

CP-666

19 March 2013

betaFIT 2.1

**A Computer Program to Fit Pointwise Potentials
to Selected Analytic Functions**

Robert J. Le Roy

*Guelph-Waterloo Centre for Graduate Work in Chemistry
University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
Electronic mail: leroy@UWaterloo.ca*

University of Waterloo

Chemical Physics Research Report

betaFIT 2.1

A Computer Program to Fit Pointwise Potentials to Selected Analytic Functions

Robert J. Le Roy

*Guelph-Waterloo Centre for Graduate Work in Chemistry
University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
Electronic mail: leroy@UWaterloo.ca*

This manual describes program `betaFIT`, which performs least-squares fits of one-dimensional (or radial) potential function values to four different types of analytic potential energy function. The families of potential functions treated in current version of `betaFIT` are: the Expanded Morse Oscillator (EMO), the Morse/Long-Range (MLR) potential, the Double Exponential/Long-Range (DELR) potential, and a wide variety of polynomial potentials including the Dunham, Simons-Parr-Finlan and Ogilvie-Tipping functions, all of which may be described as particular types of Šurkus' "Generalized Potential Energy Function (GPEF)".

©Robert J. Le Roy, 2006-2013.

1 General

It is often desirable to determine a compact analytic function to represent a set of points defining one-dimensional or radial potential energy function. This program can fit such sets of points to any of four families of analytic potential function. This code can be downloaded freely, with a PDF file of this manual, from the www site <http://leroy.uwaterloo.ca/programs/>.¹

2 Potential Function Forms

Program `betaFIT` can fit read-in potential-function points to one of four families of analytic functional forms. The first two are generalizations of familiar simple two- and three-parameter potentials, which allow the resulting functions to represent not only conventional single-well potentials, but also potentials which have double minima or ‘shelf’ behaviour. The third type of potential form (the DELR function) was developed to deal with potentials having a barrier which protrudes above the asymptote, but it should also be able to represent regular single-minimum, double-minimum, or shelf-state potentials. The fourth family of potential functions consists of polynomials expanded about the potential minimum (or equilibrium distance), for which different definitions of the radial expansion variable give a variety of particular forms.

The potential function forms described below are expressed in terms of somewhat non-standard radial expansion variables, so we begin with some remarks about those radial variables.

2.1 The Radial Expansion Variable

While potential energy functions are defined on the infinite radial domain $r \in [0, \infty)$, representing them as explicit functions of the internuclear distance r itself is ill advised, because any simple polynomial function of r will approach $\pm\infty$ as $r \rightarrow \infty$. The first three types of potential described below are based around a single exponential term whose exponent coefficient is a slowly varying function of distance, and is expressed in terms of radial variables of the form

$$y_p^{\text{eq}}(r) = y_p(r; r_e) = \frac{r^p - r_e^p}{r^p + r_e^p} \quad (1)$$

or

$$y_p^{\text{ref}}(r) = y_p(r; r_{\text{ref}}) = \frac{r^p - r_{\text{ref}}^p}{r^p + r_{\text{ref}}^p} \quad (2)$$

in which p is a small positive integer ($p = 1, 2, 3, \dots$), r_e is the usual equilibrium internuclear distance, and r_{ref} is a positive reference distance (usually set $> r_e$) chosen as the expansion centre. These variables are versions of the ‘‘GPEF’’ expansion variable discussed in §2.5, particular forms of which had been introduced by a number of authors [1, 2, 3, 4, 5].

The nature of these variables is illustrated by Fig.1 for a range of values of p [6]. The fact that $y_p^{\text{eq}}(r)$ and $y_p^{\text{ref}}(r)$ approach finite limits both as $r \rightarrow 0$ and as $r \rightarrow \infty$ means that functions of these variables will also approach finite values in these limits. At the same time, the fact that $y_p^{\text{eq}}(r) \propto (r - r_e)$ and $y_p(r, r_{\text{ref}}) \propto (r - r_{\text{ref}})$ at distances near their respective expansion centre means that they will be

¹The change in program name from that used in the initial version of this code (`phiFIT`) was made to avoid confusion between the name of the exponent coefficient parameters and the the conventional representation for polar angles (θ and ϕ) when generalized versions of the EMO or MLR potential forms are used to represent multi-dimensional potential energy surfaces.

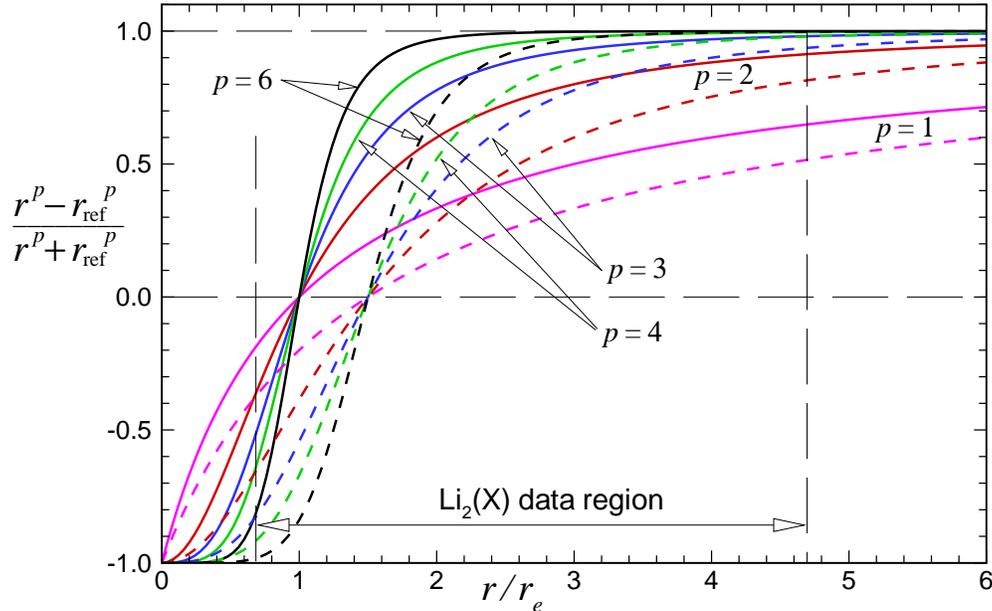


Figure 1. Illustrative plots of the expansion variables of Eqs. (1) and (2) showing the ‘data range’ associated with an analysis for the $X^1\Sigma_g^+$ state of Li_2 [6]. The solid curves are for the case $r_{\text{ref}} = r_e$ (variables $y_p^{\text{eq}}(r) = y_p(r; r_e)$), while the dashed curves are obtained for $r_{\text{ref}} = 1.5 r_e$.

effective expansion variables for properties that change significantly in those regions. This mapping of the infinite radial domain onto the finite interval $y_p(r) \in [-1, +1]$ greatly facilitates the imposition of proper theoretical constraints on the behaviour of the potential function at long range and in the very short-range region, and it means that functions defined as finite power series in $y_p(r)$ will not have singularities at either very small or very large values of r . Note that one of the models described below use two different expansion variables of this type that are defined by different values of the (integer) power p . In this case, a second (integer) label q ($q \neq p$) is introduced to identify that second radial variable.

The earlier work using this type of radial variable was based on the single variable $y_p^{\text{eq}}(r)$ of Eq. (1). [7, 8, 9, 10]. However, later work showed that use of an expansion variable $y_p^{\text{ref}}(r)$ centred at a distance $r_{\text{ref}} > r_e$ can, with no loss of accuracy, lead to much more compact and robust potential function expressions than could otherwise be obtained [6, 11, 12]. This is readily explained by the difference between solid and dashed curves for a given value of p shown in Fig. 1. For example, for $p = 4$ the solid curve for $y_4^{\text{eq}}(r)$ is flat and lies very close to its upper limit value of $+1$ over a significant fraction of the ‘data region’. As a result, expansions in that variable would be unable to accurately represent properties which vary significantly across this domain. In contrast, the corresponding variable $r_4^{\text{ref}}(r) = y_4(r; r_{\text{ref}} = 1.5 r_e)$ changes significantly across the whole data region, and hence can be expected to provide robust compact description of properties which vary across this whole domain.

The expansion variable of Eq. (1) is a special case of a more general expansion variable introduced by Šurkus *et al.* [5] (see § 2.5), who used it to represent the potential energy function as a simple power series in $y_p(r)$. In that case, the recommended value of p was based on the asymptotically-dominant inverse-power term in the long-range intermolecular potential for the state of interest. However, in other potential forms (see § 2.2–2.4) this power does not define the limiting long-range behaviour, and introduction of this parameter was based on our findings [13, 14, 15, 16, 17] that an expansion in powers of $y_p^{\text{eq}}(r)$ using some (small) integer power of $p > 1$ (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. This same concern with attaining physically reasonable extrapolation behaviour was also part of the motivation for introducing the option of setting r_{ref} at a (fixed) value differing from than the conventional molecular expansion centre of r_e .

