

Power-series Expansions as Fitting Functions of Potential-energy Curves

J. J. Camacho,* A. Pardo and J. M. L. Poyato

Departamento de Química-Física Aplicada, Facultad de Ciencias, C-XIV, Universidad Autónoma de Madrid, Cantoblanco, 28049, Madrid, Spain

A comparative study of the most important power-series expansions, Dunham, Simons–Parr–Finland, Ogilvie–Tipping, Thakkar, Engelke, Mattera, Surkus and Huffaker, as fitting functions of potential-energy curves is reported. A study of the leading terms and intervals of convergence is also shown. As an example, the calculation of the interval of convergence for an Engelke's series is given. The method is applied to the molecules: CO ($X^1\Sigma^+$), H_2 ($X^1\Sigma_g^+$) and 7LiH ($X^1\Sigma^+$ and $A^1\Sigma^+$). An analysis of the variation for the leading term of the power-series expansions with two non-linear parameters is presented for CO ($X^1\Sigma^+$). The optimum non-linear parameters are obtained when the left-hand side of the interval of convergence is very near and below the first point of the input potential. Moreover, we observed that a good fit through the leading term of a power-series expansion is obtained for Engelke, Mattera or Surkus functions with two non-linear parameters. For fitting power-series expansions with an intermediate number of basis functions it is better to use a Thakkar or Huffaker type function with only one non-linear parameter.

A model potential-energy function should have a simple analytic form. However, there is no expression capable of approximating accurately the experimental potential-energy curve. The best potentials are obtained by direct inversion of spectral data by using numerical methods such as RKR,^{1–3} IPA^{4,5} or hybrid functions (for example PMO–RKR long-range potentials⁶). Nevertheless, these experimental potentials are presented in the form of tables of numbers, that normally show the vibrational and rotational energies for the experimental vibrational levels together with the corresponding classical turning points. It is necessary to interpolate to determine the potential energy at any intermediate point. The interpolation between the given points is very critical and indeed appears to be the major source of error in the eigenvalue problem. Moreover, it is difficult to choose the interpolation method. For very accurate potentials it is observed that an interpolation by spline is usually better than a Lagrangian interpolation. Nevertheless, a Lagrangian interpolation is less sensitive to numerical noise in cases in which the potential is not very accurate. On the other hand, the most accurate potential-energy curves, obtained from experimental data, have as a basis the RKR semiclassical procedure. This method is an inversion of the first-order WKB approximation⁷ or Bohr–Sommerfeld quantization condition. This approximation is inadequate in zone of the minimum of the potential-energy curve and in the neighbourhood of the dissociation. Thus numerical noise is produced in the potential which can be detected when the successive derivatives of the potential are obtained.

Increasing attention has been given to the problem of the most convenient and accurate representation of the potential-energy curves through some type of analytic function: (i) empirical functions, (ii) Padé approximants or (iii) power-series expansions. Empirical functions as Morse,⁸ Lennard-Jones,⁹ Rydberg,¹⁰ Rosen–Mores,¹¹ Poschl–Teller,¹² Helmann,¹³ Hulbert–Hirschfelder,¹⁴ Lippincott,¹⁵ Frost–Musulin,¹⁶ Varshni,¹⁷ Linnert¹⁸ and Schubert–Certain¹⁹ are simple and easy to use but the assumption of single functional form produces important deviations of the 'true' potential-energy function. Padé approximants²⁰ have less convergence problems than power series but we must use many coefficients to fit a potential defined in a discrete set of points.²¹ Power-series expansions can be used to give a very accurate potential-energy curve close to the minimum zone

and, if the series converges, it is possible to represent the potential energy for large values of the internuclear distance, with an intermediate number of parameters. In some cases, it is possible that although there was a large convergence zone, the convergence could be slow and the corresponding approximation was not adequate. In recent years, power-series expansions for molecular potentials with improved convergence properties relative to the first Dunham expansion have been introduced by different authors. The most important power-series expansions have been reported by Dunham,²² Simons–Parr–Finlan²³ (SPF), Ogilvie–Tipping,²⁴ Thakkar,²⁵ Engelke,²⁶ Mattera,²⁷ Surkus²⁸ and Huffaker.²⁹ In this work, we present a comparative study of these power-series expansions for fitting potential-energy curves. We review the definition of these power-series expansions and present a study of the corresponding leading terms. Then we present the results of our calculations of the interval of convergence and dissociation limits for the above-mentioned power-series expansions. As an example we also show the calculation of the interval of convergence for an Engelke type power-series development with $p > 0$ and $p < 0$. The results and discussion of the different power series expansions as fitting functions for the ground state of $^{12}C^{16}O$, 7LiH and H_2 and the $A^1\Sigma^+$ state of 7LiH are presented in the final section. Here we also present a study on the variation of the standard deviation for the leading term of power-series expansions with two non-linear parameters for the ground state of CO.

