.26623 0.005 % A vibrational band from the new
 35 1 36 1 12705.94541 0.005 % chemiluminescence spectrum.
 33 1 34 1 12713.45841 0.005
 32 1 33 1 12717.06675 0.005
 30 1 31 1 12724.03656 0.005
 28 1 29 1 12730.63128 0.005
 25 1 26 1 12739.85293 0.005
 24 1 25 1 12742.74558 0.005
 20 1 21 1 12753.38391 0.005
 19 1 20 1 12755.81818 0.005
 13 1 14 1 12768.52559 0.005
 7 1 8 1 12777.95445 0.005
-1 1 -1 1 -1.0 -1.0

15 50 'FS' 'X0' 138 16 % v' J' LABLP LABLPP MN1 MN2
 0 1 49 1 37678.6 5.0 % v" p' J" p" FREQ UFREQ
 1 1 49 1 37018.0 1.7 % OODR fluorescence series R lines
 2 1 49 1 36359.8 1.7 % from Field [JCP 63,3228 (1975)].
 3 1 49 1 35706.8 1.7
.... omit 25 intermediate lines ...
32 1 49 1 18705.0 2.3
33 1 49 1 18194.3 1.5
34 1 49 1 17688.2 1.2
-1 1 -1 1 -1.1 -1.1

```

## 6.2 The Channel-5 Input File: Defining the Problem and Specifying the Fit

The logical structure and read statements governing the channel-5 data input describing the system to be treated, specifying the type of fit to be carried out, and inputting 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
#2 READ(5,*) DATAFILE
#3 READ(5,*) WRITFILE
#4 READ(5,*) UCUTOFF,NOWIDTHS,IROUND,ROBUST,LPRINT,PRINP
*****
* Loop over isotopologues
*****
DO 10 IISTP= 1,NISTP
#5 READ(5,*) MN(1,IISTP),MN(2,IISTP)
ENDDO
*****
* End loop over isotopologues
*****
* Begin loop over electronic states
*****
DO 20 ISTATE=1,NSTATES
#6 READ(5,*) SLABL(ISTATE), IOMEG(ISTATE), VMIN(ISTATE), VMAX(ISTATE),
1 JTRUNC(ISTATE), EFSEL(ISTATE)
#7 READ(5,*) PSEL(ISTATE), VLIM(ISTATE), BOBCN(ISTATE), OSEL(ISTATE)
#8 READ(5,*) nPB(ISTATE), nPu(ISTATE), nPq(ISTATE), RREF(ISTATE)

```

```

#9      READ(5,*) RMIN(ISTATE), RMAX(ISTATE), RH(ISTATE)
        IF(PSEL(ISTATE).EQ.2) THEN
c** For an MLJ potential ...
#10     READ(5,*) NcN(ISTATE), CNVAL(ISTATE), IFXCn(ISTATE), Asw(ISTATE), Rsw(ISTATE)
#11     READ(5,*) MCM(ISTATE), RCMCN(ISTATE), IFXRmn(ISTATE)
        1
        ENDDO
        IF(PSEL(ISTATE).EQ.3) THEN
c** For a DELR potential ...
#12     READ(5,*) numCm(ISTATE), RHOD(ISTATE), IDF(ISTATE)
#13     READ(5,*) (mLR(ISTATE,i), CmVAL(ISTATE,i), i=1, numCm(ISTATE))
        ENDDO
c** For a GPEF potential ...
#14     IF(PSEL(ISTATE).EQ.4) READ(5,*) AGPEF(ISTATE), BGPEF(ISTATE)
c** For all cases ...
#15     READ(5,*) DE(ISTATE), IFXDE(ISTATE)
#16     READ(5,*) RE(ISTATE), IFXRE(ISTATE)
#17     READ(5,*) NSphi(ISTATE), NLphi(ISTATE)
        DO I= 0,max(NSphi(ISTATE),NLphi(ISTATE))
#18     READ(5,*) PHI(I,ISTATE), IFXPHI(I,ISTATE)
        ENDDO
#19     READ(5,*) NUA(ISTATE)
c** Adiabatic potential energy BOB function parameters for atom-A
        IF(NUA(ISTATE).GE.0) THEN
        DO I= 0, NUA(ISTATE)
#20     READ(5,*) UA(I,ISTATE), IFXUA(I,ISTATE)
        ENDDO
#21     READ(5,*) UAinf, IFXUAinf
        ENDDO
#22     READ(5,*) NUB(ISTATE)
c** Adiabatic potential energy BOB function parameters for atom-B
        IF(NUB(ISTATE).GE.0) THEN
        DO I= 0, NUB(ISTATE)
#23     READ(5,*) UB(I,ISTATE), IFXUB(I,ISTATE)
        ENDDO
#24     READ(5,*) UBinf, IFXUBinf
        ENDDO
#25     READ(5,*) NTA(ISTATE)
c** Non-adiabatic centrifugal BOB function parameters for atom-A
        IF(NTA(ISTATE).GE.0) THEN
        DO I= 0, NTA(ISTATE)
#26     READ(5,*) TA(I,ISTATE), IFXTA(I,ISTATE)
        ENDDO
#27     READ(5,*) TAinf, IFXTAinf
        ENDDO
#28     READ(5,*) NTB(ISTATE)
c** Non-adiabatic centrifugal BOB function parameters for atom-B
        IF(NTB(ISTATE).GE.0) THEN
        DO I= 0, NTB(ISTATE)
#29     READ(5,*) TB(I,ISTATE), IFXTB(I,ISTATE)
        ENDDO
#30     READ(5,*) TBinf, IFXTBinf
        ENDDO
        IF(IOMEG(ISTATE).NE.0) THEN
c** Lambda-doubling or 2\Sigma splitting expansion parameters
#31     READ(5,*) NwCFT(ISTATE), nPw(ISTATE), efREF(ISTATE)
        IF(NwCFT(ISTATE).GE.0) THEN
        DO I= 0, NwCFT(ISTATE)
#32     READ(5,*) wCft(I,ISTATE), IFXwCft(I,ISTATE)
        ENDDO
#33     READ(5,*) wINF, IFXwINF
        ENDDO
        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
#34     READ(5,*,end=99) VP(IBAND),VPP(IBAND),LABLP,LABLPP,MN1,MN2,PP,

```

```

      IBAND= IBAND+ 1
      IF(VP(IBAND).GE.0) GO TO 70
      ENDIF
C*****
c      End of Channel-5 input data file
C*****

```

### 6.3 Definitions and Descriptions for the Channel-5 Input File Data

Read integers identifying the molecule and system.

