Interpolation and fitting of potential energy surfaces: Concepts, recipes and applications

Ralph Jaquet

March 17, 2002

1 Introduction into interpolation and fitting of PES

- molecular dynamics investigation (scattering, spectroscopy, etc.):

- need information about the interaction potential or the potential energy surface PES (Fig. 1)

- multidimensional hypersurface or single values $V(R), V(R'), V(R''), ..$

- special coordinates

- there are three possibilities to create PESs:

(1) use of data from electronic structure calculations.

(2) use of experimental information (e. g. RKR [2]), that means the PES must reproduce experimental results in a dynamical calculation.

(3) combination of the above two cases.

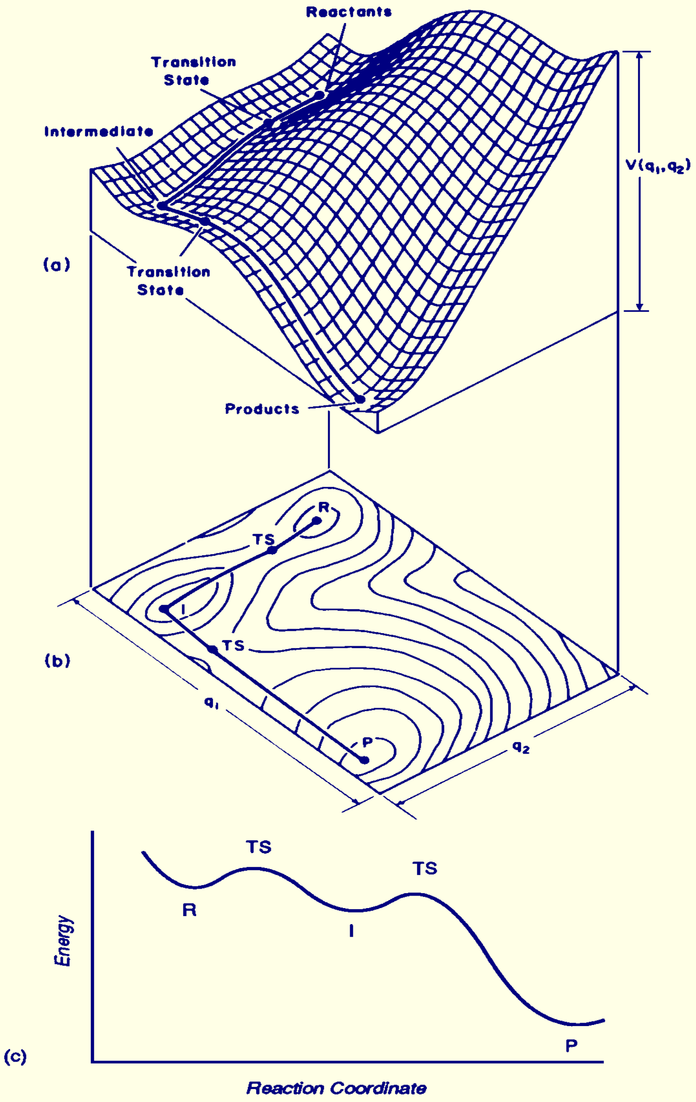


Figure 1: (a) Potential energy surface for a general reaction $R \rightarrow I \rightarrow P$ (b) Contour plot that corresponds to a. (c) Reaction coordinate for the process depicted in a and b, corresponding to the solid lines of a and b.

results of ab initio (or semiempirical) electronic structure calculations:

- tables of energy values for special geometries (commonly calculated within the Born-Oppenheimer (BO) approximation)
- in some program systems (e. g. CADPAC, GAUSSIAN94, etc.): 1st, 2nd and higher derivatives of the energy [3, 4]
- in general it is still customary to calculate single energy values, which are used for interpolation/extrapolation in order to construct a PES for a large range of nuclear geometries

kind of the dynamics to be studied:

- whether a relatively small area is needed (e. g. for spectroscopy of the lowest energy levels of a small molecule)
- or an extended area is required (e. g. in the case of reactions including the transition state region (Fig. 2), photodissociation, spectroscopy of bound states near the dissociation limit).

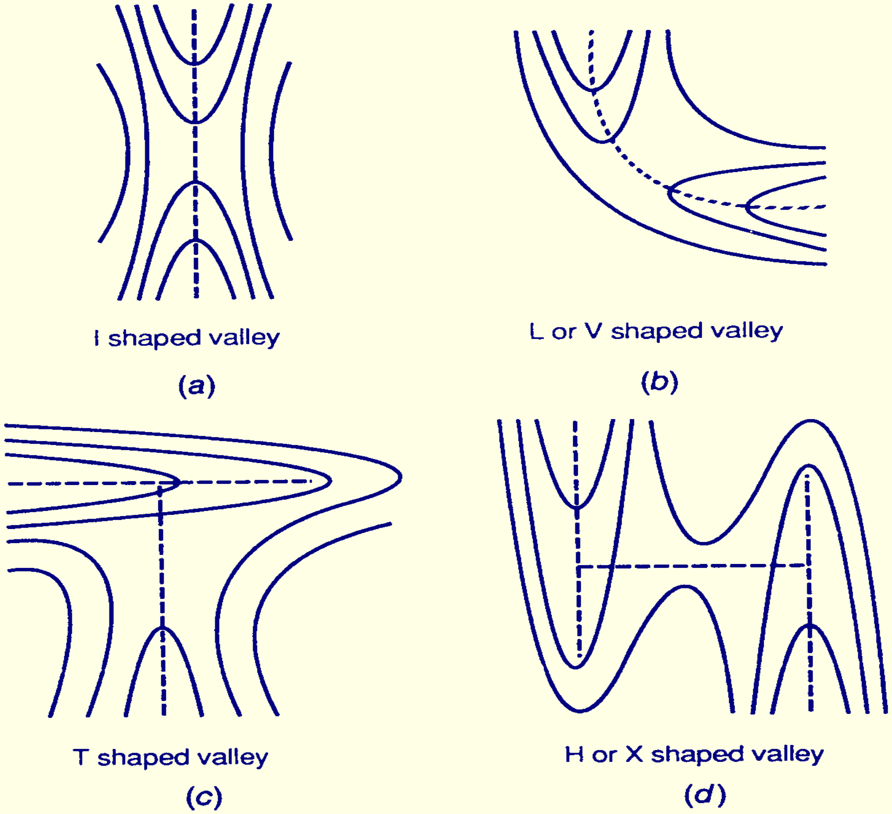


Figure 2: Different classes of potential energy surfaces in the vicinity of transition states.

- theory needed to calculate molecular properties from PESs is highly developed [5, 6, 7, 8, 9, 10, 11, 12] and computationally expensive

- one has a given set of data (i. e. atom positions, interatomic distances, internal coordinates, etc. x_i and potential energy values y_i) which one wants to condense by fitting it to a $model$ that describes the potential energy surface and that depends on adjustable parameters

\- $model$ is simply a convenient class of functions, such as polynomials, Gaussians or other specific functions and the fit supplies the appropiate coefficients

- choice:

\- use functions that perform well in a local region
\- use global functions that cover a large region with “fairly good” accuracy

- local approximations:

interpolating functions (splines), expansions in polynomials or rational functions, etc.

- local and as well global approximations:

functional forms that are special and simulate a special topography of the PES (e. g. Morse functions, separation of the many body potential into two-body, three-body, etc.-interactions)

- global methods: the function depends on the entire set of data
- local methods: a restricted number of data values are used
- or PES is searched only along the reaction path: reaction path-potential
- intrinsic reaction coordinate (from the transition state to the product or the reactant configuration)

- interpolating functions: can cover exactly or approximately the given data points

- the basic approach in all cases is usually the same:

- one chooses a ”merit function” that measures the agreement between the data and the model with a particular choice of parameters
- in case of a ”least-squares” Ansatz small values represent close aggreement
- parameters of the model are adjusted or optimized to acieve a minimum in the merit function, yielding the “best-fit” parameters. - adjustment process is a problem in minimization in many dimensions (linear or non-linear least-squares methods (LLS, NLLS: [13, 14, 15, 16])

- experimental data: for the description of PESs one has to take into account that these data are generally not exact and that one has to deal with measurement errors (i. e. systematic errors, random errors, etc.)

- important to distinguish between the terms accuracy and precision

- typical experimental data never exactly fit the model that is being used, even when that model is correct

● if each data point has its own, known standard deviation or ”measurement error” the fitting equation will be modified by this dependency (called weighting factor)

- the same is true when we deal with calculated data for the fit of the PES

● theoretical data, i. e. calculated eigenvalues, are not statistical; they are numerically ”exact” within each quantum chemical method (as long as internal parameters are correctly chosen)

- it is not easy to assign error bars to the theoretical data depending on the theoretical method and on the geometrical position on the PES

● except in few cases the theoretical data deviate from the true value by more than the standard deviation resulting from the fitting procedure; the resulting surface can be valued as a “rough” description of the true PES, although it might be the best available result

• if one fits data points (x_i, y_i) to a model one tries to predict a functional relationship between independent variables x_i and dependent variables y_i

• the independent variable x_i is not necessarily a physically meaningful coordinate, but may be a linear combination of coordinates • if the coordinate is a distance, R, many possible choices for the independent variable have been proposed:
R, $(R - R_e)/R_e$, $(R - R_e)/R$, $2(R - R_e)/(R + R_e)$, etc. (R_e= equilibrium distance)

• it is not uncommon in fitting data to discover that the merit function gives comparatively good results for different parameter values out of the parameter space and that different model-functions predict nearly the same results for the merit function
- how is one sure that there is not a very much better fit?
– this kind of problem is generally quite difficult to solve ("Modeling of Data" [80])

- if we perform the fit with theoretical data, all functions must fulfill some common features:

- the given energy values must be reproduced as accurately as possible

- the interpolated values have to be “meaningful”

– “meaningful” is not easy to specify:
– (a) mathematical relations
– (b) “chemical and physical” intuition and experience

- depending on the way of fitting the data, the outcome of the dynamics calculations will be influenced and thus can lead to different findings

Fit procedures should supply:

(a) parameters for the functional forms

(b) error estimation of the parameters

(c) a statistical measure of the quality of the fit

- if (c) is bad, the results in (a) and (b) can be classified as useless

- if the results "look good" (e. g. small variance, "chi by eye") only part (a) will be performed and the parametrization will be accepted

Summary of the criteria for interpolating functions [17, 18, 19]:

(i) an accurate fit should be achieved with the smallest number of data points

(ii) the fit should converge to the “true” PES if more data are added

(iii) the interpolating function should indicate where more data are needed

(iv) The functional Ansatz should have a minimal amount of special character

(v) the interpolating functions and derivatives should have, if possible, a simple algebraic form

(vi) the correct symmetry properties of the given system should be represented

(vii) the fit should represent the "true potential", where experimental or empirical/theoretical data are given

(viii) the fit should be "physically meaningful" where no experimental or theoretical data are given

for studying reactions it is further necessary:

(ix) the fit should smoothly connect the interaction area and the asymptotic regions

overviews:(skip this part)

till 1985 is given by Sathyamurthy [20] (especially reactive and nonreactive potentials for two- to four-atomic molecules)

Carter [21] and Schatz [22] on analytical PESs for three- and four-atomic molecules

Searles and von Nagy-Felsobuki [23, 24, 25] on local and global functional forms with detailed comparisons for different fits

Varandas [26, 27, 28] on inter- and intramolecular potentials (with "double many body expansion")

Mezey [29] on the fitting with splines, polynomials and trigonometric functions (one chapter of his book "Potential energy surfaces")

Law and Hutson [30] on interactive non-linear least-squares fitting of the parameters of physical models

book of Murrell and co-workers [31] on “molecular potential energy functions”: overview about PESs, topographies, choice of coordinates and fitting

book of Hirst [32]: relations between PESs and molecular structure and reaction dynamics

asymptotic factorization of the PES based on the global topography of molecular potentials is given in [33]

more information on topographies can be obtained from [1, 34, 35, 36]

characteristic features of the potential energy for chemical reactions (ab initio and semiempirical determination) are given in [37, 38, 39, 40, 41]

relationships between minimal energy paths, reaction paths, intrinsic reaction coordinates and gradient extremals in [42, 43, 44, 45]

use of sensitivity analysis in [46]

use of derivatives [3, 4] in a multivariate Taylor expansion of the PES in the vicinity of a reaction path or near equilibrium geometries [47, 48, 49, 50, 51]

work of Berry [52, 53, 54], especially on clusters [55], multidimensional PES and related questions are discussed:

(a) how to find important regions

(b) how the landscape depends on elementary characteristics of the parameters of the potential

(c) how certain dynamical properties are consequences of the geography of the PES, etc..