Power-series Expansions

In principle any function can be expanded in a complete set of basis functions. In practice, this set is chosen according to the physical problem to be studied, so that the series converges after a small number of terms. So any potential-energy function $V(r)$ can be expressed as a linear combination of a set of basis functions $[f_i(r)]_{i=0, 1, \dots, m}$:

$$V(r) = \sum_{i=0}^m c_i f_i(r) \quad (1)$$

where the coefficients c_0, c_1, \dots are real numbers independent of the internuclear distance r . To get $V(r_e) = 0$ and $(dV/dr)_{r=r_e} = 0$, $c_0 = c_1 = 0$ is taken. The basis functions $f_i(r)$

can be represented as a power of degree i of certain fundamental functions $f(r)$. Thus eqn. (1) can be written as

$$V(r) = d_0 f^2(r) \left[1 + \sum_{i=1}^N d_i f^i(r) \right] \quad (2)$$

The most important fundamental functions used in the approximation of potentials are shown in column 2 of Table 1. These functions $f(r)$ have different functional forms of r and they can be described by any (Dunham, SPF and Ogilvie), one (Thakkar and Huffaker) or two (Engelke, Mattera and Surkus) non-linear parameters. Some of these functions are special cases of another. In Table 2 relations between them are shown. Prior to a study of the power-series expansions it is very instructive to see the behaviour of the leading term $V_0(r) = d_0 f^2(r)$ for the different expansions. Except for Dunham's series, this leading term has an anharmonic form with an inflection point for $r > r_e$. They also have a finite asymptote as $r \rightarrow \infty$ corresponding to the dissociation limit, except for the Thakkar, Engelke and Mattera potential for $p < 0$. Owing to this fact, we have only considered these last potential functions with $p > 0$. Table 3 shows the calculated limits of $V_0(r)$ when $r \rightarrow 0$ and $r \rightarrow \infty$ and the inflection points together with their energies. We note that although the Thakkar, Engelke and Mattera potentials have different values of the internuclear distance for the inflection point their corresponding energies are equal. We see that all these simple potential functions, except the Dunham's function, represent the conventional form of a potential-energy curve with a single minimum and a smooth asymptotic rise to the dissociation limit. Although the potential-energy curves should become infinite at $r = 0$ as happens for an SPF, Thakkar ($p > 0$), Engelke ($p > 0, \beta > 0$), Mattera ($p > 0, \gamma = p$) and Surkus ($p > 0, \mu = 0$), this condition is not very strict because the results are practically the same if V becomes very large at $r = 0$, as for the leading term of Huffaker's which corresponds to a Morse potential.

Table 2 Relations between different power-series expansions

	Engelke (p, β)	Mattera (p, γ)	Surkus (p, μ)
Dunham	(-1, 0)	(-1, 1)	(-1, 0)
SPF	(1, 0)	(1, 1)	(1, 0)
Ogilvie	(1, 1)	(1, $\frac{1}{2}$)	(1, 1)
Thakkar	($p, 0$)	(p, p)	($p, 0$)

Intervals of Convergence

A fundamental requirement to approximate any potential-energy curve in terms of a power-series expansion is to determine its interval of convergence. The radius of convergence of a power-series expansion can be obtained from the singularity of the potential, which appears at $r = 0$, closest to the equilibrium internuclear distance r_e in the complex r plane. Thus the nearest singularity on the real axis gives an upper limit to the radius of convergence. The values of the singularities for the different power-series expansions considered here are shown in column 3 of Table 1. For obtaining the interval of convergence of a power-series expansion in terms of its fundamental function $f(r)$ we used the ratio test; if

$$\lim_{i \rightarrow \infty} \left| \frac{d_{i+1} f^{i+1}(r)}{d_i f^i(r)} \right| = \lim_{i \rightarrow \infty} \left| \frac{d_{i+1}}{d_i} \right| |f(r)| = L \quad (3)$$

then the series is absolutely convergent for $L < 1$ and divergent for $L > 1$, and the test fails for $L = 1$. This interval of convergence can be simply obtained by determining the values of r for which $|f(r)| < 1$. The intervals of convergence obtained by us for different $f(r)$ functions are summarized in Table 1.

As an example of the method employed here for determining the intervals of convergence we present its application to an Engelke's potential. For an Engelke's potential with $p > 0$,

Table 1 Summary of singularities, intervals of convergence and dissociation limits calculated for the most important power-series expansions used for describing potential-energy curves of bound states of diatomic molecules

function	ref.	$f(r)$	singularity	interval of convergence	dissociation limit
Dunham	22	ξ	-1	$(0, 2r_e)$	∞
SPF	23	$(r - r_e)/r$	$-\infty$	$(r_e/2, \infty)$	τ
Ogilvie	24	$(r - r_e)/(r + r_e)$	-1	$(0, \infty)$	τ
Thakkar	25	$1 - (1 + \xi)^{-p}; (p > 0)$	$-\infty$	$(r_e/2^{1/p}, \infty)$	τ
		$-(1 - (1 + \xi)^{ p }); (p < 0)$	-1	$(0, r_e 2^{1/ p })$	∞
Engelke	26	$1 - \left(\frac{1 + \xi + \beta}{1 + \beta} \right)^{-p}; (p > 0); (\beta > -1)$	$1 - \left(\frac{\beta + 1}{\beta} \right)^p$	$\left[\frac{r_e}{2^{1/p}} (\beta + 1) - \beta r_e, \infty \right]$	τ
		$- \left[1 - \left(\frac{1 + \xi + \beta}{1 + \beta} \right)^{ p } \right]; (p < 0)$	$\left(\frac{\beta}{\beta + 1} \right)^{ p } - 1$	$[0, 2^{1/ p } r_e (\beta + 1) - \beta r_e]$	∞
Mattera	27	$1 - \left(1 + \frac{\gamma \xi}{p} \right)^{-p}; (p > 0); (\gamma > 0)$	$1 - \left(\frac{p}{p - \gamma} \right)^p$	$\left[\frac{r_e p}{2^{1/p \gamma}} + \frac{r_e (\gamma - p)}{\gamma}, \infty \right]$	τ
		$1 - \left(1 + \frac{\gamma \xi}{p} \right)^{ p }; (p < 0)$	$1 - \left(\frac{p - \gamma}{p} \right)^{ p }$	$\left[\frac{2^{1/ p } r_e p }{\gamma} - \frac{r_e (\gamma + p)}{\gamma}, \frac{r_e (\gamma + p)}{\gamma} \right]$	∞
Surkus	28	$\frac{r^p - r_e^p}{r^p + \mu r_e^p}; (p > 0); (\mu > -1)$	$-\frac{1}{\mu}$	$\left[\left(\frac{1 - \mu}{2} \right)^{1/p} r_e, \infty \right]$	τ
		$-\frac{r^p - r_e^p}{r^p + \mu r_e^p}; (p < 0)$	$\frac{1}{\mu}$	$\left[0, \left(\frac{2}{1 - \mu} \right)^{1/ p } r_e \right]$	σ
Huffaker	29	$1 - \exp[-\alpha(r - r_e)]; (\alpha > 0)$	$1 - \exp(\alpha r_e)$	$\left(r_e - \frac{\ln 2}{\alpha}, \infty \right)$	τ