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

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 reduce mass for molecular ions; see Eq. (2).

NISTP is the number of isotopologues to be considered in this 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.

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 those considered in this 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 data for one isotopologue).

- If the program is being asked to predict data from a set of known input parameters (see § III.C), 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, which will have the names WRITFILE.6, WRITFILE.7, WRITFILE.8, ... , WRITFILE.16, 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.

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

#### #4 READ(5,\*) UCUTOFF, NOWIDTHS, IROUND, ROBUST, LPRINT, PRINP

UCUTOFF: causes any input data with uncertainties  $u_i > UCUTOFF$  (a real number) to be neglected.

NOWIDTHS: if  $\geq 0$ , ignore any width data in the data file.

IROUND: Setting (integer)  $IROUND \neq 0$  causes the “sequential rounding and refitting” procedure of Ref. [54] to be implemented, with each parameter being rounded at the  $|IROUND|$ 'th significant digit of its uncertainty. If  $IROUND > 0$  the sequential rounding is applied sequentially to the remaining free parameter with 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 which is set  $>0$  to cause the *robust* fitting procedure described at the end of §5.1 to be applied; otherwise (the normal case) it should be set  $\leq 0$ .

**LPRINT** is an integer specifying the level of output to be generated by the least-squares subroutine package **NLLSSRR**. Setting **LPRINT**=0 yields no internal printout except for convergence-failure warning messages; this is the recommended choice when there are no problems with the fits.

If **LPRINT**  $< 0$  print converged unrounded parameters; if **LPRINT**  $\geq 1$  also print converged rounded parameters (when **IROUND**  $\neq 0$ ); if **LPRINT**  $\geq 2$  also print parameter changes on each rounding step; if **LPRINT**  $\geq 3$  also report parameter convergence criterion satisfied; if **LPRINT**  $\geq 4$  also print convergence test on each fitting cycle; if **LPRINT**  $\geq 5$  also print the change and uncertainty in each parameter in each fitting cycle.

**PRINP** is an integer parameter which controls whether (**PRINP**  $> 0$ ) or not ( $\leq 0$ ) a summary of the experimental data is printed immediately after it is input. This option is useful only for helping locate problems in the input data; in most cases one should set **PRINP**  $\leq 0$ .

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 (**ISOT** =  $\alpha = 1$ ) for parameter mass-scaling and the calculation of BOB potential energy corrections. The mass numbers for each isotopologue must be on a different 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  $\alpha = \text{ISOT}$ . For a normal stable atomic isotope, its mass is taken from the tabulation in subroutine **MASSES**; if **MN** is outside the range for the normal stable isotopes of that atom, the abundance-averaged atomic mass is used.

**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 all of the rest of the channel-5 input data.

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

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

**SLABL** is a two-alphanumeric-character label for this electronic state, inclosed in single quotes (e.g., 'X0', 'a1', 'f+', ...), 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 in the datafile and omitted from the analysis.

**JTRUNC** is an integer data-selection parameter. If **JTRUNC**  $> 0$ , all data for this electronic state with  $J > \text{JTRUNC}$  are omitted from the analysis; if **JTRUNC**  $< 0$  omit all data with  $J < \text{JTRUNC}$ .

**EFSEL** is an integer which 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 if **EFSEL**  $< 0$ , c) all transitions if **EFSEL** = 0.