- PESs and their use in dynamics are presented in [38, 56, 57, 58, 233, 59, 60, 61, 63, 64, 65, 66, 67, 68, 69]

- vibrational PESs for ground and excited states is given by Laane [70]

- general correlations between data regression and error analysis are discussed in [15] and [71]

- EC-workshop (1995): devoted to the calculation of PESs [72]

further discussion in the literature:
- empirical force field methods [73] needed in molecular dynamics or Monte Carlo simulations [74]
- different attempts for the formulations of the complete dynamics of electrons and nuclei of a molecular system that eliminates the necessity of constructing PESs:
- END-method [75, 76], Car-Parinello-method [77] or so-called ab initio molecular dynamics simulation techniques [78]

2 General functional forms

2.1 General procedure

brief overview to proceed in modeling data for a PES:

- identify independent variables or coordinates (there are in general several possibilities) to prevent numerical problems with linear dependencies in optimizing the parameters of the model function

- the data points have to be examined for their correctness (e. g. energy values may be not converged or belong to a different electronic state) [20, 25]

- plotting of the energy points as a function of one or two coordinates might help to find erroneous input data

question:

on which variables (coordinates) the potential does depend strongly or weakly?

how carefully the optimization of the parameters with respect to an expansion in a specific variable has to be performed?

the data range of the independent variables has to be identified

it has to be checked how dense or sparse the number of data are

consequences:

depending on this information and on the qualitative behavior of the potential one chooses functions which can describe correctly a small or large range in coordinate space

one selects functions like exponentials or trigonometric functions, polynomials, etc., which can simulate the potential shape within the number of given discrete points

one has to decide for a local or global Ansatz

- if a linear Ansatz is given or the functional form is linearized from a more general non-linear Ansatz, the data (with the option to use physically or numerically motivated weighting factors) will be fitted with a linear least-squares procedure

- numerically, this means a solution of a set of linear equations which can be performed with an additional proof of quality using “singular value decomposition” (SVD) [79, 80]

- otherwise one uses non-linear concepts, where within the NLLS-method the model function is optimized iteratively and where the starting parameters can be taken from a linearized solution
- for NLLS procedures one has to make sure that a variation of the starting parameters does not lead to different results

- in case of doubts one has to use constraints for the range of values of the fitting parameters

How can one recognize the quality of the fit?

(a) one can use the residual-method [81], calculate the mean square deviation σ (i. e. difference between the fitting function and the original input data) and perform a χ^2-test [15]

- however, these tests do not always characterize the quality of the fit, even if the variance is small

- potential energy values V cannot be regarded as "statistical"

(b) help by graphical representations of the residual potential ΔV :
- V versus ΔV: always the same sign or not, do the residuals occur in clusters ? (bad!)
- plot of the fitted potential for all possible coordinates (or combinations of these)
– are minima or maxima are created in those areas where not enough data points are given?

- changing the coord. system: additional weakness of the fit can be shown

- the investigation of the dynamics will show if the known experimental or theoretical results are reproduced satisfactorily

- if the results depend strongly on the input for the PES-fit, a sensitivity analysis [61] is needed

2.2 Interpolating functions (IF)

- interpolating functions [25, 80, 82, 83] are functions which at the given data points $\{x_i, y_i\}$ reproduce the values y_i for the independent variables x_i

- for some functional types IF exactly reproduce the derivatives

\- this does not imply that the quality of the fit is maintained at any intermediate point

- the total interval for approximation is divided into subintervals, where the so-called knots, nodes or points are defined

- within each subinterval an approximation with a relatively simple function is performed

- the order of interpolation in an interpolation scheme is given by the number of points minus one

- in general smooth curves are better described by interpolation of high order; curves that change “abruptly” are better described by low order interpolations

- typically, three- or four-point interpolations are used. Irregularities in the interpolation can be found from graphical representations

- commonly, Hermite and Lagrange functions and cubic splines (and the variant of Akima) are used as interpolating functions

- splines are a compromise between polygon-line and an interpolating polynomial of higher order

$Lagrange\ interpolation$ (LI) with order N [80]:

$$V(x) = \frac{(x-x_2)(x-x_3)\ldots(x-x_N)}{(x_1-x_2)(x_1-x_3)\ldots(x_1-x_N)}y_1 + \frac{(x-x_1)(x-x_3)\ldots(x-x_N)}{(x_2-x_1)(x_2-x_3)\ldots(x_2-x_N)}y_2 + \cdots + \frac{(x-x_2)(x-x_3)\ldots(x-x_{N-1})}{(x_N-x_1)(x_N-x_2)\ldots(x_N-x_{N-1})}y_N \quad (1)$$

energy y_i given at the position x_i

$Hermite\ interpolation$ (HI) with order N [80]:

$$V(x) = \sum_{j=1}^{N}(y_j F_j(x) + g_j G_j(x)) \quad (2)$$

energy y_i and the first derivative g_i of the energy with respect to x given at the position x_i

F and G are formfunctions depending on all positions x_i

Cubic spline interpolation (SI) with order 3 [80]:

$$V(x) = y_i + a_i(x - x_i) + b_i(x - x_i)^2 + c_i(x - x_i)^3 \tag{3}$$

a_i, b_i and c_i are functions of $\{x_i, y_i\}$

Akima interpolation (AI): similar to cubic spline, can be also used for irregular grids [84, 85, 86]

Advantages and disadvantages:

- interpolating functions are normally used for a local interpolation using an equidistant discretization

- extrapolation and the use of non-equidistant grids can be problematic

- interpolating functions of high order supply quite different results, if the original data are modified a little bit (“noise”); sensitivity analysis might be helpful [61]

- comparison of different IFs can be summarized as follows (H_2: [87]): 3rd order expansions did not introduce irregularities, whereas 5th order expansions introduced errors

- SI and HI are more accurate with respect to energy than LI. SI has a distinct advantage over HI since knowledge of derivatives is not required

- cubic SI is reliable in the representation of the “true” potential

- lack of accuracy for SI depends on the number of points; in case of too few points this leads to topological errors

Alternative: a more localized interpolation of Akima; for 3D (ABC-system) there might be problems with SI in case of the wrong choice of coordinates (the triangular inequality must be fulfilled); the L-splines avoid spurious oscillations [88]

Examples:

(a) 1D cubic spline fit to a Morse potential [89] for H_2: at least 14 nodes (i. e. data points) are necessary (see table 1) [25] !

Table 1: 1D cubic spline for H_2 in comparison to the exact Morse-Ansatz [a]

nodes	$\sigma(V/eV)/10^{-3}$	$\Delta_1(V/eV)/10^{-3}$
10	3.1	—
12	0.8	2.3
14	0.5	0.3
16	0.2	0.3
20	0.1	0.1

[a] σ: variance, Δ_1: absolute variance of successive differences, fit of the Morse function in the range $0.5 \leq R \leq 2.5$ Å.

(b) Li_2: cubic spline (good!) for spectroscopic investigations ([23], see table 4.2 in [25])

(c) 3D-splines, combined with Morse functions for classical trajectories [89]. Problems with 3D-splines: see [90, 91]

higher dimensional interpolations: see [80]

discussion of different spline variants: see [82]

2.3 Power series expansions and rational functions

expansion of the PES in a polynomial form:

$$V(x_1,..,x_f) = \sum_{i_1,..,i_f}^{N} a_{i_1,..,i_f} u_1^{i_1} ... u_f^{i_f} \quad , \tag{4}$$

u_i are functions of the x_i (e. g. internal coordinates: distances, angles, etc.) for f degrees of freedom and different orders i_j.

contrary to the interpolation one has more given values for V_i than parameters a_j, so the use of LLS or NLLS in the fit is necessary

the functional form can be used for extrapolation

PES for a triatomic molecule (R_1, R_2, R_3) in a power series expansion:

$$\begin{aligned} V(R_1, R_2, R_3) \quad &= V_0 + \textstyle\sum_i^3 C_i^{(1)} x_i + \sum_i^3 \sum_j^3 C_{ij}^{(2)} x_i x \\ {}_j + \sum_i^3 \sum_j^3 \sum_k^3 C_{ijk}^{(3)} x_i x_j x_k \quad &+ \textstyle\sum_i^3 \sum_j^3 \sum_k^3 \sum_l^3 C_{ijkl}^{(4)} x_i x_j x_k x_l + \cdots \end{aligned} \tag{5}$$

different choices for the expansion variables x_i have been proposed

rational expansion: quotient $P_{m,n}(R_1, R_2, R_3)$ (Padé–approximation)

$$V(R_1, R_2, R_3) = P_{m,n}(R_1, R_2, R_3) = \frac{\sum_{i=0}^{m} \sum_{j=0}^{m} \sum_{k=0}^{m} a_{ijk} x_1^i x_2^j x_3^k}{\sum_{i'=0}^{n} \sum_{j'=0}^{n} \sum_{k'=0}^{n} b_{i'j'k'} x_1^{i'} x_2^{j'} x_3^{k'}}, \tag{6}$$

$$(i + j + k) \leq m, \quad (i' + j' + k') \leq n$$

two polynomials with different orders m and n

What is a reasonable choice for x_i?

popular forms proposed by Dunham [92], Simons-Parr-Finlan (SPF) [93], Ogilvie [94], Thakkar [95], Huffaker [96] ($R_e =$ equilibrium distance):

$$\begin{array}{l} \text{Dunham: } x = (R - R_e)/R_e \\ \text{SPF: } x = (R - R_e)/R \\ \text{Ogilvie: } x = 2(R - R_e)/(R + R_e) \\ \text{Thakkar: } x = 1 - (R_e/R)^{-a-1},\ a = \text{“Dunham-constant”} \\ \text{Huffaker: } x = 1 - e^{-a(R-R_e)} \end{array} \tag{7}$$

- advantages and disadvantages of the different expansions become more apparent when the convergence properties [97, 98] and the asymptotic behavior are discussed [93, 94, 95, 97, 98].

What are the relations between the different choices for x_i?

Dunham-SPF-Ogilvie:

$$x_i^{OGILVIE} = \frac{2x_i^{SPF}}{2 - x_i^{SPF}} = \frac{2x_i^{DUNHAM}}{2 + x_i^{DUNHAM}} = \frac{2(R_i - R_e)}{R_i + R_e} \qquad (8)$$

Nagy-Felsobuki and co-workers [23, 24, 25, 99] have laid down some “rules” for the power series expansion:

(1) the polynomial expansion used should have a “quantum mechanical basis”

(2) real plane convergence properties should suggest a reasonable (in a physical sense) region of acceptability

(3) the fit should be consistent with respect to accepted physical properties and should show a smooth behavior in case of monotonically increasing repulsive potentials

(4) the error of the fit should be within the accuracy of the ab initio points

(5) evaluation of the expansion coefficients should be systematic and amenable to a regression analysis

(6) one should prefer an analytical representation, which can accomodate several different types of experimental data

criterion 1: fulfilled; also for Morse-type expansion variables [95]

criterion 2: problematic

Dunham expansion: range of convergence $0 < R_i < 2R_e$ [97], bad for large R (e. g. vibrational energy levels near dissociation limit)

SPF-expansion: range of convergence: $R_i > 0.5R_e$ [98], shows oscillatory behavior for small values of R [93]

Ogilvie-expansion: valid for the complete range $0 < R < \infty$ (problems at R=0 and R=∞ [98])

Huffacker (Morse): good convergence properties [95, 96, 100], good for triatomics too [23, 24, 101, 102]

criterion 4: can be normally fulfilled, difficulties in the most recent calculations for highly accurate ab initio points of H_3^+ [351, 352]

criterion 5: least square fit (see eq. 9), χ^2-analysis for N data points

criterion 6: fulfilled; (Dunham, SPF and Ogilvie)- force fields are used for different experimental data

Minimization of the sum of least-squares (V^{PS}= power series expansion, V^{exact}= exact value):

$$\chi^2 = \sum_{m=1}^{N} (V^{PS}(x_{1m}, x_{2m}, x_{3m}) - V^{exact}(x_{1m}, x_{2m}, x_{3m}))^2 \qquad (9)$$

but: smallest χ^2-value does not necessarily mean the best fit

criterion 3: polynomial expansions are consistent with respect to the expected description of physical properties. There are problems with polynomials of high degree

- Ogilvie tried different expansions (Dunham, SPF, etc.) for HF [94]:

- with the Ogilvie-Ansatz he needed 5 terms in the expansion, using the Dunham-Ansatz comparable accuracy could be reached with 8 terms

- polynomials of high degree produce oscillations and singularities

Help: “Singular value decomposition SVD”: this damps the contributions of coefficients for expansions of higher order

Examples:

- 3D, LiH_2^+ [24]:

- different choices of x_i, the polynomial expansion of 6th degree with the Ogilvie-Ansatz combined with the SVD-method proved to be the best method

- Murrell et al. [103, 104]:

- diatomic molecules: the use of rational functions is not useful for the whole R-range; singularities might occur in the numerator or denominator depending on the order of the polynomial; introduction of the factor $(R_i)^{-1}$ leads to better results, nevertheless singularities do appear

- Padé-approximations:

- multidimensional cases have not been sufficiently investigated
- the Ansatz is flexible, but singularities may still occur (LiH_2^+: modified Padé-approximant [24])

- Downing et al. [105]: - potential energy values behave like roots of characteristic polynomials of a secular equation
- the method yields good results, but needs many input data for increased dimensionality - in case of extrapolation, the results are reasonable

further application: NO_2 [106].