In any case, values of p (and q , see §2.3) and r_{ref} must be selected by the user and specified in the main input data file. Some guidance regarding how to choose appropriate values of these parameters may be found below and in Refs. [8] and [11].

2.2 The Expanded Morse Oscillator (EMO) Potential Function

The first potential function form considered here is the *Expanded Morse Oscillator* or EMO function [18], which has the form of a Morse potential [19] in which the exponent coefficient varies with distance. Two other functions of this type were introduced earlier by other authors: the Generalized Morse Oscillator or ‘GMO’ potential of Coxon and Hajigeorgiou [20], and the Modified Morse Oscillator or ‘MMO’ potential of Dulick and co-workers [21]. However, because of its simpler structure and better extrapolation behaviour, only the EMO form is considered here. An EMO (or EMO_p) potential has the form

$$V_{\text{EMO}}(r) = \mathfrak{D}_e \left[1 - e^{-\beta(r) \cdot (r-r_e)} \right]^2 \quad (3)$$

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

$$\beta(r) = \beta_{\text{EMO}}(y_p^{\text{ref}}(r)) = \sum_{i=0}^{N_\beta} \beta_i y_p^{\text{ref}}(r)^i \quad (4)$$

While all currently published work based on this form used $r_{\text{ref}} = r_e$ (i.e., used $y_p^{\text{eq}}(r)$ in Eq. (4) rather than $y_p^{\text{ref}}(r)$), the latter is written here for the sake of generality.²

The EMO potential form has been used successfully in a number of demanding data analyses involving both ‘normal’ single-well potentials [18, 23, 17] and states whose potential functions have an additional ‘ripple’ [16]. However, the fact that $[\mathfrak{D}_e - V_{\text{EMO}}(r)]$ dies off exponentially at large r means that it provides a poor representation of electronic states for which the data extend fairly close to the dissociation limit. This shortcoming is addressed by the potential function forms described in § 2.3 and 2.4.

2.3 The Morse/Long-Range (MLR) Potential Function

At long range, all intermolecular potential functions may be described as a sum of inverse-power terms

$$V(r) \simeq \mathfrak{D} - \frac{C_{m_1}}{r^{m_1}} - \frac{C_{m_2}}{r^{m_2}} - \frac{C_{m_3}}{r^{m_3}} - \dots \quad (5)$$

in which the powers m_1, m_2, \dots etc., are determined by the nature of the atoms to which the given molecular state dissociates [24, 25, 26, 27, 28, 29], and the coefficients C_{m_i} may often be calculated from theory. For cases in which realistic estimates of one or more of the long-range potential coefficients C_{m_i} are available, it is always desirable to use a potential form with the limiting behaviour of Eq. (5), especially if the available experimental information extend fairly close to the dissociation limit \mathfrak{D} . These considerations instigated the development of the *Morse/Long-Range* or MLR potential energy function form [7, 8, 9, 6],

²In a previous version of this code [22], this exponent polynomial was broken into two, with different polynomial orders being used for $r > r_e$ and $r < r_e$. However, the flexibility provided by using $y_p^{\text{ref}}(r)$ as the expansion variable instead of $y_p^{\text{eq}}(r)$ has made this complication unnecessary.

$$V_{\text{MLR}}(r) = \mathfrak{D}_e \left\{ 1 - \frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} e^{-\beta(r) \cdot y_p^{\text{eq}}(r)} \right\}^2 \quad (6)$$

in which \mathfrak{D}_e is the well depth, r_e the equilibrium internuclear distance, the exponent coefficient $\beta(r) = \beta_{\text{MLR}}(y_p^{\text{ref}}(r))$ is a (fairly) slowly varying function of r , and $u_{\text{LR}}(r)$ is the attractive long-range form imposed by theory for a particular case,

$$u_{\text{LR}}(r) = \frac{C_{m_1}}{r^{m_1}} + \frac{C_{m_2}}{r^{m_2}} + \dots + \frac{C_{m_{\text{last}}}}{r^{m_{\text{last}}}} \quad (7)$$

while $u_{\text{LR}}(r_e)$ is its value at r_e . This function is an extended form of what was called the ‘Morse/Lennard-Jones’ or MLJ potential of Refs. [30, 31], which corresponded to the case in which the sum in Eq. (7) consisted of only a single inverse-power term and the pre-exponential factor collapsed to the factor $(r_e/r)^{m_1}$.³

A defining feature of the MLR function is the fact that both the exponential term in Eq. (6) and its pre-factor are equal to 1 at the equilibrium internuclear distance, r_e . Moreover, since $y_p^{\text{eq}}(r) \rightarrow +1$ and $y_p^{\text{ref}}(r) \rightarrow +1$ as $r \rightarrow \infty$, at large r Eq. (6) usually (see below) becomes simply

$$V_{\text{MLR}}(r) \simeq \mathfrak{D}_e - \left\{ \frac{2\mathfrak{D}_e e^{-\beta_\infty}}{u_{\text{LR}}(r_e)} \right\} u_{\text{LR}}(r) = \mathfrak{D}_e - u_{\text{LR}}(r) = \mathfrak{D}_e - \frac{C_{m_1}}{r^{m_1}} - \frac{C_{m_2}}{r^{m_2}} - \dots \quad (8)$$

Thus, the limiting asymptotic value (β_∞) of the exponent coefficient $\beta(r)$ is defined by the requirement that $\beta_\infty \equiv \lim_{r \rightarrow \infty} \beta_{\text{MLR}}(r) = \ln \{2\mathfrak{D}_e/u_{\text{LR}}(r_e)\}$.

In order to use the MLR potential form, it is clearly necessary to know appropriate values for the powers m_i , and to have realistic estimates of the coefficients C_{m_i} . If no realistic estimate of the leading (smallest-power) coefficient C_{m_1} is available, the MLR form has no significant advantages over the simpler EMO function, and the latter will probably be more ‘robust’. However, if the leading long-range term is the only one for which a reliable estimate of the coefficient C_{m_1} is available, experience suggests that more realistic extrapolation behaviour will be achieved if a second term with some plausible *ad hoc* estimate of C_{m_2} is also included.

The exponent coefficient function $\beta(r)$ must both asymptotically approach the value β_∞ defined above, and be sufficiently flexible that it provides an accurate description of the potential energy well. To this end, it is represented a polynomial in which the expansion variable $y_p^{\text{ref}}(r)$ effectively acts as a switching function constraining $\beta(r)$ to approach the specified asymptotic value, β_∞ [13, 14, 15, 7]:^{2,4}

$$\beta(r) = \beta_{\text{MLR}}(y_p^{\text{ref}}(r)) = y_p^{\text{ref}}(r) \beta_\infty + \left[1 - y_p^{\text{ref}}(r) \right] \sum_{i=0}^{N_\beta} \beta_i y_q^{\text{ref}}(r)^i \quad (9)$$

Note that this expression is defined in terms of two different reduced radial variables, $y_p^{\text{ref}}(r)$ and $y_q^{\text{ref}}(r)$. Although most of the early work with this model was performed with $q=p$, it has since been shown that use of a separate power $q < p$ in the power-series portion of Eq. (9) can lead more compact and robust potential functions [6, 11, 12].²

We must also take account of the limiting long-range behaviour of the exponent term in Eq. (6) [8, 6]:

³ In the early work that potential was called a *Modified Lennard-Jones* (MLJ) oscillator. However, since elimination of the exponential term yields a Lennard-Jones($2m_1, m_1$) potential, while elimination of the $(r_e/r)^{m_1}$ term yields a Morse-like potential function, its algebraic form suggests that *Morse/Lennard-Jones* is a more appropriate name.

⁴ In earlier versions of the model an exponential switching function was used [30, 32, 33, 31, 34, 35], but that form adds more complexity with no significant advantages.

$$e^{-\beta(r) \cdot y_p^{\text{eq}}(r)} \simeq e^{-\beta_\infty} \left(1 + \frac{A_p}{r^p} + \frac{A_{p,q}}{r^{p+q}} + \dots \right) = \frac{u_{\text{LR}}(r_e)}{2\mathfrak{D}_e} \left(1 + \frac{A_p}{r^p} + \frac{A_{p,q}}{r^{p+q}} + \dots \right) \quad (10)$$

In order to prevent this exponential factor from making the actual long-range behaviour differ from that specified by Eq. (7), the integer p defining the radial variable of Eq. (1) *must* be greater than the difference between the largest and smallest (inverse) powers of the terms included in the chosen definition of $u_{\text{LR}}(r)$: $p > (m_{\text{last}} - m_1)$ [6, 11]. In practice, it is often desirable to set p equal to the difference between the leading power m_1 and the power of the first long-range term predicted by theory which is *not* included in the chosen definition of $u_{\text{LR}}(r)$, $p = (m_{\text{next}} - m_1)$, as this means that the leading contribution of Eq (10) to the long-range potential would have the same qualitative radial behaviour as that first missing term, $1/r^{\text{next}}$.