Read parameters to select analytical potential model, specify the potential asymptote, define the representation to be used for BOB corrections and control output printing.

```
#7. READ(5,*) PSEL(s), VLIM(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 program LEVEL's subroutine package PREPOT [48].

If  $PSEL = 1$  use the Expanded Morse Oscillator (EMO) form of §2.2.1.

If  $PSEL = 2$  use the Morse/Long-Range (MLR) or Morse/Lennard-Jones (MLJ) potential form of §2.2.2; the choice of which of these form is to be used depends on the value of parameter MCM which is input through READ #11.

If  $PSEL = 3$  use the Double-Exponential/Long-Range (DELR) form of §2.2.3.

If  $PSEL = 4$  use Seto's modification [33] of Šurkus' Generalized Potential Energy Function (GPEF) [7], as described in §2.2.4. The parameters  $p$ ,  $a_S$  and  $b_S$  are read in below.

- Dunham expansions are generated by setting  $k = 1$ ,  $a_S = 0$  &  $b_S = 1$ .
- SPF expansions are generated by setting  $k = 1$ ,  $a_S = 1$  &  $b_S = 0$ .
- Ogilvie–Tipping expansions are generated by setting  $k = 1$ ,  $a_S = b_S = 0.5$ .
- For these polynomial-type potentials with an undefined (or at best, indirectly-defined) asymptote, parameter VLIM defines the potential minimum.

VLIM: The fixed absolute energy (in  $\text{cm}^{-1}$ ) at the potential asymptote. This sets the absolute energy scale seen in the output.

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

If  $BOBCN = 0$  choose a reference isotopologue and use mass differences following Eqs. (3) and (4).

If  $BOBCN = 1$  combine the clamped nuclei reference case with mass scaling factors  $m_e/M_A^{(\alpha)}$ , following Eqs. (26) and (27).

OSEL: if (integer)  $OSEL > 0$ , write every  $OSEL$ 'th point of the final potential energy, its exponent coefficient function  $\phi(r)$ , and of any radial BOB function arrays to channels 10-16; if  $OSEL \leq 0$ , omit such output. Smaller (positive) values of  $OSEL$  yield larger output files written on a finer radial mesh.

#8. READ(5,\*) nPB(s), nPu(s), nPt(s), RREF(s)

nPB is the power  $p$  in the definition of the radial variable  $y_p(r, r_{\text{ref}})$  of Eq. (5) used to define the potential function exponent coefficient  $\phi(y_p(r, r_{\text{ref}}))$  of Eqs. (6), (11) and (16), and in (22).

nPu is the power  $p$  defining the radial variable  $y_p(r, r_e)$  used for the “adiabatic” potential energy BOB function of Eq. (23).

nPt is the power  $p$  defining the radial variable  $y_p(r, r_e)$  used for the non-adiabatic centrifugal BOB radial function of Eq. (24).

RREF defines the reference distance in the potential-function exponent expansion variable  $y_p(r, r_{\text{ref}})$  of Eq. (5) to be:

- the (in general, variable) potential function minimum distance  $r_e(s)$ , if  $RREF(s) \leq 0$ .
- the fixed read-in value of  $RREF(s)$ , if  $RREF(s) > 0$ .

Note that for the BOB,  $\Lambda$ -doubling, and  ${}^2\Sigma$  radial strength functions, DPOTFIT sets  $r_{\text{ref}} = r_e$ .

#9. READ(5,\*) RMIN(s), RMAX(s), RH(s)

RMIN & RMAX: are the inner and outer limits, respectively, of the range of numerical integration (in Å). As zero<sup>th</sup> order estimates one may set  $RMIN \approx 0.6 \times (\text{potential inner wall position})$  and RMAX very large (say = 99 Å); see §3.

RH: the numerical integration mesh size.

If PSEL = 2 (for an MLR or MLJ potential), specify the asymptotic form of potential energy function.

#10. READ(5,\*) NCN(s), CNVAL(s), IFXCn(s), Asw(s), Rsw(s)

#11. READ(5,\*) MCM(s), RCMCN(s), IFXRmn(s)

For an MLJ function, set  $MCM \leq NCN$  and  $RCMCN = 0.0$ , and the potential will be constrained to have the asymptotic behaviour  $V(R) = VLIM - CNVAL/R^{NCN}$ .

IFXCn controls whether  $C_n$  is to be fitted ( $IFXCn \leq 0$ ) or held fixed ( $IFXCn > 0$ ) in the fit. Fitting  $C_n$  should only be considered if a substantial amount of data is available for levels lying very near dissociation.

For an MLR potential, set  $MCM > NCN$  and the potential will be constrained to have the two-term limiting behaviour  $V(R) = VLIM - CNVAL [1 + RCMCN/r^{MCM-NCN}] / r^{NCN}$ . Note that if  $nPB \leq (MCM - NCN)$ , the MLR form is reduced to the one-long-range term MLJ form (see § 2.2.2).

IFXRmn controls whether RCMCN is to be fitted ( $IFXRmn \leq 0$ ) or held fixed ( $IFXRmn > 0$ ) in the fit. While fits to this parameter can be performed by DPOTFIT, experience to date [57] suggests that it will almost always be better to fix it at a value obtained from theory.

If  $Asw \leq 0.0$  this constraint is imposed *via* the form of the potential function exponent coefficient of Eq. (15). In this case, Rsw is a dummy parameter.

If  $Asw > 0.0$  this constraint is imposed *via* the switching function constraint of Eq. (14) [20]. In this case, the distance Rsw is typically chosen to be slightly (say,  $\sim 1 \text{ \AA}$ ) larger than the outer turning point for the highest observed vibrational level.

If PSEL = 3, read in the parameters defining the long-range part  $V_{LR}(R)$  of the DELR potential; otherwise, skip READs #12-13.

#12. READ(5,\*) numCm(s), RHOD(s), IDF(s)

These parameters define the inverse-power sum contribution to  $V_{LR}(r)$  of the form:  $\sum_{m \geq n} D_m(r) C_m / r^m$  consisting of numCm(s) inverse-power terms, with damping function  $D_m(r)$ .

RHOD(s) is the exponent coefficient  $\rho_d$  in the damping function of Eqs. (20) or (21).

IDF specifies which type of term-by-term  $D_m(r)$  damping function will be used:

IDF = 1 specifies use of the Tang-Toennies form of Eq. (20).

IDF = 2 specifies use of the Douketis-Scoles form of Eq. (21).

#13. READ(5,\*) (mLR(s,i), CmVAL(s,i), i= 1, numCm(s))

Positive integer inverse-powers (mLR) and coefficients (CmVAL) of the numCm terms contribution to  $V_{LR}(r)$  of Eq. (19). Note that positive CmVAL values yield repulsive potential function contributions.

If PSEL = 4, read in the parameters defining the expansion variable in the GPEF potential of Eq. (22); otherwise, skip READ #14.

#14. READ(5,\*) AGPEF(ISTATE), BGPEF(ISTATE)

In the GPEF radial expansion variable of Eq. (22):  $a_S = AGPEF$  and  $b_S = BGPEF$ , while  $p = nPB$  was input via READ #9.

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

#15. READ(5,\*) DE(ISTATE), IFXDE(ISTATE)

DE is the dissociation energy  $\mathcal{D}_e$  for this state. This is a dummy variable for the case of a GPEF potential.

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

#16. READ(5,\*) RE(ISTATE), IFXRE(ISTATE)

RE is the equilibrium radial distance  $r_e$  for this state.

IFXRE controls whether  $r_e$  is to be fitted ( IFXRE  $\leq 0$  ) or held fixed ( IFXRE  $> 0$  ) in the fit.

Read integers specifying the order(s) of the polynomial defining the potential function  $V_{\text{ad}}^{(1)}(r)$  (or  $V_{\text{CN}}(r)$ ).

#17. READ(5,\*) NSphi(s), NLphi(s)

For PSEL=1-3, max{NSphi,NLphi} is the overall order of the potential function exponent coefficient expansion. For PSEL=4 it is the order of the GPEF polynomial expansion.

NSphi is the order of the potential function exponent coefficient expansion at distances  $r \leq r_e$ .

NLphi is the order of the potential function exponent coefficient expansion at distances  $r > r_e$  (see Eqs. (8) & (9)).

If PSEL  $> 0$ , read initial trial values of the exponent expansion parameters  $\phi_i$  of Eqs. (8), (9), (14) or (15), or of the coefficients  $c_i$  of the GPEF potential of Eq. (22). Skip this READ statement if PSEL  $\leq 0$ .