2.4 Many-body expansions

- early work by London, Eyring, Polanyi and Sato (LEPS) [107]

- “diatomics in molecules (DIM)” -method Ellison (1963) [108]

- reactivated by Murrell et al. [31, 109, 110, 111, 112]

- used this variant first for the fitting of spectroscopic data of triatomic molecules
- today different variants of this Ansatz are employed, which are not limited just to triatomic molecules
- it is possible to describe potentials with a complicated topography, several minima with different symmetries
- the repulsive, attractive and asymptotic range of the potential can be adapted differently - suitable as global fits for dynamic calculations in the full range of coordinates

Literature: [21, 31]

- large number of parameters, enough flexibility to fit the desired property with proper accuracy (energy, geometry and force constants at the minimum) - asymptotic two-body interactions can be fixed experimentally or by ab initio methods the potential for a triatomic molecule can be decomposed (one-, two- and three-body terms):

$$\begin{aligned} V(R_1, R_2, R_3) = \quad & V_A^{(1)} + V_B^{(1)} + V_C^{(1)} + V_{AB}^{(2)}(R_1) + V_{BC}^{(2)}(R_2) + V_{CA}^{(2)}(R_3) \\ & + V_{ABC}^{(3)}(R_1, R_2, R_3) \end{aligned} \tag{10}$$

for the ground state: the monoatomic terms $V^{(1)}$ can be set to zero, the two-body terms $V^{(2)}$ describe the diatomic potentials formed by adiabatic dissociation of the molecule ABC

true three-body terms are written as products of polynomials P and a range function T:

$$V_{ABC}^{(3)} = P(x_1, x_2, x_3)T, \quad T = \prod_{i=1,3} (1 - \tanh(\gamma_i x_i/2)) \tag{11}$$

$$P(x_1, x_2, x_3) = \sum_{ijk} C_{ijk} x_1^i x_2^j x_3^k, \qquad i + j + k \leq n, \qquad x_i = R_i - R_i^0 \quad (12)$$

C_{ijk}, γ_i, R_i^0: fitting parameters

- for negative x_i the function T remains finite, whereas it becomes zero for large positive x_i; the corresponding diatomic potential remains

- symmetry properties can be considered in form of proper symmetry adapted coordinates

Sorbie and Murrell (SM) [109]: original proposal to fit spectroscopic data for triatomic molecules

different approaches developed by the “Murrell-school” [26, 31] and other authors [113, 114, 115]

different functional forms tested for SO_2: [110, 111, 112]

fitting of P in a linearized form (for different combinations of γ_i):

$$[V_{tot} - V_{AB} - V_{BC} - V_{CA}]\,/\prod_{i=1,3}(1 - \tanh(\gamma_i x_i/2)) = P(x_1, x_2, x_3) \tag{13}$$

full fit will be performed with a NLLS-method

Difficulties:

SM-approach:

- known to produce small humps and wells in those regions, where not enough data points are given

- by adding gaussian functions (addition/subtraction) these errors can be reduced

- Garcia and Lagana [116] fitted first a three atomic potential term and after that matched the complete potential Ansatz to the asymptotically correct diatomic limits

Particularities:

- possible to build in these functional approaches a special non-analytical behavior: for H_3 with Jahn-Teller non-analyticities in the ground state [117]; two PE surfaces of H_3 near the conical intersection [26, 28, 118, 119]

- SM-approach: used for the fit of multi-valued PESs (ground and excited state)

- diabatical fit to SM-functions, nonadiabatic interactions to trigonometric functions: calculation of the roots of 2x2 determinants (p. 50 in [20])

Which functional forms $V(R_1, R_2, R_3)$ are generally taken in case of many body expansions?

$$V(R_1, R_2, R_3) = \sum_{i=1}^{3} V_i^{(2)}(R_i) + V^{(3)}(R_1, R_2, R_3) \qquad (14)$$

SM [109]:

use for $V^{(3)}$ the expression in equation (11).

Examples: different molecules in Ref. [20, 21, 31].

LEPS ($H + H_2 \rightarrow H_2 + H$): useful as an interpolatory function to connect reactants and products

$$V(R_1, R_2, R_3) = \sum_{i=1}^{3} Q_i(R_i) - \frac{1}{2}\sqrt{\sum_{i<j=1}^{3} (J_i(R_i) - J_j(R_j))^2}$$

$$Q_i(R_i) = \frac{1}{2}\left[{}^1E(R_i) + {}^3E(R_i)\right], \qquad J_i(R_i) = \frac{1}{2}\left[{}^1E(R_i) - {}^3E(R_i)\right]$$

$${}^1E(R_i) = {}^1D_i X_i(X_i - 2), \quad X_i = e^{-\beta_i(R_i - R_i^e)}, \qquad {}^3E(R_i) = {}^3D_i X_i'(X_i' + 2),$$

$${}^3D_i = \frac{1}{2}\frac{(1 - S_i)}{(1 + S_i)}\, {}^1D_i$$

(S_i: Sato-parameter)

DIM (based on valence bond concepts): Diagonalization of a DIM-Hamiltonian, calculations of ground and excited states are possible.

1st application: collinear reaction He + $H_2^+ \rightarrow$ HeH^+ + H: [120, 121, 122]

$$\begin{aligned} V(R_1, R_2, R_3) &= Q_1 + Q_2 + Q_3 - \sqrt{(J_1 - J_3)^2 + J_2^2} \\ Q_i(R_i) &= \frac{1}{2}\left[{}^1E(R_i) + {}^2E(R_i)\right] \\ J_i(R_i) &= \frac{1}{2}\left[{}^1E(R_i) - {}^2E(R_i)\right] \\ E(r) &= pDe^{-\beta(R-R_0)}(2 + pe^{-\beta(R-R_0)}) \end{aligned} \qquad (16)$$

($p = \pm 1$: for repulsive (1) and attractive (-1) interaction)

“extended” LEPS and residuum (NeH_2^+: [123, 124]):

$$V^{(3)} = V^{(3)}_{LEPS} + \sum_{lmn=0}^{M} a_{lmn} \frac{1}{R_2^m} \left(\frac{1}{R_1^l R_3^n} + \frac{1}{R_1^n R_3^l} \right) \tag{17}$$

Joseph and Sathyamurthy [114] (NeH_2^+: [125, 126]):

$$V^{(3)}(R_1, R_2, R_3) = \left(\sum_{i,j,k=0}^{M} C_{ijk} x_1^i x_2^j x_3^k \right) * \tag{18}$$

$$\Big(1 - \tanh\big(\gamma_1(x_1 + x_3)/2\big)\Big)\Big(1 - \tanh\big(\gamma_2 x_2/2\big)\Big),$$

$$j + k + l \leq M, \qquad R_1^0 = R_2^0 = R_3^0$$

$$V_i^{(2)}(R_i) = -D_e \left(\sum_{n=1}^{8} c_n x_i^{n-1} \right) e^{-c_9 x_i} \quad (extended\ Rydberg)$$

$$x_i = R_i - R_i^0 \tag{19}$$

Schinke [113] (NeH_2^+: [125, 126]):

$$V^{(3)}(R_1, R_2, R_3) = \left(\sum_{i,j,k=0}^{M} C_{ijk} x_1^i x_2^j x_3^k \right) \Big[\big(1 - \tanh(\gamma_1(x_1 + x_3)/2)\big) \Big]$$

$$* \left\{ (1 - \tanh(\gamma_2 x_2/2)) e^{-\alpha(R_1+R_3)^2} \right\}, \qquad j + k + l \leq M$$

$$V_i^{(2)}(R_i) = -D_e(\sum_{n=1}^{8} c_n x_i^{n-1}) e^{-c_9 x_i}$$

$$x_i = R_i - R_i^0 \tag{20}$$

Aguado and Paniagua [115] (NeH_2^+: [125, 126]):

$$V^{(3)}(R_1, R_2, R_3) = \sum_{i,j,k=0}^{M} C_{ijk} x_1^i x_2^j x_3^k,$$

$$x_i = R_i e^{-\omega_i R_i}, \qquad j + k + l \neq j \neq k \neq l, \qquad j + k + l \leq M$$

$$V_i^{(2)}(R_i) = \frac{c_o e^{-\beta_i R_i}}{R_i} + \sum_{n=1}^{N} c_i \eta_i^n, \qquad c_0 > 0, \text{ so that } \lim_{R_i \to 0} V_i^{(2)} \to \infty$$

$$\eta_i = R_i e^{-\epsilon_i R_i} \tag{21}$$

extensions of the many-body expansions of Murrell et al. [31]:

Varandas [26, 127]: many-body expansions for van der Waals and stable molecules

Aguado et al. [128]; H_4 with four-body terms

further applications: $(H_2O)_2$: [129], HeH_2: [131], $NH_3 + H \rightarrow NH_2 + H_2$: [132], Li + HF: [133], Be + HF: [295], H_4^+: [134].

Interpolation without “fixed” functional forms

Use of genetic algorithms and neural networks.

- Sumpter and Noid [135]:

- PES for macro-molecules by using a neural network to learn the relationship between vibrational spectra and a multidimensional PES

- the neural network is capable of mapping the vibrational motion from spectra onto a fully coupled PES with relatively high level of accuracy

- 51 different examples for the $g(\omega)$ spectra corresponding to a polyethylene molecule have been used for training

- the general ability of the neural network to make predictions for data, not used in the training set, was examined by calculating the relative error for potential parameters that were unknown to the neural network

– maximum error was 3.9 % with the majority being near 0 %

- Blank et al. [136]:

- use of feed-forward neural networks to model global properties of PESs from information available at a limited number of configurations
- data are error-free and geometries are selected from uniform grids of two and three dimensions
- the neural network model predicts the potential within a few hundredths of a kcal/mole at arbitrary geometries
- method has been tested to fit data from an empirical potential model of CO adsorbed on Ni(111)
- accuracy and efficiency have been demonstrated in quantum transition state theory rate calculations for surface diffusion using a MC/path integral method
- sophisticated test: interaction of H_2 with Si(100)-2 x 1 [136] in 12D at 750 geometries (DFT)
- predicting the potential at geometries outside the training set: mean absolute deviation of 2.1 kcal/mole

- Rossi and Truhlar [137]:

- genetic algorithm to fit a set of energy differences $(E_{AM1} - E_{MP2})$ yielding a set of specific reaction parameters (SRP) for the reaction Cl + CH_4

- small number of ab initio points along a distinguished-coordinate path were used as input

- the surface is well fitted both on and off the reaction path over a range of energies three times wider than the input range
– costs for the AM1-SRP surface is 8000 times lower than for the reference ab initio surface

- the PES is well suited for direct dynamics calculations
- Cl + CH_4: only 13 ab initio points (as a reference) along the reaction path, fit for a wide range of energies with an absolute error of 1.08 kcal/mole

Interpolation for a special reaction path.

- Jasien and Shepard [60] (Shepard interpolation):

- general technique that provides a systematic means for fitting polyatomic PESs

- use of both ab initio energy and gradient data to fit the surface along an N-dimensional reference curve connecting stationary points

- the reference curve may be modified iteratively during the course of fitting

- a particular iteration can specify a new set of points which are to be calculated to improve the accuracy of the surface (tested for a model PES)

- Truhlar et al. [59]: review about PESs for polyatomic reaction dynamics, global and reaction path potentials

Use of the Shepard interpolation.

- Ischtwan and Collins [138], Jordan et al. [139, 140]:

- moving interpolation technique: provides an accurate representation of the PES by using ab initio energies, energy gradients, and second derivatives and even third derivatives [140], calculated at dynamically important regions

- the interpolant of the energy and its derivatives converge to the exact value with increasing number of data

- the algorithm neither assumes a functional form for the global surface [31] nor is a numerical "surface fitting method"

- the method employs classical trajectory calculations of the reaction dynamics in the PES construction process: $NH(^3\Sigma^-) + H_2(^1\Sigma^+) \rightarrow NH_2(^2B_1) + H(^2S)$ [138, 141], $OH + H_2 \rightarrow H_2O + H$ [139]

- the resultant surface is particularly appropriate for trajectory studies, although the surface could be used in statistical reaction rate theories

– use in quantum dynamical studies: the quality might be restricted, because only a special part of the PES near the “classical trajectory reaction path” is known

- OH $+$ H_2 [139]: reaction probability may be accurately calculated using approximately 200-400 data points to define the PES

- Nguyen et al. [51]:

- dual-level approach to represent PESs in which a very small number of high-level structure calculations are combined with a lower-level global surface, e. g. one defined by a NDDO-method (AM1) with specific reaction parameters, to generate the potential at any geometry where it may be needed

- PES is interpolated with a small number of accurate data points (the higher level) that are placed along the reaction path by using information on the global shape of the potential from less accurate calculations (the lower level)

- possibility to use in addition gradients or Hessians

- dual-level interpolation can offer cost savings over single-level schemes

- the accuracy of the interpolation is lower when the potential values are predicted at points significantly removed from the reaction path

- $OH + H_2 \rightarrow H_2O + H$: a family of approaches based on the Shepard interpolation of data along distinguished-coordinate reaction path (single-level, dual-level, use of genetic codes for the NDDO-SRP parameters) hasbeen tested

- depending on the number of high-level calculations that are affordable and the type of dynamics, one or another combination of interpolation choices are preferable

- OH $+$ NH$_3$ $\rightarrow$ H$_2$O $+$NH$_2$ [142]

- improved version of a dual-level direct dynamics method for reaction rate calculations with inclusion of multidimensional tunneling effects and validation for the reaction of H with trans-N$_2$H$_2$ [143]

Roots of multidimensional polynomials.