In some cases, the above condition will require the use of relatively large values of p (e.g., $p \geq 6$). When this occurs the radial variable $y_p(r)$ may be almost flat and close to its upper limit over a relatively wide range of r . This is the problem that led to introduction of the separate integer q to define the radial variable inside the power series part of Eq.(9) with (usually) $q < p$ [6]. Equation (10) shows that if p is defined as specified above, the choice of q has no effect on the limiting long-range behaviour defined by $u_{\text{LR}}(r)$. Note, however, that for very small values of q (e.g., 1 or 2), $\beta(r)$ is more likely to misbehave in the extrapolation regions at very short distances, and/or the interval between the ‘data region’ and the long-range region where the potential finally takes on the form $\mathfrak{D}_e - u_{\text{LR}}(r)$ [13, 14]. On the other hand, for large values of q , as r increases, the variable $y_q^{\text{ref}}(r)$ will lie very close to its limiting value of $+1$ over an increasingly wide range of r , and the order of polynomial required to attain a satisfactory fit to the input points may become relatively large [6].

One final point concerns the unusual case in which the powers m_i in Eq.(7) have values such that $2 \times m_1 \leq m_2$ (for example when $m_1 = 3$ and $m_2 = 6$). In this case the quadratic term in Eq.(6) will give rise to a second $1/r^{m_2}$ term that will make the effective long-range behaviour differ from the specified $u_{\text{LR}}(r)$ function.[6]. If this occurs one should adjust the value used for the second long-range coefficient C_{m_2} in the manner illustrated by Eq. (14) of Ref. [6].

2.3.1 A More General Definition of $u_{\text{LR}}(r)$: Inclusion of Damping Functions

While all potential energy functions take on the limiting behaviour of Eq.(5) at very large r , at shorter distances, overlap of the electron distributions of the interacting atoms reduces the strength of the interaction energies associated with the even-inverse-power ‘dispersion’ terms contributing to this expression. This consideration led a number of groups to propose models for representing this ‘damping’ behaviour [36, 37, 38, 39, 40]. Another consideration here is the fact that the quadratic term in Eq. (6), which defines the short range repulsive wall of an MLR potential, contains the factor $[u_{\text{LR}}(r)]^2$. As a result, if there is no damping, at very short range the strength of this term will grow as $1/r^{2m_{\text{last}}}$ which is much steeper than the usual exponential-type behaviour expected for the repulsive wall of a normal potential energy function. These concerns led to introduction of an (optional) alternate definition for the long-range potential incorporated in Eq. (6):

$$u_{\text{LR}}(r) = D_{m_1}(r) \frac{C_{m_1}}{r^{m_1}} + D_{m_2}(r) \frac{C_{m_2}}{r^{m_2}} + \dots + D_{m_{\text{last}}}(r) \frac{C_{m_{\text{last}}}}{r^{m_{\text{last}}}} \quad , \quad (11)$$

in which $D_m(r)$ are called ‘‘damping functions’’. Following the discussion of Ref. [11], two families of damping functions are allowed here: a generalized version of a function introduced by Douketis *et al.* [38],

$$D_m^{\text{ds}(s)}(r) = \left\{ 1 - \exp \left(- \frac{b^{\text{ds}}(s)(\rho r)}{m} - \frac{c^{\text{ds}}(s)(\rho r)^2}{m^{1/2}} \right) \right\}^{m+s}, \quad (12)$$

and a generalized version of the Tang-Toennies [39] damping function,⁵

$$D_m^{\text{tt}(s)}(r) = 1 - e^{-b^{\text{tt}}(s) \cdot (\rho r)} \sum_{k=0}^{m-1+s} \frac{[b^{\text{tt}}(s) \cdot (\rho r)]^k}{k!}. \quad (13)$$

in which r has units Å, and ρ is a dimensionless, system-dependent scaling factor. For both of these families of functions the limiting short-range behaviour is given by

$$\lim_{r \rightarrow \infty} \left\{ D_m^{(s)}(r)/r^m \right\} \propto r^s. \quad (14)$$

As a result, when Eq.(11) is incorporated into an MLR potential, one must set $s \leq 0$ to prevent the potential from turning over and going to zero as $r \rightarrow 0$.

Scoles and co-workers suggested that such damping functions be defined by reference to the accurately-known [41] damping of the leading dispersion terms in the long-range potential for two ground-state H atoms [36, 38, 40]. Least-squares fits to those H-atom results yielded values of the system-independent parameters $b^{\text{ds}}(s)$, $c^{\text{ds}}(s)$, and $b^{\text{tt}}(s)$ for a range of values of the limiting short-range power s of Eq. (14) [11], and they are stored within the code. Following Ref. [38], it is suggested that the system-dependent scaling parameter for molecule AB be defined as $\rho \equiv \rho^{\text{AB}} = [2\rho^{\text{A}}\rho^{\text{B}}/(\rho_d^{\text{A}} + \rho^{\text{B}})]$, where $\rho^{\text{A/B}}$ is defined in terms of the ratio of the ionization potential of the atom of interest to that for ground-state atomic hydrogen: $\rho^{\text{A}} \equiv (I_p^{\text{A}}/I_p^{\text{H}})^{2/3}$.

Program `betaFIT` allows a user to choose to define $u_{\text{LR}}(r)$ in terms of either Eq. (7) or (11), to use either Eq. (12) or Eq. (13) to represent the damping function, and to choose a value for the limiting short-range power, s . However, Ref. [11] recommended the use of a Douketis-type damping functions Eq. (12) with $s = -1$.

2.3.2 Treatment of Interstate Coupling near the Asymptote: States of Li_2 dissociating to $\text{Li}(2S) + \text{Li}(2P)$

The above discussion of the MLR form focused on use of the inverse-power sums of Eqs. (7) or (11) to represent the long-range potential. However, there is no need to restrict $u_{\text{LR}}(r)$ to these forms, and in recent applications to states of Li_2 dissociating to the $\text{Li}(^2P_{1/2}) + \text{Li}_2(^2S_{1/2})$ asymptote, $u_{\text{LR}}(r)$ has been represented by one of the roots of a diagonalization arising from two-state [6] or three-state [12] coupling near that asymptote. In particular, the theory of this interstate mixing presented in Refs. [42, 43] shows that the expression for the 2×2 roots may be written in closed form as

$$\begin{aligned} u_{\text{LR}}^{\text{A-F}}(r) = & -\frac{A_{\text{so}}}{2} + \frac{C_3^{\Sigma} + C_3^{\Pi}}{2r^3} + \frac{C_6^{\Sigma} + C_6^{\Pi}}{2r^6} + \frac{C_8^{\Sigma} + C_8^{\Pi}}{2r^8} \\ & \pm \frac{1}{2} \left\{ \left(\frac{C_3^{\Sigma} - C_3^{\Pi}}{3r^3} + \frac{C_6^{\Sigma} - C_6^{\Pi}}{3r^6} + \frac{C_8^{\Sigma} - C_8^{\Pi}}{3r^8} - A_{\text{so}} \right)^2 \right. \\ & \left. + 8 \left(\frac{C_3^{\Sigma} - C_3^{\Pi}}{3r^3} + \frac{C_6^{\Sigma} - C_6^{\Pi}}{3r^6} + \frac{C_8^{\Sigma} - C_8^{\Pi}}{3r^8} \right)^2 \right\}^{1/2} \end{aligned} \quad (15)$$

⁵The original Tang-Toennies [39] damping function was the normalized incomplete gamma function of order $(m+1)$ which corresponds to the case $s = +1$.

in which A_{so} is the (positive) difference between the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ atomic spin-orbit level energies, and C_m^Σ / C_m^Π are the long-range coefficients associated with the relevant coupled states [6]. Use of the ‘+’ sign in front of the square root term yields the correct long-range tail for the $A^1\Sigma^+$ state, while use of the ‘-’ sign yields that for the 0_u^+ component of the $b^3\Pi_u$ state [42]. The analogous theory for the long-range tail of the $1^3\Sigma_g^+$ state potential, which involves 3-state coupling near the asymptote is described in Ref. [12].

The ease with which **betaFIT** can treat these special cases further illustrates capabilities of the MLR functional form.

2.3.3 A Spline-Pointwise Representation of the MLR Exponent Coefficient $\beta(r)$

All existing applications of the MLR potential have been based on use of a polynomial function such as Eq. (9) to represent the exponent coefficient $\beta(r)$. However, while preliminary work showed some promise [44, 45], it is not yet clear whether this form can provide a practical, compact and accurate representation of double-minimum potentials or of shelf-state potentials. A novel approach introduced by Pashov and co-workers [46, 47, 48] in which the potential is defined as a cubic spline through a set of points whose energies are the parameters of the model has proved remarkably successful for treating such systems. However, a relatively large number of points (typically $\gtrsim 50$) are required to define a potential accurately in this way, and the theoretically predicted inverse-power long-range tail may only be attached in an *ad hoc* manner.