#18. READ(5,\*) (PHI(I,s), IFXPHI(I,s), I=0, MAX(NSphi(s),NLphi(s)))

PHI(I,s) are the initial trial values of the potential exponent expansion coefficients  $\phi_i$  or (if PSEL=4) of the GPEF expansion coefficients  $c_i = \phi_i$ .

IFXPHI(I,s) controls whether  $\phi_i$  is to be fitted ( IFXPHI  $\leq 0$  ) or held fixed ( IFXPHI  $> 0$  ) in the fit.

Now, read in parameters specifying the Born-Oppenheimer breakdown radial functions. First, for the effective adiabatic functions  $\tilde{S}_{\text{ad}}^A$  and  $\tilde{S}_{\text{ad}}^B$ .

#19. READ(5,\*) NUA(ISTATE)

NUA is the (integer) order of the polynomial in  $y_{\text{nPu}}(r)$  (i.e.,  $y_p(r)$  for  $p = \text{nPu}$ ) used to define the effective adiabatic BOB radial function for atom  $A$ . If NUA  $< 0$ , omit adiabatic BOB terms for atom  $A$ , so skip READs #20 and #21.

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

UA(I,s) is the input (initial trial) value for the adiabatic BOB function coefficient  $u_i^A$ .

IFXUA(I,s) controls whether  $u_i^A$  is to be fitted ( IFXUA(I,s)  $\leq 0$  ) or held fixed ( IFXUA(I,s)  $> 0$  ).

#21. READ(5,\*) UAinf, IFXUAinf

UAinf is the limiting asymptotic value of the atom- $A$  radial BOB function  $\tilde{S}_{\text{ad}}^A(R)$  (it is stored internally as UA(NUA+1,s)).

IFXUAinf controls whether UAinf is to be fitted ( IFXUAinf  $\leq 0$  ) or held fixed ( IFXUAinf  $> 0$  ) (it is stored internally as IFXUA(NUA+1,s)).

#22. READ(5,\*) NUB(ISTATE)

NUB is the (integer) order of the polynomial in  $y_{\text{nPu}}(R)$  (i.e.,  $y_p(r)$  for  $p = \text{nPu}$ ) used to define the effective adiabatic BOB radial function for atom  $B$ . If NUB  $< 0$ , omit adiabatic BOB terms for atom  $B$ , so skip READs #23 and #24.

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

UB(I,s) is the input (initial trial) value for the adiabatic BOB function coefficient  $u_i^B$ .

IFXUB(I,s) controls whether  $u_i^B$  is to be fitted ( IFXUB(I,s)  $\leq$  0 ) or held fixed ( IFXUB(I,s)  $>$  0 ).

#24. READ(5,\*) UBinf, IFXUBinf

UBinf is the limiting asymptotic value of the atom-*B* radial BOB function  $\tilde{S}_{\text{ad}}^B(R)$  (it is stored internally as UB(NUB+1,s)).

IFXUBinf controls whether UBinf is to be fitted ( IFXUBinf  $\leq$  0 ) or held fixed ( IFXUBinf  $>$  0 ) (it is stored internally as IFXUB(NUB+1,s)).

Now, read in parameters defining the non-adiabatic centrifugal BOB radial functions  $\tilde{R}_{\text{na}}^A$  and  $\tilde{R}_{\text{na}}^B$ .

#25. READ(5,\*) NTA(ISTATE)

NTA is the (integer) order of the polynomial in  $y_{\text{nPt}}(R)$  (i.e.,  $y_p(r)$  for  $p=\text{nPt}$ ) used to define the effective adiabatic BOB radial function for atom *A*. If NTA  $<$  0, omit these terms for atom *A*, so skip READs #26 and #27.

#26. READ(5,\*) (TA(I,s), IFXTA(I,s), I=0, NTA(s))

TA(I,s) is the input (initial trial) value for the adiabatic BOB function coefficient  $t_i^A$ .

IFXTA(I,s) controls whether  $t_i^A$  is to be fitted ( IFXTA(I,s)  $\leq$  0 ) or held fixed ( IFXTA(I,s)  $>$  0 ).

#27. READ(5,\*) TAinf, IFXTAinf

TAinf is the limiting asymptotic value of the atom-*A* radial BOB function  $\tilde{R}_{\text{ad}}^A(R)$  (it is stored internally as TA(NTA+1,s)).

IFXTAinf controls whether TAinf is to be fitted ( IFXTAinf  $\leq$  0 ) or held fixed ( IFXTAinf  $>$  0 ) (it is stored internally as IFXTA(NTA+1,s)).

#28. READ(5,\*) NTB(ISTATE)

NTB is the (integer) order of the polynomial in  $y_{\text{nPt}}(R)$  (i.e.,  $y_p(r)$  for  $p=\text{nPt}$ ) used to define the effective adiabatic BOB radial function for atom *B*. If NTB  $<$  0, omit these terms for atom *B*, so skip READs #29 and #30.

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

TB(I,s) is the input (initial trial) value for the adiabatic BOB function coefficient  $t_i^B$ .

IFXTB(I,s) controls whether  $t_i^B$  is to be fitted ( IFXTB(I,s)  $\leq$  0 ) or held fixed ( IFXTB(I,s)  $>$  0 ).

#30. READ(5,\*) TBinf, IFXTBinf

TBinf is the limiting asymptotic value of the atom-*B* radial BOB function  $\tilde{R}_{\text{ad}}^B(R)$  (it is stored internally as TB(NTB+1,s)).

IFXTBinf controls whether TBinf is to be fitted ( IFXTBinf  $\leq$  0 ) or held fixed ( IFXTBinf  $>$  0 ) (it is stored internally as IFXTB(NTB+1,s)).

Finally, if the electronic angular momentum quantum number IOMEG(s) is not zero, read in parameters defining the radial  $\Lambda$ -doubling or  $^2\Sigma$  spin-splitting radial function.

#31. READ(5,\*) NwCFT(s), nPw(s), efREF(s)

NwCFT is the order of the polynomial defining the radial strength function  $f_\Lambda(r)$  or  $f_\Sigma(r)$ .

`nPw` is the integer  $p \equiv \text{nPw}$  defining the radial expansion variable  $y_{\text{nPw}}(r, r_e)$  of Eq. (30) or (33).

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

#32. `READ(5,*) (wCFT(I,s), IFXwCFT(I,s), I= 0, nLambd(s)`

`wCFT(I,s)` is the input value for the  $\Lambda$ -doubling or  $^2\Sigma$  radial strength coefficient  $w_i = \text{wCFT}(I, s)$ .  
`IFXwCFT(I,s)` controls whether coefficient  $w_i$  is to be fitted (`IFXwCFT(I,s) ≤ 0`) or held fixed (`IFXwCFT(I,s) > 0`).

#33. `READ(5,*) wINF, IFXwINF`

`wINF` is the limiting asymptotic value of the radial function  $f_\Lambda(r)$  or  $f_\Sigma(r)$ ; it is stored internally as `wCFT(NwCFT+1,s)`.

`IFXwINF` controls whether `wINF` is to be fitted (`IFXwINF ≤ 0`) or held fixed (`IFXwINF > 0`); it is stored internally as `IFXwCFT(NwCFT+1,s)`.

### Generating predictions from a set of fixed system parameters.

Loop over all bands for which predictions are desired, and for each one read the following. Last band read in is (assumed to be) end of data file.

#34. `READ(5,*) VP(IBAND), VPP(IBAND), LABLP, LABLP, MN1, MN2, PP, PPP, 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 two-alphanumeric-character names (enclosed in single quotes, as in 'XO') 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`.

## 6.4 Illustrative Sample Input Data Files

This program has been successfully applied to a wide variety of problems [12, 16, 20, 23, 4, 5, 9, 10, 11, 57]. The following subsection briefly describes two of these cases and presents the associated channel-5 instruction input data file.

### 6.4.1 Analysis to Determine the Potential Function for the Ground $X^1\Sigma_g^+$ State of $\text{N}_2$

This is the case described in Ref. [11] in which Raman and electric quadrupole pure rotational and vibration-rotation data for the three isotopologues  $^{14,14}\text{N}_2$ ,  $^{14,15}\text{N}_2$  and  $^{15,15}\text{N}_2$ , plus term values obtained from electronic spectra, are fitted to determine an  $\text{MLR}_p(N_S, N_L) = \text{MLR}_4(6, 8)$  potential function for ground-state  $\text{N}_2$ . This input data file considers only a single electronic state, since the term values determined from electronic spectra were treated as a fluorescence series. For this case, it was found that the effect of centrifugal BOB terms was negligible, so setting input parameter values `nTA = nTB = -1` tells the

program to ignore them. Also, since N<sub>2</sub> is electronically homonuclear, it was only necessary to specify the potential energy BOB function for ‘atom A’, so nuB = 0. In this listing, the % symbol appears after the last parameter of the associated READ statement, so the comments which follow it are ignored by the program.