$$\xi = (r - r_e)/r_e; \tau = d_0(1 + \sum_{i=1}^{\infty} d_i); \sigma = d_0/\mu^2[1 + \sum_{i=1}^{\infty} (d_i/\mu^i)].$$

Table 3 Limits as $r \rightarrow 0$ and inflection points for the leading term $V_0(r) = a_0 f^2(r)$ of the different power-series expansions

function	$\lim_{r \rightarrow 0} V_0(r)$	r_{inf}	$V(r_{\text{inf}})$
Dunham	a_0	—	—
SPF	∞	$\frac{3r_e}{2}$	$\frac{a_0}{9}$
Ogilvie	a_0	$2r_e$	$\frac{a_0}{9}$
Thakkar ($p > 0$)	∞	$r_e \left(\frac{2p+1}{p+1} \right)^{1/p}$	τ_1
Engelke ($p > 0$)	$a_0 \left[\left(\frac{\beta+1}{\beta} \right)^p - 1 \right]^2$	$r_e(\beta+1) \left(\frac{2p+1}{p+1} \right)^{1/p} - \beta r_e$	τ_1
Mattera ($p > 0$)	$a_0 \left[\left(\frac{p}{p-\gamma} \right)^p - 1 \right]^2$	$\left[r_e p \left(\frac{2p+1}{p+1} \right)^{1/p} + r_e(\beta-p) \right] / \beta$	τ_1
Surkus ($p > 0$)	$\frac{a_0}{\mu^2}$	σ_1	a
Huffaker	$a_0 [\exp(\alpha r_e) - 1]^2$	$\frac{\ln 2}{\alpha} + r_e$	$\frac{a_0}{4}$

$$\tau_1 = \frac{a_0 p^2}{(2p+1)^2}, \sigma_1 = r_e \left\{ \frac{\sqrt{[\mu^2(2p-1)^2 + 2\mu(2p^2+1) + (2p+1)^2 + \mu(2p-1) + 2p+1]}}{(2p+1)} \right\}^{1/p}. \text{ } ^a \text{ Expression too large.}$$

if

$$\left| 1 - \left[\frac{r_e(\beta+1)}{\beta r_e + r} \right]^p \right| < 1 \quad (4)$$

Inequality (4) can be expressed as follows

$$\left\{ \left[\frac{r_e(\beta+1)}{\beta r_e + r} \right]^p - 1 \right\} \text{sgn}\{(r + \beta r_e)^p - [r_e(\beta+1)]^p\} > -1 \quad (5)$$

The argument of the sgn function is positive for $r > r_e$, and, in this case $1/(r + \beta r_e)^p > 0$, which is true for all r . Otherwise for $r < r_e$

$$- \left\{ \left[\frac{r_e(\beta+1)}{\beta r_e + r} \right]^p - 1 \right\} > -1 \quad (6)$$

By solving inequality (6) we obtain

$$r > \frac{r_e(\beta+1)}{2^{1/p}} - \beta r_e \quad (7)$$

As all power-series expansions of the type of eqn. (2) are convergent at $r = r_e$, the interval of convergence for an Engelke's series expansion with $p > 0$ is $[r_e(\beta+1)/2^{1/p} - \beta r_e, \infty]$.

An Engelke's power-series expansion with $p < 0$ is convergent for

$$\left| \left[r_e^p - \left(\frac{\beta r_e + r}{\beta + 1} \right)^p \right] \left(\frac{\beta r_e + r}{\beta + 1} \right)^{-p} \right| < 1 \quad (8)$$

Inequality (8) is equivalent to

$$\left\{ \left[\frac{r + \beta r_e}{r_e(\beta+1)} \right]^{-p} - 1 \right\} \text{sgn} \left\{ \frac{1}{1 - \left[\frac{r_e}{(r + \beta r_e)/\beta + 1} \right]^p} \right\} > -1 \quad (9)$$

The argument of the sgn function is positive if $r < r_e$. In this case the inequality (9) leads to

$$\left[\frac{r + \beta r_e}{r_e(\beta+1)} \right]^{lp} > 0 \quad (10)$$

which is true for every r . Thus a first interval of convergence is $(0, r_e)$. For $r > r_e$, the argument of the sgn function of

inequality (9) is negative. So

$$\left[\frac{r + \beta r_e}{r_e(\beta+1)} \right]^{lp} < 2 \quad (11)$$

and hence

$$r < 2^{1/|p|} [r_e(\beta+1)] - \beta r_e \quad (12)$$

A second interval of convergence is $\{r_e, 2^{1/|p|} [r_e(\beta+1)] - \beta r_e\}$. As all power-series expansions (Table 1) are convergent for the equilibrium internuclear distance, the interval of convergence for an Engelke's series expansion with $p < 0$ is $\{0, 2^{1/|p|} [r_e(\beta+1)] - \beta r_e\}$.