An alternative approach now under investigation [49] is the ‘Spline-Exponent-MLR’ (SE-MLR) function which uses Pashov’s ‘spline-pointwise’ approach to define the exponent coefficient $\beta(r)$ in the MLR potential function form of Eq. (6). In particular, $\beta(r)$ is defined as a ‘natural’ cubic spline function passing through $\beta(r_j) = \beta(y_q^{\text{ref}}(r_j))$ values at a specified set of $y_q^{\text{ref}}(r_j)$ values, and those $\beta(r_j)$ values become the parameters defining the shape of the potential. Following the approach of Pashov [46, 50], the exponent coefficient function is written as

$$\beta(r) = \sum_{k=1}^{N_\beta} S_k(y_q^{\text{ref}}(r)) \beta_k \quad (16)$$

in which the spline ‘basis functions’ $S_k(y_p^{\text{ref}}(r))$ are completely defined by the chosen mesh of values of $y_q^{\text{ref}}(r_j)$. A very straightforward application of the chain rule of calculus then yields the partial derivatives required for the least-squares fit procedure:

$$\frac{\partial V(r)}{\partial \beta_k} = 2 \mathfrak{D}_e \left\{ 1 - \frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} e^{-\beta(r) \cdot y_p^{\text{eq}}(r)} \right\} \left(\frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} e^{-\beta(r) \cdot y_p^{\text{eq}}(r)} \right) y_p^{\text{eq}}(r) S_k(y_q^{\text{ref}}(r)) \quad (17)$$

Although the least-squares problem is non-linear, the fact that the $S_k(y_p^{\text{ref}}(r))$ functions do not depend on the parameter values $\{\beta_k\}$ leads to some computational simplifications.

In using the SE-MLR form, it is important to realize that the radial variable $y_q^{\text{ref}}(r)$ used to define $\beta(r)$ should be defined by a value of r_{ref} that is significantly greater than r_e . This is necessary in order to assure that the chosen mesh of points samples the full range of $\beta(y_q^{\text{ref}}(r))$ values appropriately. This consideration is illustrated by Fig. 2 which compares the SE-MLR exponent coefficient functions determined from fits to an extensive data set for the $X^1\Sigma_g^+$ state of Ca_2 [51, 8, 49] that were performed using, in turn $r_{\text{ref}} = r_e$ (blue points, curve and lines), and $r_{\text{ref}} = 1.5 r_e$ (red points, curve and lines). Both of these cases placed two points, equally-spaced in $y_q^{\text{ref}}(r)$, at $r < r_e$ and 14 points, equally-spaced in $y_q^{\text{ref}}(r)$ at $r > r_e$, together with one point at $r = r_e$ and one at $y_q^{\text{ref}} = 1$, which corresponds to the limit $r \rightarrow \infty$. It is intuitively clear

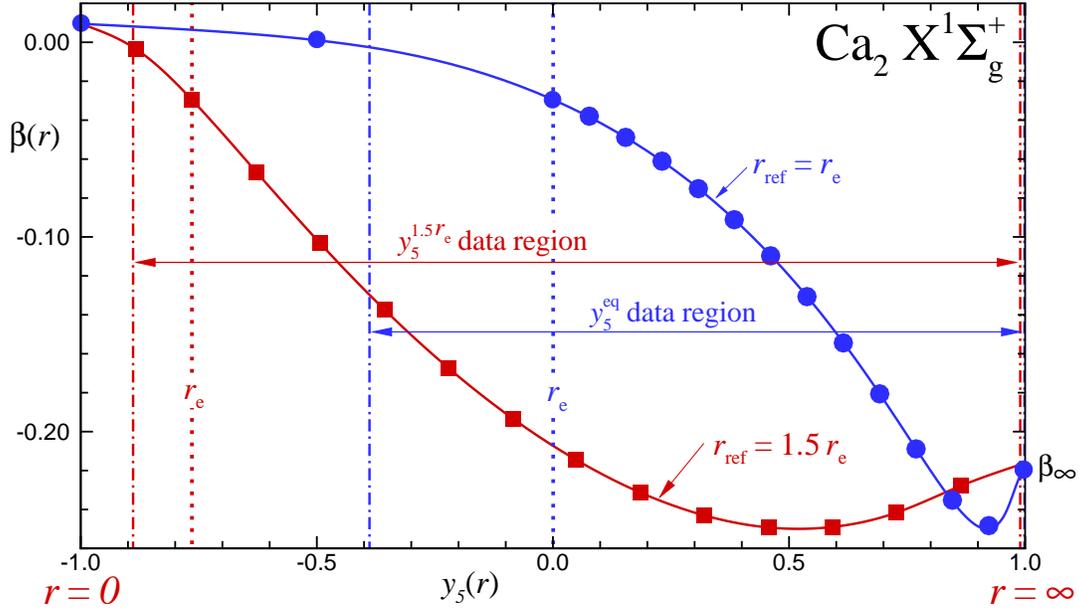


Figure 2. Comparison of $\beta(y_q^{\text{ref}}(r))$ functions for ground-state Ca_2 determined from DPFs of spectroscopic data to SE-MLR models based on $r_{\text{ref}} = r_e$ (round points, blue curve and lines), and $r_{\text{ref}} = 1.5 r_e$ (square points, red curve and lines) [Figure taken from Ref. [49], with permission].

that using the same number of spline points, it will be easier to obtain an accurate description of $\beta(r)$ using points based (in this case) on $r_{\text{ref}} = 1.5 r_e$.⁶

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

A need for a flexible analytic potential function form with a barrier that protrudes above the potential asymptote at distances $r > r_e$ instigated the development of the *double-exponential/long-range* (DELR) potential function model [13, 15].⁷ This function is written as:

$$V_{\text{DELR}}(r) = \left\{ A e^{-2\beta(r)\cdot(r-r_e)} - B e^{-\beta(r)\cdot(r-r_e)} + \mathfrak{D}_e \right\} - u_{\text{LR}}(r) \quad (18)$$

in which the exponent coefficient $\beta(r)$ is defined as the same type of simple power series in $y_p^{\text{ref}}(r)$ used for the EMO_p potential (see Eq. (4)). In its original form [15, 22], different power-series orders were used for $r \leq r_e$ and $r > r_e$. However, the subsequent introduction of a variable expansion centre r_{ref} has superseded the need for that capability.² The additive function $u_{\text{LR}}(r)$, which may be attractive or repulsive, represents the potential at large values of r . It is this term that was used to represent the repulsive barrier in the application of this function to the $B^1\Pi_u$ state of Li_2 in Ref. [15]. The pre-exponential coefficients A and B are defined in terms of the well depth \mathfrak{D}_e (relative to the potential asymptote) and equilibrium distance r_e by the expressions

$$A = \mathfrak{D}_e - u_{\text{LR}}(r_e) - u'_{\text{LR}}(r_e)/\beta_0, \quad (19)$$

$$B = 2\mathfrak{D}_e - 2u_{\text{LR}}(r_e) - u'_{\text{LR}}(r_e)/\beta_0, \quad (20)$$

⁶ Note that the SE-MLR option is not yet fully implemented.

⁷ Note that the sign convention for the long-range term $u_{\text{LR}}(r)$ in the DELR potential has been changed from that of Refs. [13, 15] in order to make it consistent with that used for the MLR potential form.

in which $u'_{\text{LR}}(r_e) \equiv [du_{\text{LR}}(r)/dr]_{r=r_e}$ [15]. If $u_{\text{LR}}(r)=0$ the DELR potential become the EMO function of Eq. (3). However, other choices of $u_{\text{LR}}(r)$ could allow it to represent the outer wall of a potential function with a barrier [15], the attractive tail of a regular single-minimum potential, or the outer well of a double-minimum or shelf-state potential. In general, $u_{\text{LR}}(r)$ should be represented by the damped long-range expansion of Eq. (11), rather than by the undamped expansion of Eq. (7), since the short-range singularities of attractive inverse-power terms in the latter would cause the potential energy function to turn over at small distances. Note, however, that one must set the damping function short-range parameter $s \geq 0$ if the higher-order C_{m_i} coefficients are positive (attractive), since otherwise the negative singularities implied by Eq. (14) would cause the potential wall to turn over at small r . Of course, other damping function expressions [37, 40] or entirely different types of expressions for $u_{\text{LR}}(r)$ could be used in the DELR type of potential form.