```

7 7 0 3 1          % AN(1) AN(2) CHARGE NISTP NSTATES
'dataN2X.4'        % experimental data filename
'68p4u1p6C8'      % output file root-name
0.1d0 1 0 0 2 0   % UCUTOFF NOWIDTHS IROUND ROBUST LPRINT PRINP
14 14             % MN1(1) MN2(2)
14 15             % MN1(1) MN2(2)
15 15             % MN1(1) MN2(2)
'X0' 0 0 20 200 0 % SLABL IOMEG VMIN VMAX JTRUNC EFSEL
2 0.d0 0 50       % PSEL VLIM BOBCN OSEL
4 6 6 0.d0        % nPB nPu nPt RREF
0.60 6.0 0.0002   % RMIN RMAX RH
6 1.16D+05 0 -1.d0 0.d0 % NCN CNVAL IFXCn Asw Bsw
8 5.5d0 1         % MCM RCMCN IFXRmn
79845.00D+00      1 % DE IFDE
1.0976793209D+00 0 % RE IFRE
6 8              % NBETAin NBETAout
-2.3441446457D+00 0 % PHI(0) IFXPHI(0)
-9.7247759140D-01 0 % PHI(1) IFXPHI(1)
-1.5618023261D+00 0 % PHI(2) IFXPHI(2)
-1.1356654112D+00 0 % PHI(3) IFXPHI(3)
-1.3958865342D+00 0 % PHI(4) IFXPHI(4)
-8.2116503593D-01 0 % PHI(5) IFXPHI(5)
-4.5566537033D-01 0 % PHI(6) IFXPHI(6)
-3.3367367368D+00 0 % PHI(7) IFXPHI(7)
2.0829634321D+00 0 % PHI(8) IFXPHI(8)

2                % nuA
0.d0             % UA(0) IFXUA(0)
-1.4177679977D+01 0 % UA(1) IFXUA(1)
0.d0             % UA(2) IFXUA(2)
0.d0             % uAinf IFuAinf
-1              % nuB
-1              % nTA
-1              % nTB

```

#### 6.4.2 Determining Potential Functions for the Ground $X^1\Sigma^+$ and $A^1\Sigma^+$ States of AgH

This is the case described in Ref. [9] in which a fit to infrared and electronic data for the  $X^2\Sigma^+$  and  $A^1\Sigma^+$  states of <sup>107</sup>AgH, <sup>109</sup>AgH, <sup>107</sup>AgD and <sup>109</sup>AgD is used to determine an EMO<sub>3</sub>(7,7) potential for the  $X^2\Sigma^+$  state, and an EMO<sub>4</sub>(5,10) function for the  $A^1\Sigma^+$  state. Because of the irregular shape of the potential for the  $A^1\Sigma^+$  state, a relatively large number of potential energy  $\{\phi_i\}$  and ‘adiabatic’ BOB radial function parameters  $\{u_i^H\}$  were required to attain a good fit.