Downing et al. [105, 144]:

- procedure for interpolation and extrapolation of multidimensional functions by a root of a low-degree polynomial

- idea: the fit of a PES results from solutions of exact or approximate Rayleigh-Ritz variational problems

– eigenvalues are given by a root of a characteristic polynomial of a usually hermitian matrix

– elements of hermitian matrix are analytical functions of the geometrical values $\mathbf{q}$

- interpolation procedure: one assumes a simple parametrized functional form, a truncated Taylor series that approximates matrix-elements

– of the electronic Hamiltonian $H_{kl}(\mathbf{q})$; k and l define different electronic states)
– of the electronic energy $E_{kl}(\mathbf{q})$ or other terms

- SCF surfaces for MgH_2, HCN, H_3 and H_2O

- method can be used for extrapolation
- problems in handling ill-conditioned equations

Multidimensional Voronoï-step representations.

Suhm [145]:

- fully anharmonic vibrational ground states of systems like $(\mathrm{HF})_2$ or $(\mathrm{HF})_3$
- method that is based on the diffusion quantum Monte Carlo formalism that does not require an analytical representation of the PES
- static variant: the algorithm exploits a pre-existing data set of potential energy points - dynamical formulation: iteratively samples arbitrarily sized batches of new optimal nuclear configurations
- in this approach the analytical potential surface is replaced by an irregular distribution of configuration points
- the PES is given only at a few number of points N

– the value of the potential energy V_L at the local site L is defined as the weighted average potential energy of the surrounding reference configurations R

– the weight is defined by a rapidly decaying function $D(L,R)$

$$D(L,R) = \sum_{i,j} a_{ij} \left(\frac{1}{\lambda_{ij}^2} - \frac{1}{\rho_{ij}^2}\right)^2 \tag{22}$$

-ρ_{ij} is the distance from site i to site j in the reference configuration R
- λ_{ij} is the same quantity in the local configuration L and a_{ij} is a scaling factor

the interpolation for the potential at the local site L

$$V_L = \frac{\sum_{i=1}^{N} D(L,i)^{-k} V_i}{\sum_{i=1}^{N} D(L,i)^{-k}}, \tag{23}$$

k influences the weighting for the contribution of each reference configuration

- Voronoï step representation (Fig. 3) is not optimal for molecular dynamics calculations

- it is well suited for a Monte Carlo algorithm

- Suhm [146]: analysis of three contributions to the fitting bias: node bias, interpolation bias and extrapolation bias and their global effect on a given property calculation

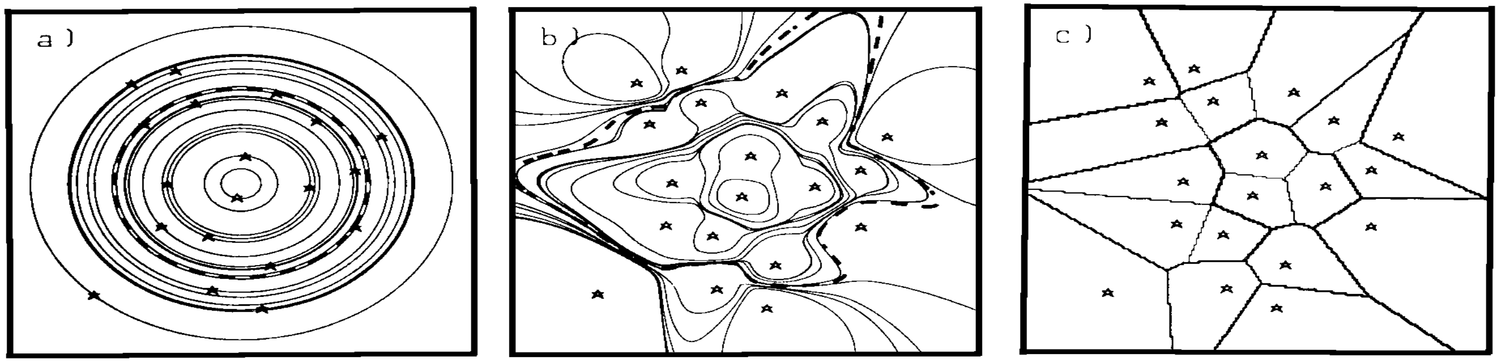


Figure 3: Illustration of the principle of Voronoï step representation (VSR) for a two-dimensional (x,y) harmonic Potential V. In (a), 19 reference configurations i (stars) and associated lines V_i are shown. The dashes mark the contour of the average ensemble energy $\bar{V}$. (b) illustrates the interpolation $V_L = \sum_{i=1}^{19} D(L,i)^{-k} V_i / \sum_{i=1}^{19} D(L,i)^{-k}$ with $D(L,i) = (x_i - x_L)^2 + (y_i - y_L)^2$ and $k = 4$, using the contour lines defined in (a). (c) shows the limit $k \to \infty$, i. e. VSR with $V_L = V_i$, where i is the reference configuration with smallest $D(L,i)$. (Suhm, M., Chem. Phys. Lett., 214 (1993) 373).

Reproducing kernel Hilbert space theory.

- Ho, Rabitz and co-workers [147, 148]:

- general interpolation method based on the reproducing kernel Hilbert space (RKHS) theory

- H_3^+: [147], O(^1D) + H_2: [148]

- the reproducing kernel of a D-dimensional tensor-product Hilbert space is a product of one dimensional kernels, which itself are made of appropiate functions with arbitrary coefficients

– the method is explained for the case that the data points are calculated on a D-dimensional grid [149]

– the ideas can also be applied to the general case, where the points are placed arbitrarily

- N(^2D) + H_2: $16 \times 16 \times 16$ grid, root mean square error of 1.32 kJ/mol

3 Specific forms for diatomic and polyatomic systems

- fitting PESs with the help of different expansions for the single degrees of freedom in diatomic - polyatomic molecules

- dependence on the distances and angles, different concepts are meaningful

- considerations, as they are made for single molecules in the gas-phase, can be transferred on descriptions of intermolecular interactions in fluids or solids.

- special functional approaches for intra/intermolecular interactions in single molecules and complexes

- recipes how to perform fitting with data points for PESs explicitly

- further detailed informations: Sathyamurthy [20].

One independent coordinate

Potential with one minimum

standard method for the expansion of functions (e. g. the potential) in one variable:

- Legendre-, Laguerre- or Hermite-polynomials
- functions are chosen on the basis of the physical problem (few terms needed)
- near the equilibrium distance R_e: potential behaves like an anharmonic oscillator $V = kx^2/2 + ax^3 + \cdots,\ x = R - R_e,\ k = (d^2V/dR^2)_{R=R_e}$

expansion has been utilized by Dunham [92]:

$$V(x) = d_0 x^2 \left(1 + \sum_{i=1}^{\infty} d_i x^i\right) \tag{24}$$

for x the expansions by Dunham [92], Ogilvie [94] and others can be used (see eq. (7))

- Dunham-Ansatz is unsatisfactory for $R \rightarrow \infty$
- SPF-Ansatz is bad for $R \rightarrow 0$ (see examples in [94])
- Ogilvie uses the F-test [150] (for RKR data) as a criterion of quality

$generalized\ expansion$ (different functional forms for $f(x)$):

$$V(x) = d_0 f^2(x) \left[1 + \sum_{n=1}^{\infty} d_n f^n(x) \right] \tag{25}$$

Thakkar [95]:

$$f(x) = \mathrm{sgn}(p) \left[1 - (1+x)^{-p} \right], \quad x = (R - R_e)/R_e, \tag{26}$$

$$\mathrm{sgn}(p) = \pm 1, \quad \text{for } p \gtrless 0$$

Engelke [151]:

$$f(x) = \mathrm{sgn}(p)\left[1 - \Big((1+x+\beta)/(1+\beta)\Big)^{-p}\right] \tag{27}$$

$$(\beta, p) = \begin{array}{cc} (0,-1) & \mathit{Dunham} \\ (0,1) & \mathit{SPF} \\ (0,p) & \mathit{Thakkar} \\ (1,1) & \mathit{Ogilvie} \end{array} \tag{28}$$

for $\beta > 0$, $p > 0$: $f(x)$ has no singularities in $[0 \leq R \leq \infty]$.

Huffaker [96]:

$$f(x) = 1 - e^{-ax}, \qquad x = R - R_e \quad \text{(Morse-like)} \tag{29}$$

Mattera [152]:

$$f(x) = 1 - (1 + \gamma x/p)^{-p}, \gamma > 0 \tag{30}$$

high flexibility of the leading term:

$$V_o(x) = d_0 \left\{ 1 - [1 + \gamma x/p]^{-p} \right\}^2 \tag{31}$$

(Lennard-Jones and Morse potentials are special cases, see (33) and (35))

Surkus [153]: use of formula (24) with

$$x = \mathrm{sgn}(p)(R^p - R_e^p)/(R^p + nR_e^p) \tag{32}$$

(n, p are real numbers; Dunham, SPF, etc. are special cases)

Empirical functional forms with minimal number of parameters:

Lennard-Jones [154]:

$$V(R) = 4D\Big[(\sigma/R)^m - (\sigma/R)^n\Big], \quad m = 12, \quad n = 6 \tag{33}$$

D is the well depth and σ is defined by $V(\sigma) = 0$.

Buckingham [155]:

$$V(R) = Ae^{-\alpha R} - BR^{-n}, \quad n = 6 \tag{34}$$

A and α can be calculated from $\ln V$ at short distance;
problem: $\lim_{R\to 0} V(R) = -\infty$

Morse [156]:

$$V(R) = D\left[e^{-2\beta(R-R_e)} - 2e^{-\beta(R-R_e)}\right] \tag{35}$$

Varshni [157]:

$$V(R) = D\left[(R_e/R)^{2m} - 2(R_e/R)^m\right] \tag{36}$$

higher terms of the dispersion forces ($R^{-n}, n \geq 6$): more flexibility (R^{-n} terms are not linearly independent):
HFD-Ansatz (Hartree-Fock-dispersion)

$$V(R) = Ae^{-\alpha R} - BR^{-6} - CR^{-8} - DR^{-10} - \cdots \tag{37}$$

Ahlrichs [158, 159], Tang and Toennies [160]: HFDD-Ansatz (Hartree-Fock with damped dispersion)

$$V(R) = Ae^{-\alpha R} - (C_6R^{-6} + C_8R^{-8} + C_{10}R^{-10})F(R),$$

$$
\begin{aligned}
F(R) &= e^{-\left[1.28(R_m/R)-1)^2\right]}, \quad R < 1.28R_m \qquad (38)\\
&= 1, \quad R \geq 1.28R_m
\end{aligned}
$$

$F(R)$: damping function, R_m: R_e of the undamped part of $V(R)$

rare gas – rare gas, halide systems: [161, 162]

Meath et al. [163]: similar to formula (38)

$$
\begin{aligned}
V(R) = &\quad [1-\gamma(1+0.1R)]E_C^{(1)} - [C_6F_6(SR)R^{-6} + C_8F_8(SR)R^{-8} \qquad (39)\\
&\quad +C_{10}F_{10}(SR)R^{-10}]G(SR)\\
G(SR) = &\quad (1+41.34e^{0.8588SR}), \quad \text{with } S = 7.82R_m^{-1} \qquad (40)
\end{aligned}
$$

$F_n(SR)$: damping functions, E_C^1: 1st order Coulomb energy

Modifications of the Morse-Ansatz:

Hulbert, Hirschfelder [164]:

$$V(x) = D\left(1 + gx^3 + hx^4\right)\left[e^{-2\beta x} - 2e^{-\beta x}\right], x = R - R_e \tag{41}$$

Schubert, Certain [165]:

$$V(R) = D\left\{(R_e/R)^2 e^{-2\beta(R^p - R_e^p)} - 2(R_e/R)e^{-\beta(R^p - R_e^p)}\right\} \tag{42}$$

Kafri, Berry [166, 167]: formula (42) with β depending on R

$$\beta = \beta_0(1 + F(x)), \quad x = R - R_e \tag{43}$$

$$F(x) = \begin{array}{ll} A_1 e^{-\beta_1 x} & x < 0 \\ (A_2 + A_3 x)e^{-\beta_2 (x - x_0)^2} & x \geq 0 \end{array} \tag{44}$$

formula (42) with: Kuntz, Roach [121]:

Kuntz, Roach [121]: $\beta = \beta_0(1 + \gamma x + \delta x^2)$Navati, Korwar [168]: $\beta(R) = \beta e^{b((R_e/}$

"Extended-Rydberg"-functions (ER):
Murrell, Sorbie [169]:

$$V(x) = -D\left[1 + a_1 x + a_2 x^2 + \cdots\right] e^{-a_1 x}, \qquad x = R - R_e \tag{46}$$

other functional forms: [170]. Fit parameters from linearizing V (using ln$V$) or directly with NLLS. Hall, Okada [171, 172]: exponential transformation of internal coordinates. *Alternative:* Lagrange-, spline-, etc.- interpolations or combinations: "exponential-spline-Morse-spline-van der Waals" [19]

Potentials with more than one minimum

symmetric double minimum (NH$_3$: [173]; x coordinate for the umbrella mode):

$$V(x) = \frac{1}{2}ax^2 + \frac{1}{2}bx^4 + V_0 e^{-cx^2} \tag{47}$$

asymmetric double minimum [174]:

$$V(R) = D\left\{1 - e^{-B(R-R_a)}\right\}^2 + Ae^{-C(R-R_b)^2} \tag{48}$$

(R_a, R_b refer to locations of minima) Huffacker (distorted Morse-potential) [175]:

$$V(R) = D(Y^2 + \sum_{n=4}^{n_{max}} b_n Y^n), \qquad Y = 1 - e^{-a(R-R_e)} \tag{49}$$

Eaker, Parr [176]: use of a modified Morse function (MM)

$$V_{MM}(x) = De^{-a\beta x} \pm af(x)e^{-\beta x} \tag{50}$$

$$f(x) = (1 - bx)e^{\frac{1}{2}bx(2-bx)}, \qquad x = R - R_e \tag{51}$$

generalized Hulbert and Hirschfelder (He* - He) [177]:

$$V(x) = (D/(t-1))\left[e^{-tx}Q_R(x) - te^{-x}Q_A(x)\right] + D' \tag{52}$$

$$x = \beta(R/R_e - 1), \qquad Q_{A,R}(x) = 1 + q_4^{A,R}x^4 + q_5^{A,R}x^5 \tag{53}$$

For $t = 2, D' = 0, q_4^{A,R} = q_5^{A,R} = 0: \quad V = V_{Morse}$

in case of humps in the potential curves as in case of a curve crossing: fitting of the diabats and solution of a 2×2 determinant problem ([178]: BeH, BeF).