Numerical Results and Discussion

For the above-mentioned series expansions we have determined the limits when r goes to infinity. These results are shown in the last column of Table 1. We have taken p for Thakkar's series; p and β for Engelke's series; p and γ for Mattera's series; p and μ for Surkus's series and α for Huffaker's series as adjustable non-linear parameters. We see that for a potential of type Thakkar, Engelke or Mattera it is better to choose the parameter p positive for obtaining a finite asymptote as $r \rightarrow \infty$ corresponding to the dissociation energy. Moreover, these power series with $p < 0$ are preferable to those with $p < 0$ because their interval of convergence is extended to infinity.

The optimum non-linear parameters are obtained by considering the best least-squares fit of the input potential. Consequently, it is necessary to determine the absolute minimum on the graph which shows the variation of the standard deviation of the fit as a function of the non-linear parameters. For each power-series expansion, by substituting the optimum non-linear parameters and the equilibrium internuclear distance into the fourth column of Table 1 we get the corresponding range of convergence.

We have carried out a comparative study of the different power-series expansions shown in Table 1 as fitting functions for approximating rotationless RKR potentials. These potentials consist of pairs of (r, V^{RKR}) points which correspond to the classical turning points for the experimental vibrational

levels. The output of the least-squares fits includes: the fitted parameters in the best fit; *F*-ratio tests for comparing the models specified in the function, as well as the degrees of freedom and sums of squares used to obtain *F*-ratios; table of confidence intervals for the best-fit parameters; the estimated covariance and correlation matrix of the fit coefficients; the variance or its square root which corresponds to the standard deviation; the mean deviation and the multiple correlation coefficient. In the results we present only the standard and mean deviations, possibly the best single statistical measures of the success of the chosen truncated series in fitting the data.

First, we have considered the ground state of the $^{12}\text{C}^{16}\text{O}$ molecule which is the most stable diatomic molecule. The available spectroscopic information for different isotopic species of carbon monoxide is very extensive and accurate. Detailed references can be found in ref. 30. Although there is accurate spectroscopic information up to the vibrational level $v = 41$ with a vibrational energy $G(41) = 68\,042.5\text{ cm}^{-1}$, this vibrational level is nevertheless far from the estimated dissociation limit $D_e = 90\,674.4\text{ cm}^{-1}$.³¹ The RKR CO ($X^1\Sigma^+$) potential curve up to $v = 37$ has been constructed by different authors^{32–37} by employing different techniques to remove the singularity that appears at the upper limit of the integration when one calculates the *f* and *g* integrals related to the classical turning points (see, *e.g.* ref. 32). All these potentials have been checked by solving numerically the radial wave equation. The self-consistency between the calculated eigenvalues with the radial wave equation. The self-consistency between the calculated eigenvalues with the experimental energy values is *ca.* 0.4 cm^{-1} . The self-consistency between the calculated eigenvalues with the experimental energy values is *ca.* 0.4 cm^{-1} . This fact supposes that this potential is employed as a test case for analysing the method for constructing potential-energy curves. We have determined the RKR potential for the electronic ground state of $^{12}\text{C}^{16}\text{O}$ up to $v = 41$ from the spectroscopic information given in ref. 30. The results are shown in Table 4 together with the corresponding eigenvalues E_v of the rotationless potential $U_0(J = 0)$ obtained by numerical solution of the radial Schrödinger equation

$$\left[-\frac{\hbar}{4\pi c\mu} \frac{d^2}{dr^2} + U_0(r) \right] \Psi_v(r) = E_v \Psi_v(r) \quad (13)$$

For the RKR potential we determined the RMS error ($\sigma = \sum_{i=1}^n (\delta E_n)^2/n$) where n is the number of terms and δE_n is the difference between the experimental vibrational energy $G(v) + Y_{00}$ and the quantum mechanical energy eigenvalue E_v . For the RKR potential defined in Table 4, $\sigma = 0.605\text{ cm}^{-1}$, whereas for the potential given in ref. 32, $\sigma = 0.263\text{ cm}^{-1}$. As the self-consistency of this last potential is better, we have considered the potential presented in ref. 32 for comparing the ability of different power-series expansions indicated above as fitting functions. So, we have carried out a least-squares fit of the tabulated RKR potential of the $X^1\Sigma^+$ state of CO³² by using eqn. (2) and considering the different fundamental functions $f(r)$ defined in Table 1. We suppose that the optimum fit is obtained when the standard and mean deviations are minima for a given number of linear parameters. We also followed the residual method.³⁸ If the residuals (algebraic deviations) plotted against r are scattered uniformly on either side of the zero line, the fit can be considered to be good. For example, in Fig. 1 we show a fit of the ground state of CO by using an SPF power-series expansion with $N = 16$. However, if the residuals occur in clusters, the fitting function has some problems. In this case we observed a behaviour such as that shown in Fig. 2 which corresponds

Table 4 RKR potential-energy curve and eigenvalues for the $X^1\Sigma^+$ state of $^{12}\text{C}^{16}\text{O}$