```

47 1 0 4 2        % AN(1) AN(2) CHARGE NISTP NSTATES
'Data_AgH.4'      % Name of PotFit input data file
'Xmlj77p3_Aemo510p4' % root name for output files
1.D0 1 0 0 5 0   % UCUTOFF NOWIDTHS IROUND ROBUST LPRINT PRINP
107 1            % MN1(1) MN2(1)
109 1            % MN1(2) MN2(2)
107 2            % MN1(3) MN2(3)
109 2            % MN1(4) MN2(4)
'X0' 0 0 11 90 0 % (1) SLABL IOMEG VMIN VMAX JTRUNC EFSEL
1 19250.0d0 0 50 % PSEL VLIM BOBCN OSEL
3 3 3 0.d0       % nPB nPu nPt RREF
0.8 9.0 0.001d0 % RMIN RMAX RH

```

1.9250000000D+04	1	% De IFXDe
1.6179161670D+00	0	% Re IFXRe
7 7		% NSphi NLphi
1.5435811526D+00	0	% PHI(0) IFXPHI(0)
3.7377771819D-02	0	% PHI(1) IFXPHI(1)
1.6642808805D-01	0	% PHI(2) IFXPHI(2)
9.8190938663D-02	0	% PHI(3) IFXPHI(3)
1.7059432062D-01	0	% PHI(4) IFXPHI(4)
5.9386199731D-02	0	% PHI(5) IFXPHI(5)
1.4250663642D-01	0	% PHI(6) IFXPHI(6)
2.2230265720D-01	0	% PHI(7) IFXPHI(7)
-1		% NUA
3		% NUB
0.0000000000D+00	1	% UB(0) IFXUB(0)
1.1749768163D+01	0	% UB(1) IFXUB(1)
1.7553993295D+01	0	% UB(2) IFXUB(2)
-1.2618688961D+01	0	% UB(3) IFXUB(3)
0.0000000000D+00	1	% UBinf IFXUBinf
-1		% NTA
2		% NTH
0.d0	1	% TB(0) IFXTB(0)
1.4851142822D-04	0	% TB(1) IFXTB(1)
9.3302644949D-04	0	% TB(2) IFXTB(2)
0.d0	1	% TBinf IFXTBinf
'A1' 0 0 7 90 0		%(2) SLABL IOMEG VMIN VMAX JTRUNC EFSEL
1 48802.05 0 50		% PSEL VLIM BOBCN OSEL
4 4 4 0.d0		% nPB nPu nPt RREF
0.75 7.0 0.001d0		% RMIN RMAX RH
1.8830645993D+04	0	% De IFXDe
1.6447948537D+00	0	% Re IFXRe
5 10		% NSphi NLphi
1.4516696726D+00	0	% PHI(0) IFXPHI(0)
-2.5093751948D-01	0	% PHI(1) IFXPHI(1)
-2.6892797056D-01	0	% PHI(2) IFXPHI(2)
-4.0519788744D-01	0	% PHI(3) IFXPHI(3)
-1.1183274297D+00	0	% PHI(4) IFXPHI(4)
-1.5751057028D+00	0	% PHI(5) IFXPHI(5)
2.6097077067D+01	0	% PHI(6) IFXPHI(6)
-9.6955732594D+01	0	% PHI(7) IFXPHI(7)
1.6317499720D+02	0	% PHI(8) IFXPHI(8)
-1.2748346982D+02	0	% PHI(9) IFXPHI(9)
3.8202389384D+01	0	% PHI(10) IFXPHI(10)
0		% NUA
-6.1532403636D-01	0	% UA(0)
0.d0	1	% UAinf IFXUAinf
7		% NUB
-2.0990806299D+01	0	% UB(0) IFXUB(0)
1.1855118102D+02	0	% UB(1) IFXUB(1)
-1.5172266409D+02	0	% UB(2) IFXUB(2)
1.3266145502D+02	0	% UB(3) IFXUB(3)
-5.9275261121D+02	0	% UB(4) IFXUB(4)
-5.4137300903D+02	0	% UB(5) IFXUB(5)
3.1572792242D+03	0	% UB(6) IFXUB(6)
-2.1427337370D+03	0	% UB(7) IFXUB(7)
0.d0	1	% UBinf IFXUBinf
-1		% NTA
3		% NTB
0.0000000000D+00	1	% TB(0) IFXTB(0)
2.8801232707D-04	0	% TB(1) IFXTB(1)
2.9670189368D-03	0	% TB(2) IFXTB(2)
8.0194859562D-03	0	% TB(3) IFXTB(3)
0.0000000000D+00	1	% TBinf IFXTBinf

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## Appendix A. 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 which 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 [53] 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 which reads in and writes out the parameters and properties of the potential energy, BOB, and (as appropriate)  $\Lambda$ -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.

**PREPOT**: A subroutine package described in detail in the manual for program LEVEL [48] which 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.

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

**NLLSSRR**: A general non-linear (or linear) least-squares fitting subroutine package which can also implement (when input parameter `IROUND`  $\neq 0$ ) the “sequential rounding and refitting” procedure of Ref. [54].

**DYIDPJ**: The key user-supplied subroutine required by NLLSSRR, which 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.

**INITDD**: Prior to each cycle of fit, this subroutine updates the sets of band constants used to generate 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 of a given potential energy curve.

**SCHRQ**: This is the core Schrödinger solver subroutine which provides the eigenvalue and radial wavefunctions required for the data simulation and partial derivative calculations. Some special aspects of this routine are described in the manual for program LEVEL [48].

**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 of each datum, this routine generates and returns the eigenvalue and the 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.

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.

## Appendix B. Sample Program Output

Channel-6 output file yielded by the fit to data for ground-state N<sub>2</sub> described in §6.4.1.