Repulsive potentials

Anti-Morse (Sato [107]: ${}^3\Sigma_u^+$ (H$_2$)):

$$V(x) = \frac{1}{2}D\left[e^{-2\beta x} + 2e^{-\beta x}\right], x = R - R_e \tag{54}$$

Pedersen, Porter [179]:

$$\begin{aligned} V(x) &= A\left[e^{-2\beta x} + 2e^{-\beta x}\right], R \leq 1.6a_0 \\ &= b(R+c)e^{-\alpha R}, R > 1.6a_0 \end{aligned} \tag{55}$$

Berces [180]:

$$V(x) = (D/\alpha)e^{-2\beta x}\left[1 + \beta x\right]^{2\alpha} \tag{56}$$

Kafri, Berry [166]:

$$V(R) = e^{-(a_0+a_1R+a_2R^2+a_3R^3+a_4R^4+a_5R^5)} \tag{57}$$

Varandas, Brandao [181]:

$$V(x) = AR^{-1}e^{-bx} \tag{58}$$

Further examples: different functional forms for proton transfer potentials: $(H_2O)_2$ - H^+ - $(H_2O)_2$, $(NH_3)_2$ - H^+ - $(NH_3)_2$ [182].

Multi-valued potentials

if nonadiabatic interaction is substantial:
calculate the adiabatic surfaces $V_\pm$

$$V_\pm(R) = \frac{1}{2}\Big[V_{11}(R) + V_{22}(R)\Big] \pm \frac{1}{2}\left(\Big[V_{11}(R) - V_{22}(R)\Big]^2 + 4V_{12}^2(R)\right)^{\frac{1}{2}} \tag{59}$$

$V_{11}(R)$ and $V_{22}(R)$: diabatic states
$V_{12}(R)$: potential coupling between the states [183]
V_{11}, V_{22} and V_{12}: can be fitted individually

more general way: calculation of the roots of multidimensional polynomials describing ground and excited states [105]

Two and more coordinates: Non-reactive scattering

PES in higher dimensions:
- expansion in a polynomial like form
- for radial coordinates : different expansions possible
- angular coordinates: expansion in Legendre polynomials

for systems with few degrees of freedom special forms have been developed:
Atom (A) - linear rigid rotor (BC)

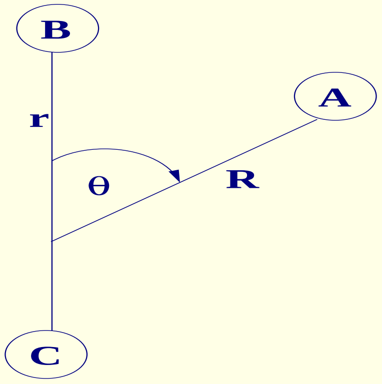


Figure 4: Jacobi coordinates for “atom – diatomic vibrotor” system

potential for the collision of an atom in a ^1S-state with a rigid rotor molecule in a $^1\Sigma$ or $^1\Pi$ state [184, 185]
expansion in terms of *Legendre polynomials* P_λ (see Fig. 4)

$$V(R,\theta) = \sum_\lambda V_\lambda(R) P_\lambda(cos\theta) \tag{60}$$

- $V_\lambda(R)$: fitted as explained before 3.1 (as V or ln$V$)
- spline- or Lagrange interpolation often do not result in sufficiently reliable 1st derivatives for quasi classical trajectories (QCT), but are good for quantum mechanical calculations

$V_\lambda(R)$ is calculated by numerical *integration:*

$$V_\lambda(R) = \frac{(2\lambda+1)}{2} \int_{-1}^{1} P_\lambda(cos\theta) V_\lambda(R,\theta) d(cos\theta) \tag{61}$$

- it is sensible to choose the points for θ as in a Gauss-Legendre-quadrature otherwise a system of linear equations has to be solved ($matrix\text{-}inversion$) for each value of R:

$$V(R,\theta_i) = \sum_{\lambda=0}^{n} V_\lambda(R) P_\lambda(cos\theta_i), \qquad i = 1, \ldots, n \tag{62}$$

How does one proceed?

- if the system is overdetermined (i. e. there are more data than Legendre terms), a least-squares fit has to be performed.

- for weakly anisotropic systems: H_2–He, short expansion (n=2) [186]

- for strongly anisotropic systems: CO_2–Ar, long expansion (n=10) [187]

- alternative: numerical interpolation for irregular grids (Akima [85], Schagen [188])

- sequence of fitting: 1) angle, 2) distance
- changing the sequence can lead to different results
- different concepts have to be tried!

fitting for *fixed angles* can be tried: Ewing [189]:

$$V(R,\theta) = A(\theta)e^{-\alpha(\theta)R} - B(\theta)e^{-\beta(\theta)R} \tag{63}$$

attention: one has to be careful that the fit does not produce wells and humps and that the functions are continuous and go smoothly into each other

other concepts for model potentials: Lösch [190], Gordon and Kim (electron gas-potentials) [187, 191], comparison of different models [192]

applications: Table 2 in [20], O_2-He: [193]

Three variables: atoms - diatomic vibrotor

Legendre expansion (e. g. ^1S (A) – $^1\Sigma$ (BC)) (Fig. 4):

$$V(R,\theta,r) = \sum_{\lambda} V_\lambda(R,r) P_\lambda(cos\theta) \tag{64}$$

(1) fit of $V_\lambda(R,r)$ as in (60, 61) for fixed R, r (2) fit of each $V_\lambda(R,r)$, where $V_\lambda(R,r)$ can be expanded in a *Taylor series* in r:

$$V_\lambda(R,r) = V_\lambda(R) \mid_{r=r_e} + \partial V_\lambda(R)/\partial r \mid_{r=r_e} (r - r_e) + \tag{65}$$
$$\frac{1}{2}\partial^2 V_\lambda(R)/\partial r^2 \mid_{r=r_e} (r - r_e)^2 + \cdots$$

- near the equilibrium distance ($r \approx r_e$): only V_λ and the 1st derivatives have to be fitted in one dimension
- for a regular grid in (R, r) a 2D numerical fit of $V_\lambda(R,r)$ is possible

Alternative:

(1) Taylor expansion in r

$$V(R,r,\theta) = V(R,\theta)\mid_{r=r_e} + \partial V(R,\theta)/\partial r \mid_{r=r_e} (r-r_e) + \frac{1}{2}\partial^2 V(R,\theta)/\partial r^2 \mid_{r=r_e} (r-r_e)^2 + \cdots \quad , \tag{66}$$

(2) fit of the coefficients in Legendre polynomials - if one keeps only the linear term

$$V(R,r,\theta) = V(R,\theta)\mid_{r=r_e} [1 + \partial \ln V(R,\theta)/\partial r \mid_{r=r_e} (r-r_e)] \quad , \tag{67}$$

- ln$V(r)$ reveals the strength of vibrational coupling [194]

Simple expansion in r, R, θ:

$$V(R,r,\theta) = \sum_{\lambda,m} V_\lambda^m(R) x^m P_\lambda(cos\theta), \qquad x = (r - r_e)/r_e \tag{68}$$

Ewing [189]: “fixed angle”-fit ($A, B, \alpha, \beta, \gamma, \delta$: parameters to be fitted)

$$V(R,r,\theta) = A(\theta)e^{\gamma(\theta)(r-r_e)-\alpha(\theta)R} - B(\theta)e^{\delta(\theta)(r-r_e)-\beta(\theta)R} \tag{69}$$

(1) “rigid rotor”-fit ($r = r_e$)
(2) fit of the rest: HF-He, Ar; CO-He, Li^+; Li^+-H_2, N_2 [189]; SiO-He [195]

other applications: Table 3 in [20], (He,Ne)-CO: [196, 197, 198], C(^{3}P) + H_2: [199], O(^{3}P) + H_2: [200], $HeCl_2$: [201], H_2Ar: [202], HCN/HNC: [203], ArHF: [204]

with Morse-like expansions (29): H_3^+: [99, 101, 205], H_2O: [206, 207, 208, 209], Na^+-H_2: [210], Ar-NO^+: [211], LiH-He: [212].

Three coordinates: Atom - rigid nonlinear polyatomic system

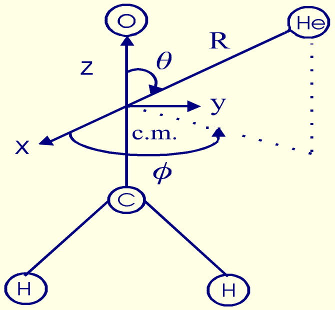


Figure 5: Coordinates for "atom – rigid nonlinear polyatomic"- system

Expansion in spherical harmonics $Y_l^m(\theta,\phi)$ (see Fig. 5):

$$V(R,\theta,\phi)=\sum_{l=0}^{l_{\max}}\sum_{m=-l}^{l}\left[4\pi/(2l+1)\right]^{\frac{1}{2}}V_l^m(R)Y_l^m(\theta,\phi) \tag{70}$$

He-H$_2$CO [213]: $l_{max} = 12$

$$\begin{aligned} V_l^m(R) = \quad & Ae^{-BR} - CR^{-6} - DR^{-2} \quad & , R \leq 10.5a_0 \\ & = 0 & , R > 10.5a_0 \end{aligned} \tag{71}$$

He-NH$_3$ [214]: symmetry in ϕ allows for reduction in the number of terms in the expansion

$$\begin{aligned} & V(R,\theta,\phi) = \\ & V(R,\theta,-\phi) = \sum_{\lambda \geq \mu > 0} V_\lambda^\mu(R) \left[Y_\lambda^\mu(\hat{R}) + (-1)^\mu Y_\lambda^{-\mu}(\hat{R}) \right] (1 + \delta_{\mu 0})^{-1} \\ & = \sum_{\lambda \geq \mu > 0} (2\pi)^{-\frac{1}{2}} V_\lambda^\mu(R)(2 - \delta_{\mu 0}) P_\lambda^\mu(cos\theta) \cos(\mu\phi), \qquad \hat{R} = (\theta, \phi) \end{aligned} \tag{72}$$

He-NH$_3$ [214]: for V_λ^μ, 5th order Lagrange interpolation, exponential Ansatz, R^{-n} expansion

Atom-atom-fit: without Legendre expansion

CO$_2$-He [215, 216, 217]: $R_1 = R_3 = R_{He-O}, R_2 = R_{He-C}$

$$V(R_1, R_2, R_3) = A\left[e^{-BR_1} + e^{-BR_3}\right] + Ce^{-DR_2} \tag{73}$$

H$_2$O-He [216, 217]: $R_1 = R_3 = R_{He-H}, R_2 = R_{He-O}$

$$V(R_1, R_2, R_3) = \sum_{i=1}^{3}\left[A_i e^{-a_i R_i} - B_i e^{-a_i R_i/2}\right] \tag{74}$$

Four coordinates $(R, \theta_1, \theta_2, \phi)$: rigid rotor (r_1) - rigid rotor (r_2)

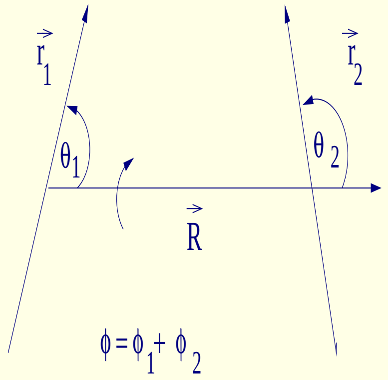


Figure 6: Coordinates for "linear molecule – linear molecule" system

- R defines center-of-mass separation between two molecules oriented with respect to θ_1, θ_2, ϕ
- an expansion in a radial (A, B) and an angular part $(I, \bar{I})$ can be further expanded in Legendre polynomials P_λ or spherical harmonics Y_l^m
- the angular part can be described by either a body-fixed (BF) or space-fixed (SF) expansion