<i>c</i>	$G(v) + Y_{00}$ $/\text{cm}^{-1}$	$r_-/\text{\AA}$	$r_+/\text{\AA}$	E_v/cm^{-1}
0	1081.776	1.083 269 6	1.178 725 0	1081.820
1	3 225.047	1.053 410 7	1.219 597 7	3 225.149
2	5 341.838	1.034 222 1	1.249 885 5	5 341.975
3	7 432.215	1.019 399 6	1.275 916 1	7 432.375
4	9 496.245	1.007 121 5	1.299 525 0	9 496.418
5	11 533.998	0.996 555 54	1.321 547 8	11 534.175
6	13 545.545	0.987 241 46	1.342 450 8	13 545.720
7	15 530.957	0.978 890 91	1.362 523 4	15 531.129
8	17 490.311	0.971 311 47	1.381 962 1	17 490.481
9	19 423.680	0.964 366 48	1.400 907 1	19 423.852
10	21 331.144	0.957 954 66	1.419 462 7	21 331.322
11	23 212.781	0.951 998 04	1.437 708 8	23 212.969
12	25 068.671	0.946 436 73	1.455 709 6	25 068.871
13	26 898.896	0.941 222 69	1.473 517 5	26 899.109
14	28 703.538	0.936 316 39	1.491 175 4	28 703.764
15	30 482.681	0.931 683 79	1.508 718 2	30 482.918
16	32 236.409	0.927 299 21	1.526 178 6	32 236.655
17	33 964.807	0.923 138 74	1.543 583 1	33 965.060
18	35 667.960	0.919 182 56	1.560 955 7	35 668.219
19	37 345.951	0.915 413 95	1.578 318 2	37 346.218
20	38 998.867	0.911 817 32	1.595 689 4	38 999.142
21	40 626.790	0.908 380 08	1.613 087 5	40 627.078
22	42 229.805	0.905 090 22	1.630 528 5	42 230.109
23	43 807.991	0.901 938 60	1.648 029 2	43 808.316
24	45 361.430	0.898 915 34	1.665 603 2	45 361.779
25	46 890.198	0.896 012 42	1.683 265 0	46 890.576
26	48 394.372	0.893 222 80	1.701 028 3	48 394.780
27	49 874.022	0.890 540 01	1.718 906 7	49 874.462
28	51 329.218	0.887 957 34	1.736 912 6	51 329.690
29	52 760.024	0.885 470 63	1.755 060 4	52 760.523
30	54 166.499	0.883 073 39	1.773 361 6	54 167.037
31	55 548.700	0.880 762 14	1.791 830 7	55 549.273
32	56 906.673	0.878 532 43	1.810 481 0	56 907.287
33	58 240.462	0.876 380 85	1.829 326 9	58 241.126
34	59 550.102	0.874 303 63	1.848 382 6	59 550.829
35	60 835.620	0.872 297 28	1.867 663 1	60 836.427
36	62 097.035	0.870 359 39	1.887 184 7	62 097.943
37	63 334.356	0.868 486 31	1.906 063 6	63 335.388
38	64 547.581	0.866 676 71	1.927 018 6	64 548.763
39	65 736.698	0.864 947 30	1.947 387 9	65 738.053
40	66 901.681	0.863 282 31	1.968 078 5	66 903.227
41	68 042.491	0.861 675 12	1.989 107 9	68 044.236

$r_e = 1.128\,323\,2\text{ \AA}$.

to a fit of the $X^1\Sigma^+$ state of CO by a Dunham power-series development with $N = 6$. We also note the difference of scale for the residual in both figures. Some results for different fits of the ground state of CO potential are shown in Table 5. As the input potential is defined between $r_-(v = 37) = 0.868\,176\,7\text{ \AA}$ and $r_+(v = 37) = 1.906\,655\,5\text{ \AA}$, in principle, any $f(r)$ contains the full potential inside its interval of convergence. We see that the interval of convergence depends only on r_e and the non-linear parameters. From the results in Table 5 we observe that the worse fit corresponds to an

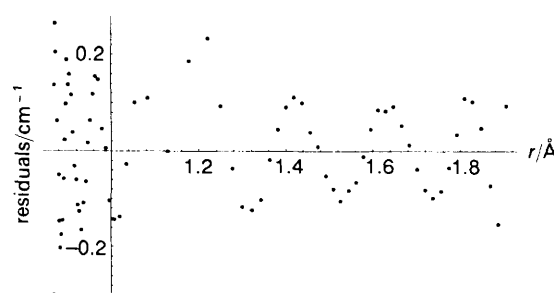


Fig. 1 Residuals for the ground state of the CO molecule using as fitting function an SPF power-series expansion with $N = 16$

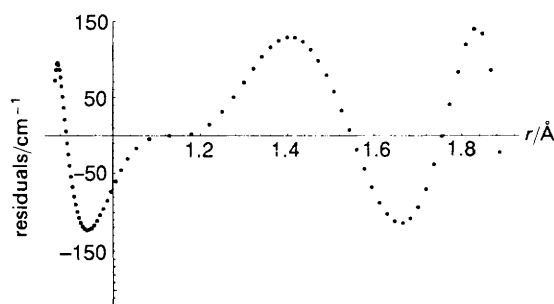


Fig. 2 Residuals for the ground state of the CO molecule using as fitting function a Dunham power-series expansion with $N = 6$

Ogilvie function which has the greater interval of convergence. This is because the convergence of an Ogilvie's potential is very slow and its limit when $r \rightarrow 0$ gives a finite small number (see Table 3). Moreover we see that the optimum non-linear parameters for different power-series expansions and for all the potentials studied had values such that the lower limit of the interval of convergence is somewhat smaller than the first internuclear distance of the input potential. For example, for the ground state of ^7LiH the best fit is obtained for a Thakkar's potential with $p = 1.48$ corresponding to an interval of convergence of $(0.998\,898\,\text{\AA}, \infty)$ whereas the inner first point of the input potential³⁹ is $r_-(v = 22) = 1.004\,707\,\text{\AA}$. For the potential with two non-linear parameters ($p > 0$) an interval of convergence $(0, \infty)$ is obtained for $\beta = \{1/[2^{(1/p)} - 1]\}$ defined in the range $0 < r < \infty$, then one would think these values were optima. The optimum parameters are obtained when the left-hand side of the interval of convergence is very near to or less than the first point of the input potential.