2.5 Šurkus' Generalized Potential Energy Function (GPEF)

The fourth family of potential functions implemented in `betaFIT` is a generalization of the familiar Dunham polynomial potential [1] which Šurkus *et al.* [5] introduced and called the *Generalized Potential Energy Function* (GPEF). Using the modified (but exactly equivalent) expression for his expansion variable devised by Seto [52], the GPEF potential form is

$$V_{\text{GPEF}}(r) = c_0 z_p^2 \left[1 + \sum_{m=1}^N c_m z_p^m \right] \quad \text{where} \quad z_p = \frac{(r^p - r_e^p)}{(a_S r^p + b_S r_e^p)} . \quad (21)$$

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 the Dunham expansion variable:
 $z = (r - r_e)/r_e$ [1].
- Setting $p=1$, $a_S=1$ and $b_S=0$ yields the Simons-Parr-Finlan (SPF) expansion variable:
 $z = (r - r_e)/r$ [2].
- Setting $p = 1$, $a_S = b_S = 0.5$ yields the Ogilvie-Tipping (OT) potential expansion variable:
 $z = 2(r - r_e)/(r + r_e)$ [4].
- Setting $a_S=b_S=1$ yields the expansion variable of Eq. (1).
- Setting $p = 1$, $a_S = 1$ and fixing b_S at some small value yields the type of asymmetric expansion variable used by Tiemann and coworkers [51, 53].

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, this type of expansion can in principle be required to have the theoretically predicted limiting long-range behaviour of Eq. (5) [5, 54]. However, except for the relatively simple case in which p is set equal to the power of the leading long-range term in Eq. (5) [5], such constraints have proved to be too unwieldy for practical use.

3 Using betaFIT

3.1 Methodology

The first three of the potential function forms described above are based on an exponential term whose exponent coefficient $\beta(r)$ is expanded as a power series in a radial variable with the form of $y_p^{\text{ref}}(r)$ of Eq. (2). Such potentials are non-linear functions of the expansion coefficients β_i , so an approximate method must be used to produce the realistic initial trial values of these parameters required to initiate the non-linear least-squares fits. In **betaFIT** this is done by first fitting to a linearized version of the potential function equation. For example, Eq. (3) for the EMO potential may be re-arranged to yield the expression:

$$-\ln \left\{ 1 \pm \sqrt{\frac{V(r) - \text{VMIN}}{\mathfrak{D}_e}} \right\} = (r - r_e) \beta(r) = (r - r_e) \sum_{i=0} \beta_i y_p^{\text{ref}}(r)^i, \quad (22)$$

in which the + and - signs, respectively, correspond to points on the inner ($r < r_e$) and outer branches of the potential. Values of the logarithmic term in Eq. (22) are defined by the input data points, and the resulting expression is a linear function of the expansion parameters β_i . Thus, if plausible initial values of the physical parameters $r_e = \text{Re}$, $\mathfrak{D}_e = \text{De}$ and the energy of the potential minimum VMIN are supplied in the input data file, a simple linear fit to Eq. (22) yields realistic values of the β_i parameters for use in the subsequent direct non-linear fits to Eq. (3). While the algebra is a little more complicated, essentially the same approach is used to determine expansion parameters for an MLR potential, with Eq. (9) being used to represent the exponent coefficient $\beta(r)$. In particular:

$$\begin{aligned} -\ln \left\{ \left(1 \pm \sqrt{\frac{V(r) - \text{VMIN}}{\mathfrak{D}_e}} \right) \frac{u_{\text{LR}}(r_e)}{u_{\text{LR}}(r)} \right\} &= y_p^{\text{eq}}(r) \beta(r) \\ &= y_p^{\text{eq}}(r) \left\{ y_p^{\text{ref}}(r) \beta_\infty + [1 - y_p^{\text{ref}}(r)] \sum_{i=0} \beta_i y_q^{\text{ref}}(r)^i \right\} \end{aligned} \quad (23)$$

As was the case for the EMO potential, the logarithmic term on the left-hand side of Eq. (23) is a simple linear function of the β_i exponent expansion parameters.

For the case of an SE-MLR potential, in which the $\beta(r)$ is represented by a spline function passing through a specified set of $y_q^{\text{ref}}(r_i)$ values,⁶ essentially the same linearization procedure applies. However, this step must avoid use of a mesh point corresponding to $r = r_e$ (or $y_p^{\text{eq}}(r) = 0$), since division of the left-hand side of Eq. (23) by $y_p^{\text{eq}}(r)$ would lead to division by zero.

For the DELR potential the situation is a little more complicated, since in the analog of Eq. (22),

$$\beta(r) (r - r_e) = -\ln \left\{ \frac{B}{2A} \pm \sqrt{\frac{V(r) - \text{VMIN} - \mathfrak{D}_e + u_{\text{LR}}(r)}{A} + \left(\frac{B}{2A} \right)^2} \right\} = (r - r_e) \sum_{i=0} \beta_i y_p^{\text{ref}}(r)^i, \quad (24)$$

the logarithmic term depends on the value of β_0 through the definitions of A and B (see Eqs. (19) & (20)). Thus, it is necessary to use Eq. (24) iteratively to generate a self-consistent set of trial β_i values. However, experience indicates that virtually any non-zero initial trial value of β_0 will serve as an adequate starting point, so this apparent problem presents no practical difficulty.

3.2 Uncertainties and Parameter Rounding

In general, in any least-squares fit each datum should be weighted by the inverse square of its uncertainty. The current version of `betaFIT` allows all input potential points to be equally weighted by the common read-in uncertainty `UNC`, but if the value input for `UNC` is set ≤ 0.0 , the program will read in a separate uncertainty u_i for each datum i . The quality of a fit of an M -parameter model to N input data which yields the predicted quantities $\{y_{\text{calc}}(i)\}$, is indicated by the value of the dimensionless root mean square deviation

$$\text{DRMSD} \equiv \overline{dd} = \left\{ \frac{1}{N} \sum_{i=1}^N \left[\frac{y_{\text{calc}}(i) - y_{\text{obs}}(i)}{u(i)} \right]^2 \right\}^{1/2} \quad (25)$$

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

In addition to reporting the 95% confidence limit (approximately ‘two-sigma’) uncertainty in each fitted parameter, `betaFIT` follows the approach of Ref. [55] by always also listing the associated ‘‘parameter sensitivity’’ (identified as `PS` in the output). This quantity is defined (see Eq. (4) of Ref. [55]) 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 uncertainties) on the ability of the resulting parameter set to accurately predict the input data. For the illustrative cases considered in Ref. [55], 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 `betaFIT` is its (optional) implementation of the automated ‘‘sequential rounding and refitting’’ (SRR) procedure of Ref. [55], 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 is turned on or off by the value of the flag `IROUND` which is set by the user in the input data file. One might choose to turn this flag off (set `IROUND=0`) for preliminary analyses, and turn it on when one wishes to generate a final parameter set to report and distribute. However, in the present application the difference in absolute computation time for these two cases is very small. As discussed in Ref. [55], in most cases setting `IROUND=±1` yields a maximum degree of rounding without significant loss of precision (the author prefers `IROUND=-1`). However, in some cases it may be necessary to set $|\text{IROUND}| > 1$.

3.3 Input/Output Conventions, and Program Execution

The array dimensions assumed by `betaFIT` are set by parameter statements in lines #8, 1093, and 1623 of the code, and may be changed by a user, as needed. The current settings allow for up to 1501 input potential function points and up to 40 expansion parameters, while the long-range tail of Eq. (7) or (11) may include up to 15 terms.

`betaFIT` requires one input data file, which is read on Channel 5, and it writes its main output to Channel 6. A compact supplementary listing of the results of each fit in a form that facilitates their being incorporated into input instruction files for program `DPOTFIT` [56] is also written to channel 7. If desired, listings of values of the resulting functions are written to Channel 8. The structure of the input data file and the definitions of and options for the various input quantities are presented in Section 4.

4 Data File Structure and Input Parameter Definitions

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

The logical structure and read statements governing the parameters describing the system to be treated, specifying the type of fit to be carried out, and specifying any necessary system parameters, is shown below. The following subsection then provides a detailed description of the nature and/or options associated with each of the input variables.

```
#1  READ(5,*) PSEL, NTP, UNC, IROUND, LPPOT, prFIT, prDIFF
#2  READ(5,*) Re, De, VMIN
#3  READ(5,*) IFXRe, IFXDe, IFXVMIN
    IF(PSEL.EQ.2).OR.PSEL.EQ.3) THEN
#4      READ(5,*) NCMM, rhoAB, sVSR2, IDSTT, APSE yMIN
        DO m=1, NCMM
#5          READ(5,*) (MMLR(m), CmVAL(m)
            ENDDO
        ENDIF
#6  IF(PSEL.EQ.4) READ(5,*) as, bs
#7  IF(UNC.GT.0.d0) READ(5,*) (RTP(i), VTP(i), i= 1,NTP)
#8  IF(UNC.LE.0.d0) READ(5,*) (RTP(i), VTP(i), uVTP(i), i= 1,NTP)
20  CONTINUE
#9  READ(5,*, END= STOP) p, q, NS, NL, Rref
#10 IF(LPPOT.GT.0) READ(5,*) NPR, RPR1, dRPR
    {perform fit, and then repeatedly return for another case}
    GO TO 20
```

4.2 Definitions and Descriptions for the Channel-5 Input File Data

Read integers identifying the molecule or system.