BF ("body-fixed") [218]:

$$V(R,\theta_1,\theta_2,\phi) = \sum_{\lambda_1\lambda_2\lambda} B_{\lambda_1\lambda_2\lambda}(R)\bar{I}_{\lambda_1\lambda_2\lambda}(\hat{r}_1,\hat{r}_2,\hat{R}) \tag{75}$$

$$\bar{I}_{\lambda_1\lambda_2\lambda}(\hat{r}_1,\hat{r}_2,\hat{R}) = P_{\lambda_1}(\hat{r}_1 * \hat{R})P_{\lambda_2}(\hat{r}_2 * \hat{R})P_{\lambda}(\hat{r}_1 * \hat{r}_2)$$

with three dot products:

$$\hat{r}_1 * \hat{R} = \cos(\theta_1), \hat{r}_2 * \hat{R} = \cos(\theta_2) \tag{76}$$

$$\hat{r}_1 * \hat{r}_2 = \cos(\theta_1)\cos(\theta_2) + \sin(\theta_1)\sin(\theta_2)\cos(\phi) \tag{77}$$

($\hat{r} = (\theta,\phi)$: angular part of vector r)

SF ("space-fixed"):

$$V(\hat{r}_1, \hat{r}_2, R) = \sum_{l_1 l_2 l} A_{l_1 l_2 l}(R) I_{l_1 l_2 l}(\hat{r}_1, \hat{r}_2, \hat{R}) \tag{78}$$

$$I_{l_1 l_2 l}(\hat{r}_1, \hat{r}_2, \hat{R}) = \sum_{m_1 m_2 m} \langle l_1 m_1 l_2 m_2 \mid lm \rangle Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2) Y_l^m(\hat{R}) \tag{79}$$

$m_1 + m_2 = m$
$l_1 + l_2 + l =$ even
$\langle l_1 m_1 l_2 m_2 \mid lm \rangle$: Clebsch-Gordan coefficients

<u>Relations</u>: BF – SF with $\hat{R} = (0,0)$ and $Y_0^0 = 1$

expansion in spherical harmonics Y_l^m:

$$I_{l_1 l_2 l} = [(2l+1)/4\pi]^{\frac{1}{2}} \sum_{m=-l_m}^{l_m} \langle l_1 m l_2 - m \mid l0 \rangle Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2),\; l_m \leq l_1, l_2 \tag{80}$$

expansion in associated Legendre functions P_l^m:

$$I_{l_1 l_2 l} = [(2l+1)/4\pi]^{\frac{1}{2}} [\langle l_1 0 l_2 0 \mid l0 \rangle P_{l_1}^0(\theta_1) P_{l_2}^0(\theta_2) +$$

$$\sum_{m=1}^{l_m} (-1)^m 2 \langle l_1 m l_2 - m \mid l0 \rangle P_{l_1}^m(\theta_1) P_{l_2}^m(\theta_2) \cos\left(m(\phi_1 - \phi_2)\right)],\; l_m \leq l_1, l_2 P_l^m($$

- SF expansion is preferred over above BF expansion (generally)
- radial coefficients are fitted or interpolated numerically

Flower et al. (CO-H_2: [219]): alternative BF expansion

$$V(\hat{r}_1, \hat{r}_2, R) = \sum_{l_1 l_2 \mu \geq 0} V_{l_1 l_2 \mu}(R) \tilde{Y}_{l_1 l_2 \mu}(\hat{r}_1, \hat{r}_2), \qquad \hat{r}_1, \hat{r}_2 : \text{BF angular coordinates} \tag{82}$$

$$\tilde{Y}_{l_1 l_2 \mu} = 4\pi \left[2(1+\delta_{\mu 0})\right]^{-\frac{1}{2}} \left[Y_{l_1}^{\mu}(\hat{r}_1) Y_{l_2}^{-\mu}(\hat{r}_2) + Y_{l_1}^{-\mu}(\hat{r}_1) Y_{l_2}^{\mu}(\hat{r}_2)\right] \tag{83}$$

- expansion is equivalent to the SF expansion (78):

$$A_{l_1 l_2 l}(R) = 4\pi \left[4\pi/(2l+1)\right]^{\frac{1}{2}} \sum_{\mu \geq 0} V_{l_1 l_2 \mu}(R) \langle l_1 \mu l_2 - \mu \mid l 0 \rangle (2/(1+\delta_{\mu 0}))^{\frac{1}{2}} \tag{84}$$

$examinations$: there is no simple check for the accuracy of the fit

(a) performing a fit using a reduced number of potential values (e. g. 5 out of 6 orientations) and using additional potential values (e. g. the 6th orientation) as a check

- Berns and v.d.Avoird found in that case poor results for the systems N_2-N_2 [220] and CO_2-H_2 [221] !

(b) plot of the residual values shows the quality of the angular convergence

- accurate analysis for CO_2-H_2 [221]: 36 orientations ($1.5 \leq R \leq$ 4 Å) were necessary *“site – site” potential:* Berns, v.d.Avoird [220]; (N_2-N_2)

$$\triangle E^{AB} = \sum_{i \epsilon A} \sum_{j \epsilon B} V_{ij} \tag{85}$$

$$V_{ij}(R_{ij}) = q_i q_j R_{ij}^{-1} - C_{ij} R_{ij}^{-6} + A_{ij} e^{-B_{ij} R_{ij}} \tag{86}$$

i, j: sites (e. g. atoms, position of charges q_i, etc.) of molecules A and B
examples: $(CO_2)_2$: [222], $(O_2)_2$: [223]

further examples:
overview: general [224], applications: Table 4 in [20], H_2-CO [225, 226], CO-CO: [227], H_2-OH: [228], O_2-O_2: [229, 230, 231, 232], dimers of CO, HF, H_2O, NH_3: [234], $(HF)_2$: [235, 236], $(H_2O)_{3,4}$: [237, 238], $(H_2O_2)_2$: [239], $(H_2O)_2$ (atom-atom potential and many-body expansion): [129], Ar_2-HF: [130]

More than four variables

H_2-H_2: [240], with $A_{l_1 l_2 l}(R, r_1, r_2)$ spline fit; [241], $(HF)_2$(6D): [236], $(HCl)_2$ (6D): [242, 243, 244]

further examples: [20]

“Larger molecules” and other vdW-systems

general: [229, 245], intermolecular interactions in crystals (atom-atom, site-site): [246]

Ar-C_6H_6: [247], Rg(rare gas)-CH_4: [248], H_2O-H_2: [249], Ar-C_2H_2: [250], (He,Ne)-SF_6: [251], Ar-CH_4: [252], He-C_2H_2: [253]

overview: molecules with up to 10 atoms [59]

Two and more coordinates: Reactive scattering

Three-atomic systems

- difficulty in fitting PESs for reactive scattering in comparison to non-reactive problems

- interaction region and the different asymptotic regions have to be described with the same accuracy

- mostly one set of coordinates (e. g. Jacobi coordinates) is not satisfactory

- hyperspherical coordinates can manage the full description of the PES

- in case of dynamical calculations hyperspherical coordinates are not the optimal one in the limit of the asymptotic region

($H + H_2$) reaction: probably most detailed investigated system

- for the electronic ground state:
[254], SLTH: [255, 256], DMBE: [257, 258]

- excited states: [258, 259, 260]

- more details: see the introduction in [258]

● generally, the chemical accuracy of ± 1 kcal/mol is needed for A + BC → AB + C PESs

- applications till 1984: Tables 5 and 6 in [20]

LEPS-, DIM- Ansatz

LEPS (London, Eyring, Polanyi, Sato) [261, 262, 263]
- LEPS-functions favor collinear reaction-paths
- errors in the determination of barrier heights [117]
- problems in the case of several reactive channels
- examples: review [17], modified LEPS: H_2O [264], Cl+HCl [265]
- LEP for HXY-systems (X,Y= hydrogen or other elements): [266]

DIM (diatomics-in-molecules): Kuntz [17, 122, 267], Brown and Hayes [120]: $He + H_2^+ \rightarrow HeH^+ + H$, [268]: $NH_3 \rightarrow NH_2 + H$, [269]: HO_2, [270]: rare gas clusters

DIM and LEPS:
- yield reasonable PE-values at geometries, where not many ab initio data are available - in case of scattering calculations LEPS and "spline-fitted" potentials show different results: HeH_2^+ [271], NeH_2^+ [272]

“Rotated-Morse-curve-spline” (RMCS) [273]

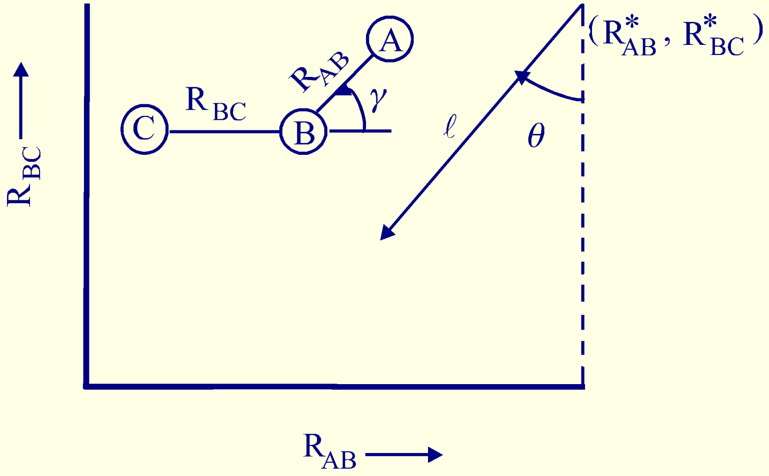


Figure 7: Coordinates for rotated Morse-curves

Wall, Porter [274]:

$$V(R_{AB}, R_{BC}) = V(l, \theta) = D(\theta) \left[e^{2\beta(\theta)(l - l_e(\theta))} - 2e^{\beta(\theta)(l - l_e(\theta))} \right] \quad (87)$$

$l_e(\theta)$: equilibrium value as a function of θ (see Fig. 7)

$$l = \sqrt{(R^0_{AB} - R_{AB})^2 + (R^0_{BC} - R_{BC})^2} \quad (88)$$

$$\theta = \tan^{-1} \left[(R^0_{AB} - R_{AB}) / (R^0_{BC} - R_{BC}) \right] \quad (89)$$

many calculations by Kuppermann et al. [275, 276] and Connor, Jakubetz et al. [273, 275, 276, 277, 278]

H_3: [258], Cl + HCl: [279]

Sorbie-Murrell-type [109]

H_3: [117]; O(^3P)+ H_2: [280, 281], O(^1D)+ H_2: [282], H_3^+: [283, 284], LiFH: [285], NH_2^+: [286], CH_2^+: [287], HeH_2^+: [288], O_3: [289]

further applications:
different functional forms and comparative study of the reaction dynamics: O(^3P) + H_2 [290, 291]

further examples: Zn + H_2: [292], Ar_3^+: [293, 294], Li+HF [295], He+LiH [212], H_3 [256, 258, 296], H_3^+: [205, 297, 298, 299],H_3^-: [300]

excited states: HeH_2^+: [301], N_2O: [302], triplet H_3^+ (hyperspherical coordinates): [303]

Multi-valued potentials

- topography of PESs in the vicinity of intersection points and seams

- in chemical reactions [258, 304], molecular spectroscopy [305] and organic photophysics [306, 307].

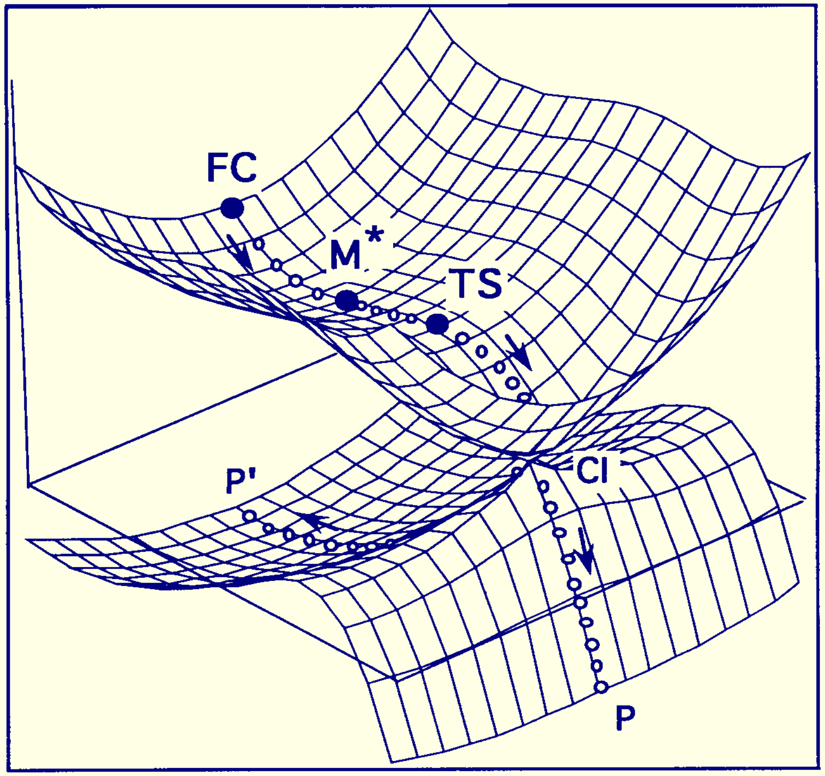


Figure 8: Model conically intersecting PES plotted along the branching space (x_1,x_2). The arrows indicate the direction of the minimum energy path connecting the FC point to the photoproducts P and P'. M*: excited state intermediate; TS: transition state connecting M* to the conical intersection (CI) (Bernardi, F., Olivucci, M., Robb, M.A., Chem. Soc. Rev. **25** (1996) 321).