On the other hand, when we fit potentials defined very near to the dissociation limit (for example, the ground state of ^7LiH and H_2) we must see expressions for the potential whose upper extreme of the interval of convergence is infinity. For a potential defined distant to the dissociation limit (for example the ground state of CO) it is not important to use functions with an interval of convergence defined up to infinity. For definitions of $f(r)$ whose right extreme in the interval of convergence is not infinity we have an asymptotic behaviour of the potential going to infinity. However, if the functions have a right extreme in the interval of convergence of infinity, the potential tends toward a finite limit corresponding to the dissociation.

On the other hand, we have observed that it is almost equivalent to fit any $V(r)$ by $N + 1$ basis functions to eqn. (2) and determine the optimum non-linear parameters of $f(r)$ by fitting with only one basis function (the leading term) and from these last non-linear parameters to fit using eqn. (2). This procedure allows us to economize on the time of calculation when we are looking for various non-linear param-

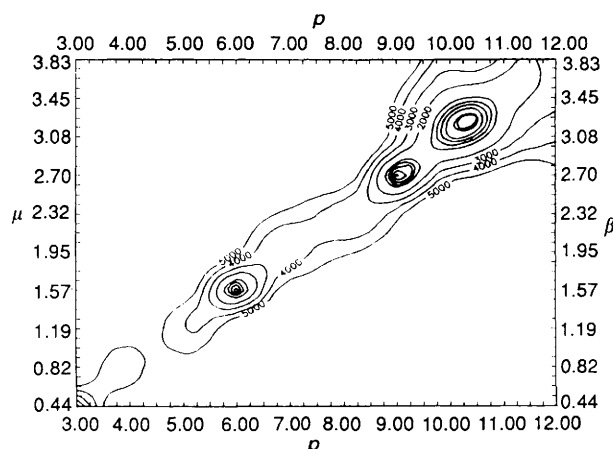


Fig. 3 Contour lines of the standard deviation of fits of the ground state of the CO molecule using as fitting function the leading term of an Engelke's potential

eters. Evidently the coefficients d_i are different but the accuracy of the fits is the same. For example, when we fit the ground state of CO by a Thakkar's potential to eqn. (2) at $N = 19$, with an optimum value of $p = 1.90$, a standard deviation of $0.0126\,\text{cm}^{-1}$ is obtained whereas by fitting using only the leading term, the optimum value of p is 1.81, and if we employed this last optimum p value and now fitted to eqn. (2) a standard deviation of $0.0127\,\text{cm}^{-1}$ is obtained. For Engelke, Mattera and Surkus type functions we must construct a grid for determining their two non-linear parameters. As we have described above it is sufficient to use the leading term of the series for obtaining the optimum non-linear parameters and after that to fit to eqn. (2). As an example, in Fig. 3 we have shown the contour lines of the standard deviation of fits of the ground state of CO by using the leading term of an Engelke's potential $[\xi = (r - r_e)/r_e]$

$$V_0(r) = d_0 \left[1 - \left(\frac{1 + \xi + \beta}{1 + \beta} \right)^{-p} \right]^2 \quad (14)$$

as a function of the non-linear parameters for $3 \leq p \leq 12$ and $0.44 \leq \beta \leq 3.83$. In this case, the optimum parameters are $p = 10.1$ and $\beta = 3.11$, with a fitted linear parameter of $d_0 = 101\,184.019\,\text{cm}^{-1}$. This minimum corresponds to a standard deviation of $20.71\,\text{cm}^{-1}$ and a mean deviation of the residuals of $15.85\,\text{cm}^{-1}$. Thus, we see that with only one term in the power-series expansion it is possible to fit the starting CO potential in a manner which is sufficiently accurate up to an energy of $63\,334.1\,\text{cm}^{-1}$. The results shown in Table 6 were obtained by fitting with these last p and β optimum parameters by eqn. (2), varying the number of basis functions. The optimum number of linear parameters for an Engelke's potential as a fitting function of the ground state of CO is at $N = 18$. The introduction of more linear parameters does not

Table 5 Statistical values for the least-squares fit of the $X^1\Sigma^+$ state of $^{12}\text{C}^{16}\text{O}$ defined between $r_-(v = 37) = 0.868\,176\,\text{\AA}$ and $r_+(v = 37) = 1.906\,655\,5\,\text{\AA}$ for different truncated power series expansions

function	N	optimum parameters	interval of convergence/ \AA	standard deviation/ cm^{-1}	mean deviation/ cm^{-1}
Dunham	20		(0, 2.256 646)	0.697	0.477
SPF	20		(0.564 161 5, ∞)	0.018	0.012
Ogilvie	20		(0, ∞)	1.38	0.96
Thakkar	19	$p = 1.81$	(0.769 340 3, ∞)	0.013	0.008 1
Engelke	18	$p = 10.1$; $\beta = 3.11$	(0.820 740 1, ∞)	0.013	0.008 0
Mattera	18	$p = 10.8$; $\gamma = 2.47$	(0.821 632 7, ∞)	0.012	0.008 0
Surkus	18	$p = 2.8$; $\mu = 0.234$	(0.800 895 5, ∞)	0.013	0.008 1
Huffaker	19	$\alpha = 2.35$	(0.833 366 7, ∞)	0.013	0.008 1

$$r_e = 1.128\,323\,3\,\text{\AA}.$$

Table 6 Standard mean deviations of least-squares fits to different number of fundamental basis Engelke and Mattera type functions for the $X^1\Sigma^+$ state of CO