```

Input data for 3 isotopomer(s)
*****
-----
Isotopomer      Mass of atom-1    Mass of atom-2    Reduced mass
-----
N( 14) - N( 14)  14.003074005      14.003074005      7.001537002
N( 14) - N( 15)  14.003074005      15.000108898      7.242227023
N( 15) - N( 15)  15.000108898      15.000108898      7.500054449

Use experimental data input file: ../dataN2X.4
For homonuclear diatomics, BO correction terms are the same for both atoms.
Only the first set of correction terms will be used, UA(R) and TA(R),
with a mass scaling factor equal to the sum of the two individual terms.

For state X0 use a Morse/Lennard-Jones MLJ(n;p= 4) potential function with
===== radial expansion variable   y_p = (R^p - Re^p)/(R^p + Re^p)
& coefficient exponent given by: phi(R)= phiINF*y_p + (1-y_p)*Sum{phi*y_p^i}
For our n= 6 MLJ potential C6= 116000.00000
and C8 defined by R_{8,6}= C8/C6 = 5.5000

Integrate from RMIN= 0.60 to RMAX= 6.00 with mesh RH= 0.00020
=====

State X0 represented by an MLJ(n= 6;p= 4) function defined in terms of an
===== exponent power series of order 6 for R < Re and 8 for R > Re
with C6= 1.16000D+05[cm-1 Ang^6] defining phiINF= -0.837608
and C8 defined by R_{8,6}= C8/C6 = 5.5000
using radial expansion variable: y_p = (R^p - Re^p)/(R^p + Re^p)
Adiabatic BOB functions are scaled by DELTA{M(A)}/M(A) and expanded as:
dV_ad( N;R) = u(inf)*y6 + (1 - y6)*Sum{u_i * [y6]^i} for i= 0 to 1

Parameter:  Initial Value:  Uncertainty:  Sensitivity:
VLIM       0.000000000D+00    --          --
De         7.984500000D+04    --          --
Re         1.0976793209D+00    0.0D+00     0.0D+00
phi( 0)    -2.3441446457D+00    0.0D+00     0.0D+00
phi( 1)    -9.7247759140D-01    0.0D+00     0.0D+00
phi( 2)    -1.5618023261D+00    0.0D+00     0.0D+00
phi( 3)    -1.1356654112D+00    0.0D+00     0.0D+00
phi( 4)    -1.3958865342D+00    0.0D+00     0.0D+00
phi( 5)    -8.2116503593D-01    0.0D+00     0.0D+00

```

```

phi( 6) -4.5566537033D-01    0.0D+00    0.0D+00
phi( 7) -3.3367367368D+00    0.0D+00    0.0D+00
phi( 8)  2.0829634321D+00    0.0D+00    0.0D+00
phi_INF -8.3760839776D-01    --        --
C( 6)   1.1600000000D+05    --        --
u N( 0)  0.0000000000D+00    --        --
u N( 1) -1.4177679977D+01    0.0D+00    0.0D+00
u_inf( N) 0.0000000000D+00    --        --

```

```

=====
Neglect data with: Uncertainties > UCUTOFF= 0.100 (cm-1)
and State X0 data with J > JTRUNC= 200 or v outside range 0 to 20
State X0 Energy Convergence criterion EPS is 2.0D-06 cm-1

```

Fit uses standard 1/[uncertainty(i)]\*\*2 data weighting

```

Fit of 1221 data to 1 parameters yields RMS(residuals)= 1.444
PV( 1) = -7.86691580066135D+04 (+/- 8.7D-03) PS= 1.5D-02 PC= 1.3D-10

```

```

Fit of 1221 data to 12 parameters yields RMS(residuals)= 1.444
PV( 1) = 1.09767932091232D+00 (+/- 8.2D-07) PS= 5.8D-09 PC=-8.4D-14
PV( 2) = -2.34414464573982D+00 (+/- 2.2D-06) PS= 9.0D-09 PC=-1.3D-13
PV( 3) = -9.72477591396618D-01 (+/- 8.6D-05) PS= 9.6D-07 PC= 1.3D-13
PV( 4) = -1.56180232605478D+00 (+/- 1.7D-04) PS= 3.0D-07 PC=-3.7D-12
PV( 5) = -1.13566541145535D+00 (+/- 3.2D-03) PS= 8.8D-06 PC= 4.3D-12
PV( 6) = -1.39588653459165D+00 (+/- 4.0D-03) PS= 3.7D-06 PC= 2.0D-10
PV( 7) = -8.21165032955729D-01 (+/- 2.7D-02) PS= 2.5D-05 PC=-6.9D-10
PV( 8) = -4.55665365232550D-01 (+/- 5.7D-02) PS= 2.5D-05 PC=-3.1D-09
PV( 9) = -3.33673676526657D+00 (+/- 2.5D-01) PS= 7.0D-05 PC= 1.3D-08
PV( 10) = 2.08296345833923D+00 (+/- 2.3D-01) PS= 1.4D-04 PC=-1.2D-08
PV( 11) = -1.41776800433599D+01 (+/- 7.3D-01) PS= 7.9D-02 PC=-5.1D-07
PV( 12) = -7.86691580071866D+04 (+/- 1.1D-02) PS= 1.3D-03 PC= 9.6D-11

```

```

=====
For fit of 12 parameters to 1221 transitions, DSE= 1.4508526

```

The following Fluorescence Series Term Values were determined.