#1. READ(5,*) PSEL, NTP, UNC, IROUND, LPPOT, prFIT, prDIFF

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

If PSEL = 1 use the Expanded Morse Oscillator (EMO) form of § 2.2. For $N = 0$ this yields the conventional 3-parameter Morse function.

If PSEL = 2 use the Morse/Long-Range (MLR) potential form of § 2.3 which has one or more specified inverse-power long-range terms.

If PSEL = 3 use the Double-Exponential/Long-Range (DELR) form of § 2.4 which has one or more specified inverse-power long-range terms.

If PSEL = 4 use Seto's modification [52] of Šurkus' Generalized Potential Energy Function (GPEF) [5] of § 2.5. The parameters p , a_S and b_S are input through READs #6 and 9.

- Dunham expansions are generated by setting $p = 1$, $a_S = 0$ & $b_S = 1$.
- SPF expansions are generated by setting $p = 1$, $a_S = 1$ & $b_S = 0$.
- Ogilvie-Tipping expansions are generated by setting $p = 1$, $a_S = b_S = 0.5$.
- 'Hannover'-type polynomials [51, 53] are generated by setting $p = 1$ and $a_S = 1$

NTP is the (integer) number of potential function points to be read in.

If UNC > 0.0 it is the (real number) uncertainty assigned to all input potential function values.

If the input value of UNC ≤ 0.0, read in an independent uncertainty for each datum.

IROUND: Setting (integer) IROUND ≠ 0 causes the "sequential rounding and refitting" procedure of Ref. [55] to be implemented, with each parameter being rounded at the |IROUND|'th significant digit of its uncertainty. If IROUND > 0 the 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 (recommended). If `IROUND=0` the fit simply stops after full convergence and performs no parameter rounding.

`LPPOT` controls whether (`LPPOT > 0`) or not (`LPPOT ≤ 0`) `betaFIT` will print to Channel 8 a listing of potential energy and exponent coefficient values, on the range and mesh specified in `READ #10`.

`prFIT` is an integer flag which controls the level of printout by `betaFIT`. For `prFIT ≤ 0` print only the final results for each case (normal setting). If `prFIT = 1` also print results of the initial linearized fit and of subsequent intermediate non-linear fits; the latter option creates more output, which may prove illuminating in cases for which the final fit fails to converge. If `prFIT = 2 – 5` also print parameter changes and convergence tests in every non-linear fitting cycle. Normally set `prFIT=0`.

`prDIFF` is an integer specifying whether (for `prDIFF > 0`) or not (for `prDIFF ≤ 0`) the output will include a listing of the residual discrepancies $\{y_{\text{calc}}(i) - y_{\text{obs}}(i)\}$ for each case. Normally set `prDIFF = 0`.

#2. `READ(5,*) Re, De, VMIN`

`Re, De & VMIN` are the (real number) initial trial values of the equilibrium distance, well depth, and absolute energy at the potential minimum. Realistic (but not necessarily accurate) values of these parameters are required for the approximate linearized fit which precedes non-linear fitting to Eq. (3), (6), or (18).

#3. `READ(5,*) IFXRe, IFXDe, IFXVMIN`

`IFXRe, IFXDe & IFXVMIN` are integers which control whether the values of `Re, De` and `VMIN`, respectively, are to be varied in the fit (`IFXxx ≤ 0`), or to be held fixed at the input trial value (`IFXxx > 0`). While one would normally want to set all three `≤ 0`, high-order fits with \mathcal{D}_e free may sometimes be unstable.

For the case of an MLR or DELR potential (`PSEL=2` or `3`), read parameters specifying properties of the long-range tail function $u_{\text{LR}}(r)$; for other cases, skip `READ` statements #4 & 5.

#4. `IF((PSEL.EQ.2).OR.(PSEL.EQ.3)) READ(5,*) NCMM, rhoAB, sVSR2, IDSTT, APSE, yMIN`

`NCMM` is the number of inverse-power long-range terms to be incorporated into $u_{\text{LR}}(r)$ via Eq. (7) or (11), or to be included in the terms defining the 2×2 $u_{\text{LR}}(r)$ function of Eq. (15) or the 3×3 diagonalization of Ref. [12]. For the two latter Li_2 cases, set `NCMM = 6` with `MMLR(i) = 3, 0, 6, 6, 8, & 8`, where the input value of `CmVAL(i)` are $C_3^\Sigma, A_{\text{so}}, C_6^\Sigma, C_6^\Pi, C_8^\Sigma$ and C_8^Π for $i = 1 - 6$, respectively.

- For the $A^1\Sigma_u^+$ state of Li_2 , set `MMLR(2) = 0`.
- For the $1^3\Sigma_g$ state of Li_2 , set `MMLR(2) = -1`.
- For the $b^3\Pi_u$ state of Li_2 , set `MMLR(2) = -2`.

`rhoAB` is the dimensionless system-dependent parameter $\text{rhoAB} = \rho = \rho^{\text{AB}}$ appearing in the damping function of Eqs. (12) and (13). If the read-in value of `rhoAB ≤ 0.0`, omit damping functions and define the long-range tail of the MLR potential by Eq. (7).

If integer `IDSTT > 0` the damping functions are represented by the generalized Douketis-Scoles type function of Eq. (12).

If integer `IDSTT ≤ 0` the damping functions are represented by the generalized Tang-Toennies function of Eq. (13).

If damping functions are used, integer `sVSR2` is twice the value of the very-short-range power parameter ‘*s*’ of Eqs. (12)-(14) (`sVSR2 = 2s`). For generalized Tang-Toennies type functions its allowed values are -4 -2, 0, 2, or 4, while for generalized Douketis-type functions, its allowed values are -4, -3, -2, -1, or 0.

If integer `APSE` ≤ 0 , use Eq.(9) to define $\beta(r)$ for an MLR potential, and `yMIN` is a dummy parameter.

If integer `APSE` > 0 , the exponent coefficient in the MLR potential is defined by a spline-pointwise function, as outlined in §2.3.2.⁶ In this case, $\beta(r)$ is defined by a natural cubic spline function through its values at N_S equally spaced points on the interval $y_q^{\text{ref}}(r) \in [\text{yMIN}, 0)$, a point at $y_q^{\text{ref}} = 0.0$, and N_L equally spaced points on the interval $y_q^{\text{ref}}(r) \in (0, +1]$. Note that $-1.0 \leq \text{yMIN} < 0.0$, and that the total number of spline points is $N_S + N_L + 1$. Values of N_S and N_L are input via `READ #9`.

For an MLR or DELR potential (`PSEL` = 2 or 3), loop over the NCMM inverse-power terms, reading in the power `MMLR(m)`, and a value for that coefficient `CmVAL(m)`.

```
IF((PSEL.EQ.2).OR.(PSEL.EQ.3)) THEN
  DO m= 1,NCMM
#5. IF((PSEL.EQ.2).OR.(PSEL.EQ.3)) READ(5,*) (MMLR(m), CmVAL(m)
    END DO
  END IF
```

If `PSEL` = 4, read in the parameters defining the expansion variable in the GPEF potential of Eq. (21). For other cases, skip `READ #6`.

```
#6. IF(PSEL.EQ.4) READ(5,*) as, bs
  In the GPEF radial expansion variable of Eq.(21):  $a_S = \text{as}$  and  $b_S = \text{bs}$ , while p is input below via READ #9.
```

Read the NTP distances `RTP(i)` and energies `VTP(i)` defining the potential function to be fitted. If `UNC` < 0.0 also read in an uncertainty `uVTP(i)` for each point.

```
#7. IF(UNC.GT.0.d0) READ(5,*) (RTP(i), VTP(i), i = 1,NTP)
#8. IF(UNC.LE.0.d0) READ(5,*) (RTP(i), VTP(i), uVTP(i), i= 1,NTP)
```

Finally, read in parameters specifying the type of fit to be performed. This `READ` statement is in a loop which allows *any* number of different fits to be performed in the same run. The loop stops when the end of the data file is reached, or if the input value of `p` is < 0 .

```
#9. READ(5,*) p, q, NS, NL, RREF
  p and q are the integer powers  $p$  and  $q$  defining the radial variables  $y_p^{\text{eq}}(r)$  of Eq. (1),  $y_p^{\text{ref}}(r)$  and  $y_q^{\text{ref}}(r)$  of Eqs. (2), (4) and (9), or  $z_p(r)$  of Eq. (21). Except for the case of an MLR potential,  $q$  is a dummy parameter.
```

For `PSEL` = 1 – 3 and `APSE` ≤ 0 , `NL` = N_β is the polynomial order of the potential function exponent coefficient expansion of Eq. (4) or (9), and `NS` is a dummy variable.