<i>N</i>	Engelke ($p = 10.1, \beta = 3.11$)		Mattera ($p = 10.8, \gamma = 2.4$)	
	standard deviation /cm ⁻¹	mean deviation /cm ⁻¹	standard deviation /cm ⁻¹	mean deviation /cm ⁻¹
2	20.7	15.8	30.2	24.7
3	20.6	15.9	30.1	24.6
4	19.7	14.2	19.8	13.0
5	19.8	14.1	18.6	12.7
6	11.9	8.30	12.2	8.51
7	9.93	7.33	9.79	7.26
8	5.45	3.86	5.47	3.91
9	4.21	3.21	4.20	3.19
10	1.99	1.45	2.01	1.45
11	1.39	1.06	1.39	1.06
12	0.60	0.44	0.60	0.45
13	0.39	0.29	0.38	0.29
14	0.15	0.11	0.15	0.11
15	0.090	0.066	0.088	0.068
16	0.032	0.023	0.033	0.024
17	0.020	0.014	0.020	0.015
18	0.013	0.0080	0.013	0.0081
19	0.013	0.0081	0.013	0.0080
20	0.013	0.0080	0.013	0.0079
21	0.013	0.0081	0.013	0.0080
32	0.013	0.0079	0.013	0.0080

give any significant improvement. For any power-series expansion studied here this last result can be extrapolated. From Table 6 we see that the fits are not improved by increasing the number of basis functions from 2 to 5. However, the linear basis terms with $N = 3, 4$ and 5 must be considered in the fits because their omission produces important deviations. For example, if the basis terms with $N = 2, 6$ and 7 are considered, the fit is equivalent in accuracy to that considering only the term with $N = 2$ with a standard deviation of 19.84 cm⁻¹ (mean deviation 15.19 cm⁻¹). Similarly other power-series expansions with two non-linear parameters were studied.

In Fig. 4 the contour map of the standard deviation of fits of CO (ground state) by the leading term of a Mattera's potential

$$V_0(r) = d_0 \left[1 - \left(1 + \frac{\gamma_5^c}{p} \right)^{-p} \right]^2 \quad (14)$$

as a function of its non-linear parameters $4 \leq p \leq 13$ and $2.20 \leq \gamma \leq 2.50$ is shown. By comparing Fig. 4 with Fig. 3,

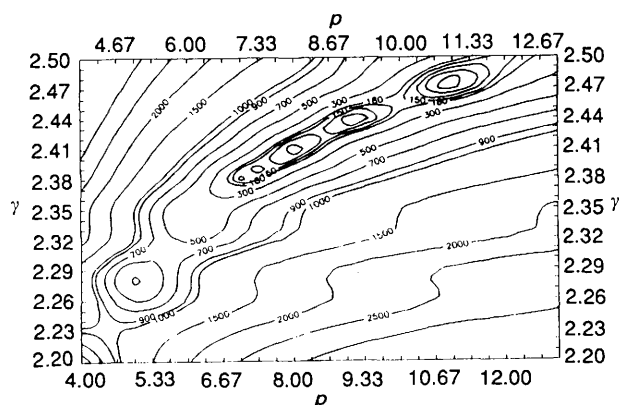


Fig. 4 Contour lines of the standard deviation of fits of the ground state of CO molecule using as fitting function the leading term of a Mattera's potential

the zone of the minimum is now very well defined with respect to the second parameter γ . The standard deviation of the minimum is now 30.2 cm⁻¹ (mean deviation 24.7 cm⁻¹) corresponding to the optimum parameters: $p = 10.8$ and $\gamma = 2.47$. From Table 6 we can see that both Engelke and Mattera potentials are equivalent for $N \geq 4$ as fitting functions. In Fig. 5 we show a three-dimensional representation of the variation of the standard deviation of the fit of the $X^1\Sigma^+$ state of CO by using the leading term of a Surkus potential as a function of its non-linear parameters for $2.70 \leq p \leq 2.90$ and $0.20 \leq \mu \leq 0.26$. The minimum is at 118 cm⁻¹ for $p = 2.80$ and $\mu = 0.234$. We see that the leading terms of an Engelke or Mattera potential function are preferable to a Surkus's function, although for an intermediate number of basis functions ($N \approx 8$) all these functions are equivalent.

We have also considered potential-energy functions defined very near to the dissociation of the ground state of ^7LiH ³⁹ and H_2 ⁴⁰ molecules. The statistical parameters of the least-squares fits for these potentials are shown in Tables 7 for H_2 , and 8 for ^7LiH . In general, we see that the accuracy of these fits is worse than for CO, with a standard deviation *ca.* 0.7 cm⁻¹ for H_2 and *ca.* 9 cm⁻¹ for ^7LiH . In the fits we have only considered power-series expansions with an interval of convergence up to infinity except for the Dunham function which as we saw presents serious convergence problems. For H_2 we see that the fits by different power-series expansions using the same number of parameters are similar. For ^7LiH there is little oscillation between the fits; the better fit is obtained for a Thakkar's potential with $p = 1.48$. The explanation of the difference between the fits for H_2 and ^7LiH may be that the ^7LiH potential is a mixture of two ionic and covalent potentials.⁴¹ This mixture of states is most clear when considering the first excited state $A^1\Sigma^+$,³⁹ with an unusual form of the potential curve and anomalous negative values of the anharmonicity constants $\omega_e x_e$ and α_e . The statistical parameters of the least-squares fits of this potential are shown in Table 9. The standard deviation is *ca.* 4.8 cm⁻¹ when using 11–13 basis functions. We see that the methods discussed here are also useful for abnormal potential-energy curves such as the $A^1\Sigma^+$ state of alkali hydrides.