```

T(v', J', p';ISTP) Final Value: Uncertainty: Sensitivity:
T( 0, 0, +1; 1) -7.8669158007D+04 1.1D-02 1.3D-03

```

```

=====
State X0 represented by an MLJ(n= 6;p= 4) function defined in terms of an
===== exponent power series of order 6 for R < Re and 8 for R > Re
with C6= 1.16000D+05[cm-1 Ang^6] defining phiINF= -0.837608
and including C8 with C8/C6 = 5.5000
using radial expansion variable: yp = (R^p - Re^p)/(R^p + Re^p)
Adiabatic BOB functions are scaled by DELTA{M(A)}/M(A) and expanded as:
dV_ad( N;R) = u(inf)*y6 + (1 - y6)*Sum{u_i * [y6]^i} for i= 0 to 1

```

```

Parameter: Final Value: Uncertainty: Sensitivity:
VLIM 0.0000000000D+00 -- --
De 7.9845000000D+04 -- --
Re 1.0976793209D+00 8.2D-07 5.8D-09
phi( 0) -2.3441446457D+00 2.2D-06 9.0D-09
phi( 1) -9.7247759140D-01 8.6D-05 9.6D-07
phi( 2) -1.5618023261D+00 1.7D-04 3.0D-07
phi( 3) -1.1356654115D+00 3.2D-03 8.8D-06
phi( 4) -1.3958865346D+00 4.0D-03 3.7D-06
phi( 5) -8.2116503296D-01 2.7D-02 2.5D-05
phi( 6) -4.5566536523D-01 5.7D-02 2.5D-05
phi( 7) -3.3367367653D+00 2.5D-01 7.0D-05
phi( 8) 2.0829634583D+00 2.3D-01 1.4D-04
phi_INF -8.3760839776D-01 -- --
C( 6) 1.1600000000D+05 -- --
u N( 0) 0.0000000000D+00 -- --
u N( 1) -1.4177680043D+01 7.3D-01 7.9D-02
u_inf( N) 0.0000000000D+00 -- --

```

```

=====
*** Discrepancies for 16 bands/series of N( 14)- N( 14) ***
=====

```

```

=====
19 State X0 N( 14)- N( 14) MW transitions in 1 vib. levels
===== Avge. =====
v' v" #data J"min J"max Av.Unc. Max.Unc. Err/Unc DRMSD
=====

```

```

0 0 19 0 20 1.3D-03 3.0D-03 1.00217 1.602
----- For these 19 lines, overall: 1.00217 1.602

```

```

=====
317 State X0 N( 14)- N( 14) InfraRed transitions in 14 bands
===== Avge. =====
v' v" #data J"min J"max Av.Unc. Max.Unc. Err/Unc DRMSD
-----
1 0 42 4 48 1.0D-02 1.0D-02 0.09219 1.065
2 1 24 4 30 2.0D-02 2.0D-02 0.92024 1.163
1 0 15 0 47 1.3D-03 4.3D-03 -0.67198 0.950
2 1 24 2 26 2.2D-03 3.6D-03 1.93787 2.174
2 1 15 0 14 1.4D-03 1.4D-03 2.26928 2.508
3 2 21 0 20 1.8D-03 1.3D-02 0.99549 1.745
4 3 21 0 20 4.1D-03 1.3D-02 0.22134 0.886
5 4 19 0 18 1.4D-03 1.4D-03 -0.49775 1.680
6 5 16 2 17 1.6D-03 1.6D-03 0.80113 1.239
7 6 21 2 22 3.5D-03 1.9D-02 -1.21607 1.425
8 7 6 6 12 2.2D-03 2.2D-03 -2.95924 3.069
1 0 56 0 24 5.4D-04 1.0D-03 -0.80918 1.006
1 0 18 6 21 4.3D-03 1.0D-02 -0.15766 0.624
1 0 19 4 22 6.3D-04 2.4D-03 -0.16047 2.053
----- For these 317 lines, overall: 0.09731 1.489

```

```

=====
525 Fluorescence transitions into State X0 N( 14)- N( 14) in 1 series
===== Avge. =====
v' j' p' #data v"min v"max AvgeUnc Max.Unc. Err/Unc DRMSD
-----
0 0 e 525 0 19 7.0D-02 1.0D-01 -0.00042 1.141
----- For these 525 lines, overall: -0.00042 1.141

```

```

=====
*** Discrepancies for 3 bands/series of N( 14)- N( 15) ***
=====

```

```

=====
18 State X0 N( 14)- N( 15) MW transitions in 1 vib. levels
===== Avge. =====
v' v" #data J"min J"max Av.Unc. Max.Unc. Err/Unc DRMSD
-----
0 0 18 0 19 3.4D-03 2.0D-02 0.21486 0.667
----- For these 18 lines, overall: 0.21486 0.667

```

```

=====
97 State X0 N( 14)- N( 15) InfraRed transitions in 2 bands
===== Avge. =====
v' v" #data J"min J"max Av.Unc. Max.Unc. Err/Unc DRMSD
-----
1 0 37 5 48 2.0D-02 2.0D-02 0.84262 1.315
1 0 60 0 26 5.5D-04 1.1D-03 -0.16165 1.018
----- For these 97 lines, overall: 0.22142 1.141

```

```

=====
*** Discrepancies for 10 bands/series of N( 15)- N( 15) ***
=====

```

```

=====
20 State X0 N( 15)- N( 15) MW transitions in 1 vib. levels
===== Avge. =====
v' v" #data J"min J"max Av.Unc. Max.Unc. Err/Unc DRMSD
-----
0 0 20 0 21 2.5D-03 1.5D-02 0.59843 1.508
----- For these 20 lines, overall: 0.59843 1.508

```

```

=====
225 State X0 N( 15)- N( 15) InfraRed transitions in 9 bands
===== Avge. =====
v' v" #data J"min J"max Av.Unc. Max.Unc. Err/Unc DRMSD
-----
2 1 11 7 29 2.0D-02 2.0D-02 -0.77657 1.096
1 0 25 1 25 9.6D-04 9.6D-04 2.08586 3.079
2 1 27 1 27 1.6D-03 1.6D-03 -1.23240 1.585
3 2 25 1 25 1.7D-03 1.7D-03 -2.80495 3.084
4 3 24 1 25 4.3D-03 1.7D-02 -0.91014 1.454
5 4 21 3 23 3.0D-03 2.1D-02 -0.11639 1.200
6 5 25 1 25 3.2D-03 1.9D-02 1.59373 1.982
7 6 12 3 25 1.8D-03 1.8D-03 0.60307 1.139
1 0 55 1 25 5.6D-04 1.5D-03 0.25965 1.807
----- For these 225 lines, overall: -0.10098 2.033

```

```

=====
For overall fit to 1221 data, DRMS(deviations)= 1.44371
=====

```