For `PSEL` = 2 and `APSE` > 0 ,⁶ N_S and N_L are the numbers of exponent-coefficient spline points on the intervals $y_p^{\text{eq}}(r) \in (\text{yMIN}, 0.0)$ and $y_p^{\text{eq}}(r) \in (0.0, +1.0]$, respectively (see `READ #4`).

For `PSEL` = 4, perform a series of fits with the order of the GPEF polynomial expansion ranging from `NS` to `NL`. For this case, `q` and `RREF` = r_{ref} are dummy parameters.

`RREF` defines the reference distance in the potential function exponent expansion variable $y_p^{\text{ref}}(r) = y_p(r; r_{\text{ref}})$ of Eq. (2) to be:

- the (in general variable) potential function equilibrium distance r_e , if `RREF` ≤ 0 .
- the fixed read-in value of `RREF`, if `RREF` > 0 .

For a GPEF potential, `RREF` is a dummy variable.

```
#10. IF(LPPOT.GT.0) READ(5,*) NPR, RPR1, dRPR
```

`NPR` specifies the number of distances at which the fitted potential function is to be calculated and written to Channel 8.

- If $\text{NPR} \leq 0$, omit generation of potential function printout for this case.
- If $\text{NPR} > 0$, calculate and print potential function at NPR distances starting from $r = \text{RPR1}$ with a step size of $\Delta r = \text{dRPR}$.

4.3 Sample Input Data Files

This data file is a set of RKR turning points for ground-state NaH used to generate initial trial values of the EMO potential function parameters used in the direct-potential-fit data analysis of Ref. [57].

```

1 101 1.0 0 0 0 0 % PSEL NTP UNC IROUND LPPOT prFIT prDIFF
1.88653358d0 15795.1d0 0.d0 % Re De VMIN
0 0 0 % IFXRe IFXDe IFXVMIN
1.27263185744278 15779.01494490216
1.27327384018599 15733.75964567196 1.27435125787419 15658.02169863633
1.27583333934101 15554.27115742115 1.27769354944942 15424.75760065909
1.27990913199516 15271.52292783471 1.28246073055685 15096.41408441944
1.28533207261631 14901.09564985342 1.28850970563499 14687.06222657656
1.29198277636327 14455.65057295593 1.29574284668412 14208.05142760175
1.29978374089745 13945.32097720924 1.30410142064656 13668.39192470874
1.30869388475278 13378.08411915137 1.31356109212164 13075.11471340259
1.31870490666139 12760.10782036122 1.32412906385398 12433.60364306624
1.32983915927281 12096.06705869898 1.33584265998404 11747.89564113306
1.34214894042987 11389.42711132992 1.34876934510735 11020.94620952222
1.35572269569781 10642.69098777300 1.36303003514904 10254.85852614313
1.37071534769550 9857.61008034484 1.37880637457872 9451.07567340393
1.38733552236517 9035.35814849868 1.39634088170374 8610.53670478794
1.40586739970834 8176.66994268661 1.41596828170263 7733.79844969106
1.42670674238721 7281.94696250262 1.43815829029988 6821.12614584201
1.45041382625359 6351.33403299273 1.46358399081091 5872.55717775632
1.47780545428256 5384.77157214772 1.49325029754690 4887.94338880370
1.51014047711566 4382.02961172252 1.52877103890559 3866.97862359792
1.54954930328844 3342.73082265578 1.57306554959751 2809.21934654652
1.59444609265762 2375.69130719870 1.60622288307612 2156.67406538804
1.61888488247225 1936.14783396631 1.63259897575096 1714.10737152743
1.64759065095732 1490.54737204525 1.66417732548816 1265.46248700455
1.68283083085370 1038.84734984010 1.70430799871312 810.69660285449
1.72997038943680 581.00492678794 1.76279951083522 349.76707321686
1.81307314119747 116.97789996057 1.88705009889396 0.00000000000
1.96769517603239 116.97789996057 2.03135827083286 349.76707321686
2.07764630024764 581.00492678794 2.11683564094010 810.69660285449
2.15190683637149 1038.84734984010 2.18422086769690 1265.46248700455
2.21453432471999 1490.54737204525 2.24331909085724 1714.10737152743
2.27089288956752 1936.14783396631 2.29748173332110 2156.67406538804
2.32325321765905 2375.69130719870 2.37283030205624 2809.21934654652
2.43199189394290 3342.73082265578 2.48887793654518 3866.97862359792
2.54410043041310 4382.02961172252 2.59808980397705 4887.94338880370
2.65116528053317 5384.77157214772 2.70357417354405 5872.55717775632
2.75551556411033 6351.33403299273 2.80715551742447 6821.12614584201
2.85863744680374 7281.94696250262 2.91008957427635 7733.79844969106
2.96163060477349 8176.66994268661 3.01337429158559 8610.53670478794
3.06543333049125 9035.35814849868 3.11792288728003 9451.07567340393
3.17096399277721 9857.61008034484 3.22468700777581 10254.85852614313
3.27923535597148 10642.69098777300 3.33476974130368 11020.94620952222
3.39147310688556 11389.42711132992 3.44955665990463 11747.89564113306
3.50927324791250 12096.06705869898 3.57092188821601 12433.60364306624
3.63486041027552 12760.10782036122 3.70152187572707 13075.11471340259
3.77143637617311 13378.08411915137 3.84526064710088 13668.39192470874

```

```

3.92381932238662 13945.32097720924 4.00816402293421 14208.05142760175
4.09966068317251 14455.65057295593 4.20012335281574 14687.06222657656
4.31202810411714 14901.09564985342 4.43887297528275 15096.41408441944
4.58582336531524 15271.52292783471 4.76096746621319 15424.75760065909
4.97804002053615 15554.27115742115 5.26332726810017 15658.02169863633
5.67804681677814 15733.75964567196 6.43542911797951 15779.01494490216

```

```

5 0 0 10 -1.0
5 0 0 10 1.9
5 0 0 10 2.0
5 0 0 10 2.1
5 0 0 10 2.2
5 0 0 10 2.4
5 0 0 10 2.6
5 0 0 10 2.8

```

```

5 3 0 11 -1.0
5 0 0 11 1.9
5 0 0 11 2.0
5 0 0 11 2.1
5 0 0 11 2.2
5 0 0 11 2.4
5 0 0 11 2.6
5 0 0 11 2.8

```

```

5 3 0 12 -1.0
5 0 0 12 1.9
5 0 0 12 2.0
5 0 0 12 2.1
5 0 0 12 2.2
5 0 0 12 2.4
5 0 0 12 2.6
5 0 0 12 2.8

```

To fit the same set of turning points to an MLR potential with the damped, three-term long-range tail, $u_{LR}(r) = D_6(r) \frac{C_6}{r^6} + D_8(r) \frac{C_8}{r^8} + D_{10}(r) \frac{C_{10}}{r^{10}}$ the first three lines in the above data set are replaced by the following:

```

2 101 1.0 0 0 0 0 % PSEL NTP UNC IROUND LPPOT prFIT prDIFF
1.88653358d0 15795.1d0 0.d0 % Re De VMIN
0 0 0 % IFXRe IFXDe IFXVMIN
3 0.687d0 -2 1 0 -0.8 % NCMM rhoAB sVSR2 IDSTT APSE yMIN
6 357502.d0 % MMLR(1) CmVAL(1)
8 5.41796d6 % MMLR(2) CmVAL(2)
10 1.1292d8 % MMLR(3) CmVAL(3)

```

To fit the same set of turning points to a DELR potential with the same damped three-term long-range tail used for the MLR potential, the first five lines in the above MLR data file remain unchanged except that the value of PSEL in the first line is set equal to 3 rather than 2:

```

3 101 1.0 0 0 0 0 % PSEL NTP UNC IROUND LPPOT prFIT prDIFF
1.88653358d0 15795.1d0 0.d0 % Re De VMIN
0 0 0 % IFXRe IFXDe IFXVMIN
3 0.687d0 -2 1 0 -0.8 % NCMM rhoAB sVSR2 IDSTT APSE yMIN
6 357502.d0 % MMLR(1) CmVAL(1)
8 5.41796d6 % MMLR(2) CmVAL(2)
10 1.1292d8 % MMLR(3) CmVAL(3)

```

To fit the same set of turning points to a GPEF potential using the Šurkus $p = 1$ expansion variable, the first three lines in the EMO data file above are replaced by the following:

4	101	1.0	0	1	0	0	% PSEL NTP UNC IROUND LPPOT prFIT prDIFF
1.	88653358d0	0.	d0	0.	d0		% Re De VMIN
0	1	0					% IFXRe IFXDe IFXVMIN
1.	d0	1.	d0				% a_S b_S

Acknowledgements

I am grateful to Professor George McBane of Grand Valley State University for helpful suggestions.