Conclusions

Eight different power-series expansions are compared both by consideration of convergence properties and by fitting experimental potential-energy curves. The quality of fits

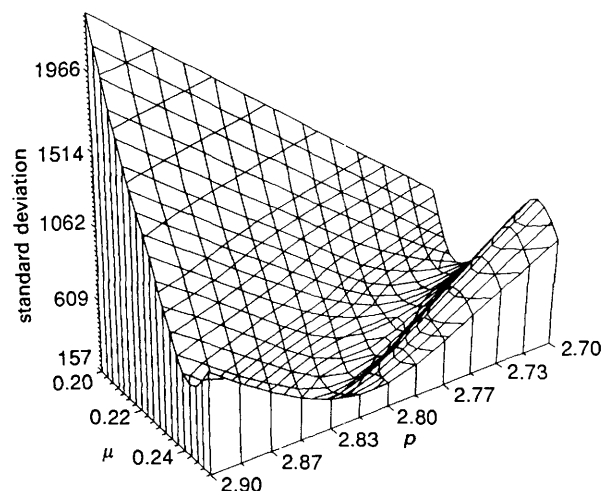


Fig. 5 Three-dimensional representation of the variation of the standard deviation of fits of the ground state of the CO molecule using as fitting function the leading term of a Surkus's potential

Table 7 Statistical values for the least-squares fit of the $X^1\Sigma_g^+$ state of H_2 defined between (0.268 50 Å, 5.652 15 Å), using different truncated power-series expansions

function	N	optimum parameters	interval of convergence/Å	standard deviation/cm ⁻¹	mean deviation/cm ⁻¹
Dunham	20		(0, 1.483)	13 540	8 567
SPF	20		(0.370 75, ∞)	0.72	0.49
Ogilvie	20		(0, ∞)	0.76	0.43
Thakkar	19	$p = 0.5$	(0.185 375, ∞)	0.74	0.48
Engelke	18	$p = 1; \beta = 0.9$	(0.037 075, ∞)	0.77	0.45
Mattera	18	$p = 5; \gamma = 1$	(0.261 566, ∞)	0.63	0.38
Surkus	18	$p = 2; \mu = 1$	(0, ∞)	0.61	0.41
Huffaker	19	$\alpha = 1$	(0.048 352 5, ∞)	0.70	0.40

$$r_e = 0.741\,499\text{ Å}.$$

Table 8 Statistical values for the least-squares fit of the $X^1\Sigma^+$ state of $^7Li\ ^1H$ defined in the interval (1.004 70 Å, 5.204 851 Å) for different truncated power-series expansions

function	N	optimum parameters	interval of convergence/Å	standard deviation/cm ⁻¹	mean deviation/cm ⁻¹
Dunham	20		(0, 3.191 168)	12 901	5 672
SPF	20		(0.797 792, ∞)	11.18	5.76
Ogilvie	20		(0, ∞)	14.81	7.82
Thakkar	19	$p = 1.48$	(0.998 897 7, ∞)	8.07	4.79
Engelke	18	$p = 4; \beta = 1$	(1.087 857, ∞)	11.21	7.22
Mattera	18	$p = 4; \gamma = 2$	(1.087 857, ∞)	12.60	7.23
Surkus	18	$p = 0.5; \mu = -0.5$	(0.897 515, ∞)	11.5	7.74
Huffaker	19	$\alpha = 1.36$	(1.085 916, ∞)	9.79	5.41

$$r_e = 1.595\,584\text{ Å}.$$

Table 9 Statistical values for the least-squares fit of the $A^1\Sigma^+$ state of $^7Li\ ^1H$ defined in the interval (1.4162 Å, 4.9538 Å) for different truncated power-series expansions

function	N	optimum parameters	interval of convergence/(Å)	standard deviation/cm ⁻¹	mean deviation/cm ⁻¹
Dunham	13		(0, 5.1926)	175.3	139.8
SPF	13		(1.2982, ∞)	4.95	3.95
Ogilvie	13		(0, ∞)	5.35	4.27
Thakkar	12	$p = 0.85$	(1.1487, ∞)	4.83	3.95
Engelke	11	$p = 2.2; \beta = 1$	(1.1929, ∞)	4.72	3.94
Mattera	11	$p = 2.3; \gamma = 1.1$	(1.1838, ∞)	4.72	3.95
Surkus	11	$p = 1.7; \mu = 0.6$	(1.0074, ∞)	4.75	3.97
Huffaker	12	$\alpha = 1.0$	(1.9032, ∞)	4.79	3.91

$$r_e = 2.5963\text{ Å}.$$

which can be achieved for accurately known RKR potentials is shown for a range of examples.

We observed that a good fit with only the leading term of a power-series expansion may be obtained more accurately from an Engelke, Mattera or Surkus function with two non-linear parameters. For fitting power-series expansions with an intermediate number of fundamental basis functions it is better to use a Thakkar or Huffaker type function with only one non-linear parameter because the effort in calculating the second optimum non-linear parameter of an Engelke, Mattera or Surkus function does not compensate the precision of the fits (see Tables 5–9). In conclusion, we feel that the power-series expansions can be used, with sufficient accuracy, as fitting functions of potential-energy curves whose definition rank is within the interval of convergence of the series. Moreover, in the zone of short distances it is preferable that the interval of convergence includes the first right point of the input potential and its lower extreme is in the neighbourhood of that point. For potentials defined far away from the dissociation, by using power-series expansions with an intermediate number of linear parameters, it is possible to fit the

starting potential with an accuracy of *ca.* tenths of cm⁻¹. For potentials defined near the dissociation, by using power-series expansions with an intermediate number of linear parameters, it is possible to fit the starting potential with an accuracy *ca.* tenths of cm⁻¹. For potentials defined up to the dissociation, it is possible to fit with an accuracy of a few cm⁻¹.

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