Ruedenberg et al.:
- detailed investigations of the fitted multi-valued potentials for O_3, S_3, SO_2, S_2O [308, 309, 310]
- analysis general PESs near intersection points [308, 311]
- influence of the neighborhood of a conical intersection and other specific regions, like bifurcating transition regions (e. g. ring opening of cyclopropylidene to allene [312, 313, 314, 315]), on chemical reactions
- the use of perimetric coordinates might help to get a better insight in viewing the PESs in three dimensions [316] - different approaches for fitting the region near the intersection point (seam, etc.) [308, 310, 311, 317, 318]

further examples:
FH_2: [285], H_2O: [319], CH_2: [320, 321], four electronic states of H_3: [258], H_3^+: [299]

double many body expansion (DMBE): H_3 [322], H_3, FH_2, NO_2: [28]

reactions at an avoided crossing: $A + B_2 \rightarrow AB + B$ [323]

(conical, Jahn-Teller, Renner-Teller, etc.) intersections: [324], SO_2: [325], O_3^+: [199, 326], $C_6H_6^+$: [327], NO_2: [328]

some PESs for photodissociation problems: HCO (with Renner-Teller coupling) [329, 330], H_2O: [331], O_3: [332], HNCO: [333], H_2O_2: [239]

Four- and polyatomic systems

review: [45, 22, 41], $OH + H_2$ [334, 335, 336], $H_2^+ + H_2$ [337], $OH + CO$ [338], $NH + NO$ [41], $CN + H_2$ [339, 340, 341], H_4: [128, 342, 343], $Cl^- + CH_3Cl$: [344, 345]

Spline and other interpolation schemes and comparison in dynamics calculations

2D: [42, 272, 346, 347, 348, 349, 350]; 3D: [89, 90, 91]
H_3^+: symmetry coordinates, polynomial Ansatz (Morse-type for distances)
special choice of points [101, 205, 351, 352]
NeH_2^+: diff. forms for a fit-Ansatz: influence on rovibr. frequencies [126]

Miscellaneous

Reaction-path potentials: [59, 45]
Interpolation for a special reaction-path: [59, 60, 138, 139, 140, 51, 45, 143]
Voronoï step representation: [145, 146]
Piecewise tessalation (with Clough-Tocher interpolant): [292]
Genetic algorithms and neural networks: [135, 136, 137]
Distributed approximating functional fit: [353]
Reproducing kernel Hilbert space: [147, 148, 149]
Multiperturbation approach to PESs for polyatomic molecules: [354]
Permutation-inversion-group invariant representation: [355]

Description for fluids, solids and biochemical problems

large number of applications to the subject of PESs:
- fluids, solids, atomic and molecular interactions on solid surfaces, biochemical problems
- with few exceptions these studies are performed with empirical functions or force field methods

intra/intermolecular potentials for molecular dynamics investigations in condensed phase:
Ne [356, 357], Ar [358], CH_4/N_2 [359], CCl_4 [360], NH_3 [361], N_2 [362], CH_4, CH_3F, CHF_3, CH_3Cl, CH_2Cl_2, CH_3CN, CO_2 [363], H_2O [129, 364], HF [365, 366, 367], HCl [242], CO_2 [222]

polyatomic molecular ions: [103]

atomic solids: [368, 369]

solids: general: [370, 371], N_2-N_2: [372], O_2-O_2: [223], O_4^+/Ne: [373], Li^+/F^- [374]

clusters: general: [52, 53, 54], H_2O: [375]

solid surfaces: review: [376], H_2/Cu(100) [377], H_2/Hg(liquid surface): [378]

biochemistry: topology of multidimensional PES of a peptide [379]

Which area of the PES influences which property?

	range	properties
(1)	very short	cross sections at high scattering energies
(2)	$R < R_e, V(R) \approx 0$	description of fluids (molecular dynamics)
(3)	$R \approx R_e$	rotation/vibration frequencies (spectroscopy of stable molecules), rotationally inelastic cross sections (van der Waals (vdW) molecules)
(4)	$R > R_e$	polarizabilities (C_6-, C_8-, etc. terms of vdW molecules), spectroscopic properties
(5)	barriers	reaction cross sections (vib., rot. or trans. excitation of the reaction products)
(6)	minima	equidistribution of energy for single degrees of freedom, spectroscopic properties
(7)	FC-region	photodissociation (excited potential energy surface), reaction probabilities (vib., rot. or trans. excitation of the reaction products)

Fitting procedures for PESs

(a) one variable (R)

create a plot for given energy points and resulting fitting function

(1) in case of a minimum, calculate $R_e, D_e, (\frac{d^2V}{dR^2})|_{R=R_e}$

- (i) only three points given: fit to Morse-function
- (ii) more then three points given: fit to ER- or mod. Morse-f.
- (iii) many points: like in (ii) or interpolation (spline, Lagrange, polynomial) with correct choice of expansion variables

(2) van der Waals minimum: choose a HFD-Ansatz

(3) more than one minimum: in case of enough points choose an interpolation (e. g. splines)

(4) no extremum: fitting with ER-Ansatz, anti-Morse or ln$V$ with interpolation scheme

- quality of interpolation can be checked by omission of some data points; this elucidates, how sensitive the fitting reacts on single points

(b) two variables (R, θ): atom – rigid rotor

- regular grid: Legendre-functions have to be expanded for every R

- calculate V_λ from a GL-quadrature (or one chooses a matrix inversion or a LLS-procedure)
- convergence of the Legendre-expansion has to be checked

alternative: one can perform a "fixed angle"-fit for an analytical function Ansatz in R (e. g. as in **(a)**)

- $V_\lambda(R)$ has to be fitted as in **(a)**

alternative: explicit 2D-fitting (e. g. spline) with the original data or one uses in addition interpolated data for explicit 2D-fit (especially, if there are only a few (R, θ)-data points)

- irregular grid: Akima method can be used or with the help of interpolation a regular grid can be created

- good choice for testing the fit: perform 1D- and 2D-contour plots
- visually it is easier to discern, if a fit makes sense (additional humps, small oscillations)

(c) Two variables (R_1, R_2): ABC-system for fixed angles
regular, dense grid: 2D-spline
few points: many body expansion Ansatz (e. g. SM)
irregular grid: Akima-interpolation or analytical Ansatz (e. g. of SM-type)

(d) Three variables (R, r, θ): atom – vibrotor
regular grid:
(1) Legendre expansion: $V_\lambda(R, r)$ or Taylor-expansion in r (diatom): "r^k" for given R: then $V_{\lambda,k}(R)$ has to be calculated
(2) "fixed angle"-fit: 2D-spline or analytical Ansatz
(3) 3D-spline

- check the quality of the fit: plot V, compare the different fit-variants, e. g. if there are oscillations depending on the fitting scheme

irregular grid: create a regular grid with the help of 1D-interpolations or use an analytical Ansatz (of SM-type)

(e) Four variables $(R, \theta_1, \theta_2, \phi)$: rotor – rotor
regular grid: space-fixed (SF) expansion and fitting of $V_{\lambda_1,\lambda_2,\lambda}(R)$ in 1D (interpolation, analytical Ansatz) or alternatively the body-fixed (BF) version

(f) Reactions: three variables (R_1, R_2, R_3) or (R, r, θ)
regular grid:
(1) 3D-spline (very seldom one has so many points !)
(2) for fixed coordinates (from which the potential does not depend strongly) perform a 2D-spline or a 2D-functional Ansatz (RCMS) for the other coordinates
(3) many-body expansion (e. g. SM), "site-site"-Ansatz
attention: asymptotic potential energy curves (diatom) have to be fitted independently and have to be fitted to the interaction range (many body expansion) by spline or a NLLS-method irregular grid:
(1) create points for a regular grid (as mentioned in **(a)**)
(2) many body expansion, "site-site"-Ansatz, RMCS-fit

(g) Where do we have to create data points?

- great advantage if a dense regular grid of data points can be created

- costs for each ab initio point limits the number of data to be calculated

- therrefore, it is not possible to create enough points for a regular grid in case of high dimensionality ($> 3D$)

- one has to think in advance how many angles are needed in the corresponding Legendre-quadrature
  - an arbitrary choice of points will make the fitting difficult

- for distance-coordinates: number of points should be large enough that strong changes in the potential can be described correctly

- for a strong anisotropic atom-rotor potential: many angular points are needed

- dynamical calculations can give hints beforehand (e. g. test calculations with a model potential can be performed), in which area points are needed (e. g. with a reaction path potential)

- tests with trajectories can show, which area of the potential can be reached for a given collision energy
  - quantum dynamics calculations: a large range for the PE is needed

- choosing the points: take care of the correct symmetry and the correct choice of coordinates
  - change of the coordinate-system within a dynamical calculation can imply that a high quality of the fit in those part of potential energy area is needed, where in the original coordinate system not enough data were given

- important to perform in between (i. e. before all points are generated) fits and plots (to see if more or less points will be needed)

short summary:

- no clear-cut concept for a minimal and additionally optimal choice of points
- because for no system the “true” potential (except perhaps H_2) is known, there is also no guarantee for the definitions of the fit
- an unequivocal estimate of the error of the fit is not possible (e. g. χ^2-partition function, see also [15, 80])
- spline-type fits reproduce input values (e. g. given energy points, gradients and higher derivatives); newly calculated (i. e. added) points will show how good the interpolated regime is
- comparison between different fit-variants and a comparison of calculated properties and experimental results supplies additional information about the quality of the fit
- a good fit for a special property is not necessarily a good for the calculation of other properties

- different properties are sensitive with respect to special parts of the potential energy area
- a multi-property-fit might help: (O_2-rare gas: [380], Ar_2: [127], N_2-Ar: [381])

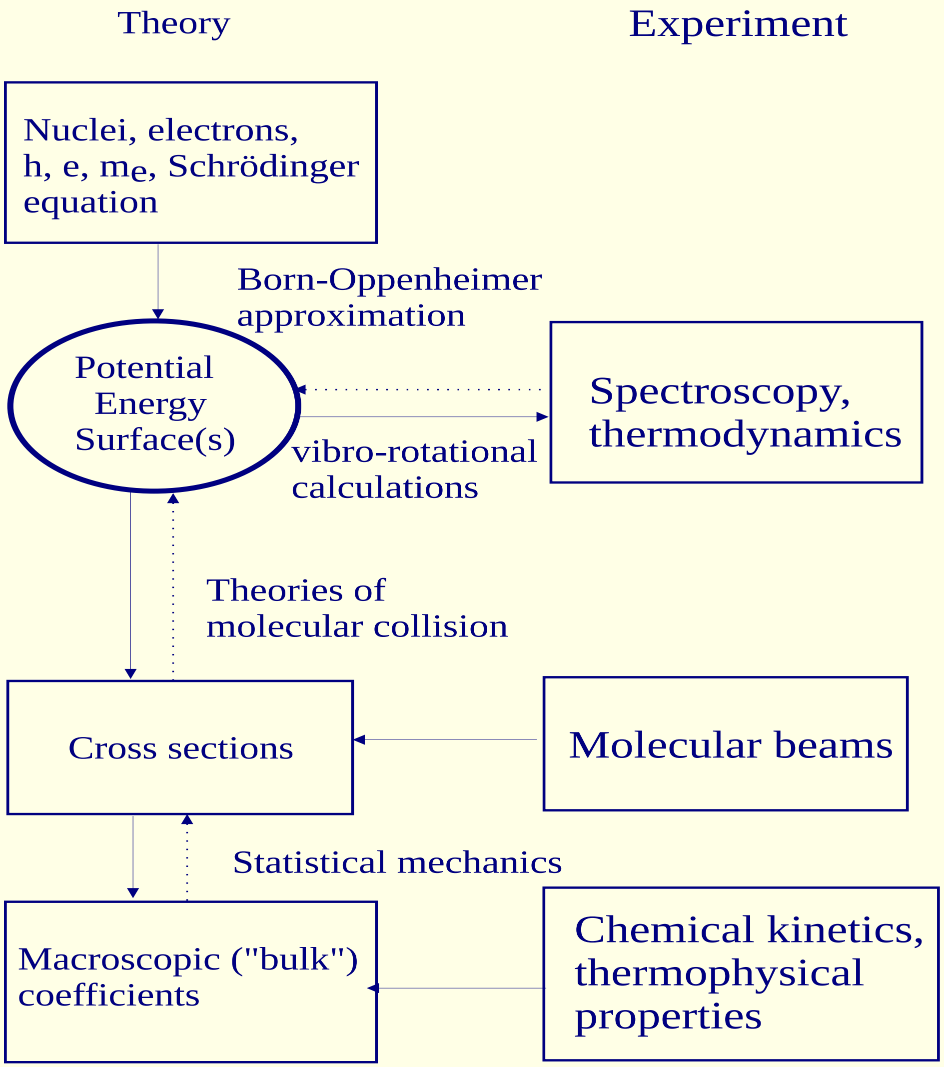
4 Combination of theoretical and experimental data for the construction of PESs

- accurate PESs without experimental information:

- diatomic molecules
- H_3 [256, 296], FH_2, H_3^+ [205])

- improvement:

- use of data derived from spectroscopical and scattering experiments
- interrelation between theory and experiment necessary



Theory

Experiment

Nuclei, electrons, h, e, m_e, Schrödinger equation

Born-Oppenheimer approximation

Potential Energy Surface(s)

Spectroscopy, thermodynamics

vibro-rotational calculations

Theories of molecular collision

Cross sections

Molecular beams

Statistical mechanics

Macroscopic ("bulk") coefficients

Chemical kinetics, thermophysical properties

Figure 9: The molecular potential as connecting link between theory and experiment.