References

- [1] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
- [2] G. Simons, R. G. Parr, and J. M. Finlan, J. Chem. Phys. **59**, 3229 (1973).
- [3] A. J. Thakkar, J. Chem. Phys. **62**, 1693 (1975).
- [4] J. F. Ogilvie, Proc. Roy. Soc. (London) **A 378**, 287 (1981).
- [5] A. A. Šurkus, R. J. Rakauskas, and A. B. Bolotin, Chem. Phys. Lett. **105**, 291 (1984).
- [6] R. J. Le Roy, N. Dattani, J. A. Coxon, A. J. Ross, P. Crozet, and C. Linton, J. Chem. Phys. **131**, 204309 (2009).
- [7] R. J. Le Roy, Y. Huang, and C. Jary, J. Chem. Phys. **125**, 164310 (2006).
- [8] R. J. Le Roy and R. D. E. Henderson, Mol. Phys. **105**, 663 (2007).
- [9] H. Salami, A. J. Ross, P. Crozet, W. Jastrzebski, P. Kowalczyk, and R. J. Le Roy, J. Chem. Phys. **126**, 194313/1 (2007).
- [10] A. Shayesteh, R. D. E. Henderson, R. J. Le Roy, and P. F. Bernath, J. Phys. Chem. A **111**, 12495 (2007).
- [11] R. J. Le Roy, C. C. Haugen, J. Tao, and H. Li, Mol. Phys. **109**, 435 (2011).
- [12] N. Dattani and R. J. Le Roy, J. Mol. Spectrosc. **268**, 199 (2011).
- [13] Y. Huang, *Determining Analytical Potential Energy Functions of Diatomic Molecules by Direct Fitting*, M.Sc. Thesis, Department of Chemistry, University of Waterloo (2001).
- [14] R. J. Le Roy and Y. Huang, J. Mol. Struct. (Theochem) **591**, 175 (2002).
- [15] Y. Huang and R. J. Le Roy, J. Chem. Phys. **119**, 7398 (2003); erratum: *ibid* **126** 169904 (2007).
- [16] R. J. Le Roy, D. R. T. Appadoo, K. Anderson, A. Shayesteh, I. E. Gordon, and P. F. Bernath, J. Chem. Phys. **123**, 204304 (2005).
- [17] R. J. Le Roy, D. R. T. Appadoo, R. Colin, and P. F. Bernath, J. Mol. Spectrosc. **236**, 178 (2006).
- [18] E. G. Lee, J. Y. Seto, T. Hirao, P. F. Bernath, and R. J. Le Roy, J. Mol. Spectrosc. **194**, 197 (1999).
- [19] P. M. Morse, Phys. Rev. **34**, 57 (1929).
- [20] J. A. Coxon and P. G. Hajigeorgiou, J. Mol. Spectrosc. **139**, 84 (1990).
- [21] H. G. Hedderich, M. Dulick, and P. F. Bernath, J. Chem. Phys. **99**, 8363 (1993).
- [22] R. J. Le Roy, (a) R. J. Le Roy. betaFIT 2.0, University of Waterloo Chemical Physics Research Report CP-665 (2009); b) *ibid*, phiFIT 1.1, CP-663R (2006).
- [23] J. Y. Seto, Z. Morbi, F. Charron, S. K. Lee, P. F. Bernath, and R. J. Le Roy, J. Chem. Phys. **110**, 11756 (1999).
- [24] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).
- [25] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).
- [26] J. O. Hirschfelder and W. J. Meath, in *Intermolecular Forces*, Vol. 12 of *Adv. Chem. Phys.*, edited by J. O. Hirschfelder (Interscience, New York, 1967), Chap. 1, pp. 3–106.
- [27] R. J. Le Roy and R. B. Bernstein, J. Chem. Phys. **52**, 3869 (1970).

- [28] W. J. Meath, *Am. J. Phys.* **40**, 21 (1972).
- [29] R. J. Le Roy, in *Molecular Spectroscopy*, edited by R. N. Barrow, D. A. Long, and D. J. Millen (Chemical Society of London, London, 1973), Vol. 1, Specialist Periodical Report 3, pp. 113–176.
- [30] P. G. Hajigeorgiou and R. J. Le Roy, in *4th Ohio State University International Symposium on Molecular Spectroscopy* (Columbus, Ohio, 1994), paper WE04.
- [31] P. G. Hajigeorgiou and R. J. Le Roy, *J. Chem. Phys.* **112**, 3949 (2000).
- [32] J. A. Coxon and R. Colin, *J. Mol. Spectrosc.* **181**, 215 (1997).
- [33] J. A. Coxon and P. G. Hajigeorgiou, *J. Mol. Spectrosc.* **193**, 306 (1999).
- [34] J. Y. Seto, R. J. Le Roy, J. Vergès, and C. Amiot, *J. Chem. Phys.* **113**, 3067 (2000).
- [35] J. A. Coxon and P. G. Hajigeorgiou, *J. Mol. Spectrosc.* **203**, 49 (2000).
- [36] J. Hepburn, G. Scoles, and R. Penco, *Chem. Phys. Lett.* **36**, 451 (1975).
- [37] A. Koide, W. J. Meath, and A. R. Allnatt, *Chem. Phys.* **58**, 105 (1981).
- [38] C. Douketis, G. Scoles, S. Marchetti, M. Zen, and A. J. Thakkar, *J. Chem. Phys.* **76**, 3057 (1982).
- [39] K. T. Tang and J. P. Toennies, *J. Chem. Phys.* **80**, 3726 (1984).
- [40] C. Douketis, J. M. Hutson, B. J. Orr, and G. Scoles, *Mol. Phys.* **52**, 763 (1984).
- [41] H. Kreek and W. J. Meath, *J. Chem. Phys.* **50**, 2289 (1969).
- [42] F. Martin, M. Aubert-Frécon, R. Bacis, P. Crozet, C. Linton, S. Magnier, A. Ross, and I. Russier, *Phys. Rev. A* **55**, 3458 (1997).
- [43] M. Aubert-Frécon, G. Hadinger, S. Magnier, and S. Rousseau, *J. Mol. Spectrosc.* **188**, 182 (1998).
- [44] Y. Huang and R. Le Roy, in *55th Ohio State University International Symposium on Molecular Spectroscopy* (Columbus, Ohio, 2000), paper RA01.
- [45] J. Y. Seto and R. J. Le Roy, in *55th Ohio State University International Symposium on Molecular Spectroscopy* (Columbus, Ohio, 2000), paper RA02.
- [46] A. Pashov, W. Jastrzębski, and P. Kowalczyk, *Comp. Phys. Comm.* **128**, 622 (2000).
- [47] A. Pashov, W. Jastrzębski, and P. Kowalczyk, *J. Chem. Phys.* **113**, 6624 (2000).
- [48] A. Pashov, W. Jastrzębski, W. Jaśniecki, V. Bednarska, and P. Kowalczyk, *J. Mol. Spectrosc.* **203**, 264 (2000).
- [49] J. Tao, R. J. Le Roy, and A. Pashov, in *65th Ohio State University International Symposium on Molecular Spectroscopy* (Columbus, Ohio, 2010), paper MG07.
- [50] M. Ivanova, A. Stein, A. Pashov, H. Knöckel, and E. Tiemann, *J. Chem. Phys.* **134**, 024321 (2011).
- [51] O. Allard, C. Samuelis, A. Pashov, H. Knöckel, and E. Tiemann, *Eur. Phys. J. D* **26**, 155 (2003).
- [52] J. Y. Seto, *Direct Fitting of Analytic Potential Functions to Diatomic Molecule Spectroscopic Data*, M.Sc. Thesis, Department of Chemistry, University of Waterloo (2000).
- [53] H. Knöckel, B. Bodermann, and E. Tiemann, *Eur. Phys. J. D* **28**, 199 (2004).
- [54] J. F. Ogilvie, *J. Chem. Phys.* **88**, 2804 (1988).
- [55] R. J. Le Roy, *J. Mol. Spectrosc.* **191**, 223 (1998).
- [56] R. J. Le Roy, J. Seto, and Y. Huang, *DPotFit 1.2: A Computer Program for fitting Diatomic Molecule Spectra to Potential Energy Functions*, University of Waterloo Chemical Physics Research Report CP-664 (2007); see <http://leroy.uwaterloo.ca/programs/>.
- [57] R. J. Le Roy, S.-D. Walji, and K. M. Sentjens, in *68th International Symposium on Molecular Spectroscopy at the Ohio State University* (Columbus, Ohio, June 2013), paper XXXX.