- PESs fitted to experimental results:

the PES now includes relativistic effects, adiabatic and non-adiabatic corrections

in light systems (H_3^+) a good fit to experimental, spectroscopic results [383] helps to analyze new available experimental data

-this procedure does not necessarily describe the correct potential energy form, i. e. the Born-Oppenheimer and adiabatic contributions and the non-local effect of the non-adiabatic contributions

-the parameters of the fit are influenced by the choice of mass used for the nuclear motion
- which mass? depends on the "level of theory" [351, 352]

- empirical evaluation of adiabatic and nonadiabatic corrections in small molecules: [384, 385, 386, 387].

review articles:

- relations between spectroscopy and PESs [66, 388]
- inversion of experimental data for the determination of inter- and intra-molecular potentials [61, 389], difficulties to derive potentials from experimental results

for diatomic systems: special methods
Rydberg-Klein-Rees method (RKR) [61]

larger molecules:
“Fitting molecular potential energy surfaces”
(Law, Hutson and Ernesti [63])

“Fashioning a Model: Optimization methods in chemical physics”
(Ernesti, Hutson and Wright [62])

PESs constructed using experimental data from spectroscopy and scattering cross sections:

- LeRoy et al.: anisotropic potentials from van der Waals spectra, e. g. He-C_2H_2 [390, 391], H_2-Ar, Kr, Xe [202, 392], He-CO [393]
- Bowman et al.: $ArOH^*$ [394] and HCN [395] potentials from experimental spectroscopical data
- Carter et al. [396]: used experimental spectroscopical data of stable molecules like SO_2, CO_2, CS_2 [31], HCN [21], Renner-Teller system NH_2 [397], for the global generation of PESs
- Howard et al. [398] used micro-wave and infrared data for the determination of PESs of NeCO-, $ArSiH_4$ complexes
- Hutson et al. [388]: fitting of van der Waals complexes like Ar-HCl [399], Ar-HF [400], Ar-H_2O [401], Ar-OH [402], Ar_2-HF, HCl [403, 404], $HeAr^+$ [405], Li^+-H_2O [406], CO_2-Ar [407, 408], He-HCN [409]
- Keil [410, 411]: “multi-property” -methods, determination of anisotropic potentials and quantum effects in case of rotationally inelastic cross-sections

- Jensen [412]: developed the program MORBID to improve potentials for H_2O, CH_2, H_2Se (information from rotation-vibration spectra)
- Halberstadt et al.: energy transfer data for the fitting of vdW interactions, e. g. in $HeCl_2$ [413, 201], HeICl [414], $ArCl_2$ [415], $HgAr_2$ [416]
- Tennyson et al. [417]: improved present potentials for H_3^+ [418], H_2O [419], fit of the potentials to experimental data
- Ernesti et al. [420]: investigated the possibility to use information given in rotational rainbows for the fitting of anisotropic potentials
- Battaglia et al. [380]: fitting the potential curves of Rg-O_2-systems (Rg$\,=\,$rare gas). "multi-property" -analysis
- Saykally et al.: determine the potentials from rotation-vibration spectra: $(HCl)_2$: [243], Ar-H_2O: [401, 421], Ar-NH_3: [343]
- Mills et al.: determine PESs, harmonic and anharmonic force fields from rotation-vibration-data [13, 422, 423]
- Rasmussen et al.: optimize force fields for alkens [424]

5 Comparison of different fits in some test cases [31, 21]

- test example

(1) typical one-dimensional fits for diatomics:

- H_2: splines: [23, 89]; Lagrange-, Hermite- and spline-interpolation: [87]; Taylor expansions and extended Rydberg functions: [31]

- test example for the qualitative difference of Taylor expansions of highest order, splines and the test function

- Taylor expansions, Morse and extended Rydberg functions with experimental RKR points for the $^1\Sigma_g^+$ ground state of H_2

- Lagrange-, Hermite- and spline-interpolation of the Kolos and Wolniewicz $E, F^1\Sigma_g^+$ double minimum potential of H_2

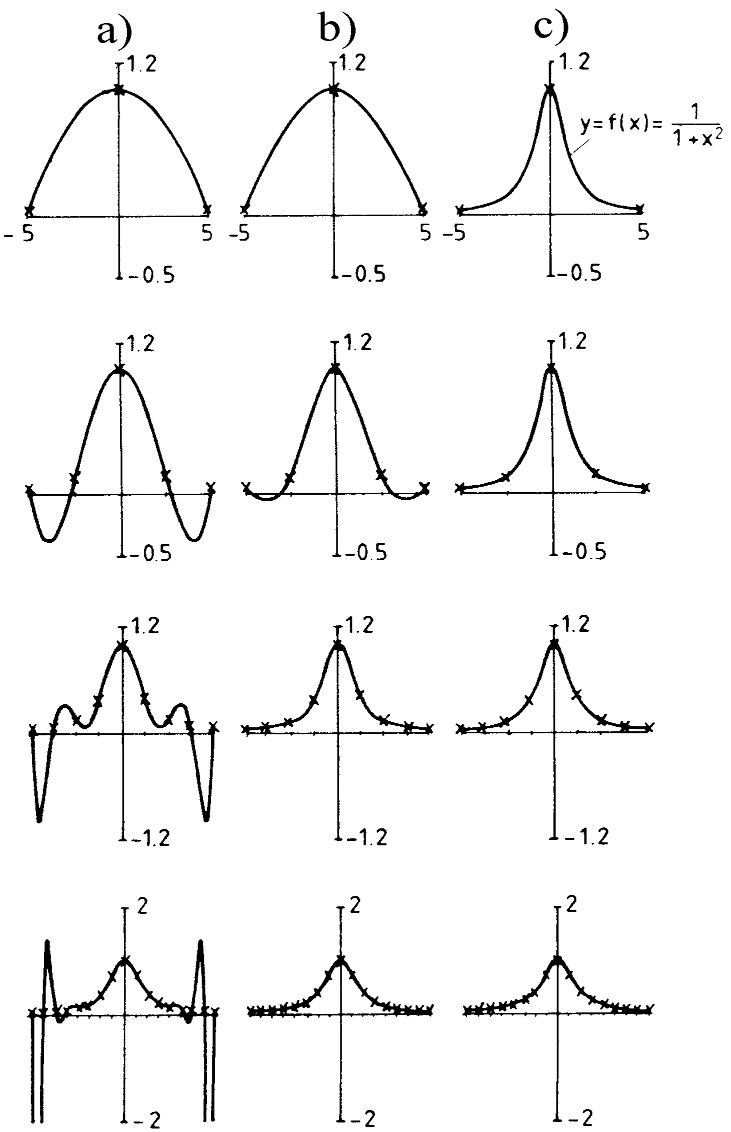


Figure 10: Comparison of (a) interpolational polynomial of highest order, (b) cubic spline with (c) the test function $y = \frac{1}{1+x^2}$ for 3, 5, 9 and 17 data points.

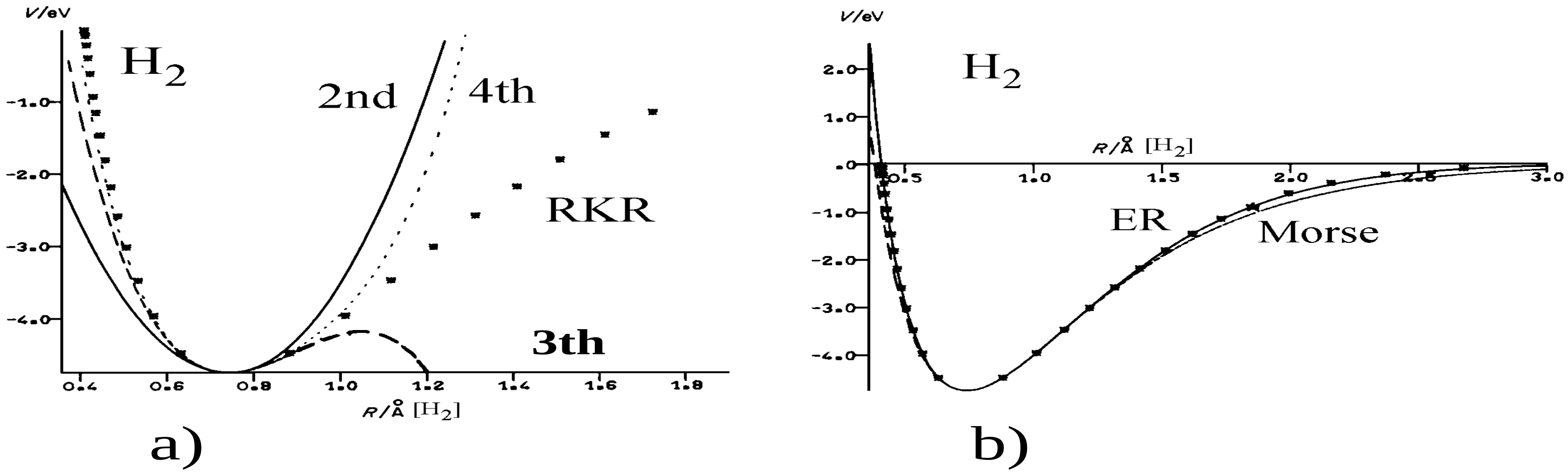


Figure 11: (a) Comparison of the Taylor expansions to the H_2 potential with the RKR points. (b) Comparison of the Morse function and the Extended Rydberg function (ER) with the RKR points for H_2. (Murrell, J.N., Carter, S., Farantos, S.C., Huxley, P., Varandas, A.J.C.: Molecular potential energy functions (1984)).

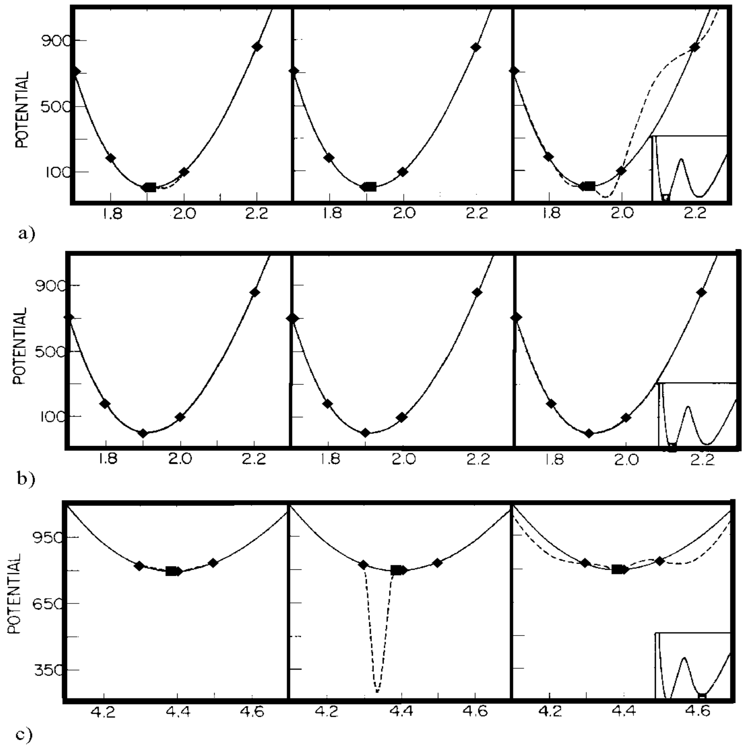


Figure 12: Interpolated inner ((a), (b)) and outer (c) minima of the $E, F\ ^1\Sigma_g^+$ potential of H_2. Shown are Lagrangian (left panel), Hermite (center), and spline (right) interpolation points. Third (solid line) and fifth (dashed line) order functions were used [cm^{-1}]. (a) All tabulated points, shown as rhombs, including the 6 points represented by the squares, are used. (b) As in (a), but 15 points clustered around the extrema have been deleted. (c) As in (a), but for the outer minimum. (Malik, D.J., Eccles, J., Secrest, D.: J. Comput. Phys. **38** (1980) 157)

- Ar$_2$:

Ogilvie [94]:
test of different expansion variables $x_{mn} = \frac{(R-R_e)(m+n)}{(mR+nR_e)}$
$(m, n$: integer)

- $m = 0, n = 1$: Dunham
- $m = 1, n = 0$: SPF
- $m = 1, n = 1$: Ogilvie
- leads to excellent results depending on the type of the functional form (defined by m, n) and the order of expansion in ρ_{mn}

Varandas and da Silva [127]:
very sophisticated fit; multiproperty fit including spectroscopic and scattering results and second virial coefficients, combination of different methods

- fitting the R dependence of the CO-HCl van der Waals interaction

- two most attractive arrangements (Fig. 14 and 13)

- energy points are calculated on the CEPA-level [425]

- different expansion variables

- four point Lagrange, Padé and spline interpolation schemes

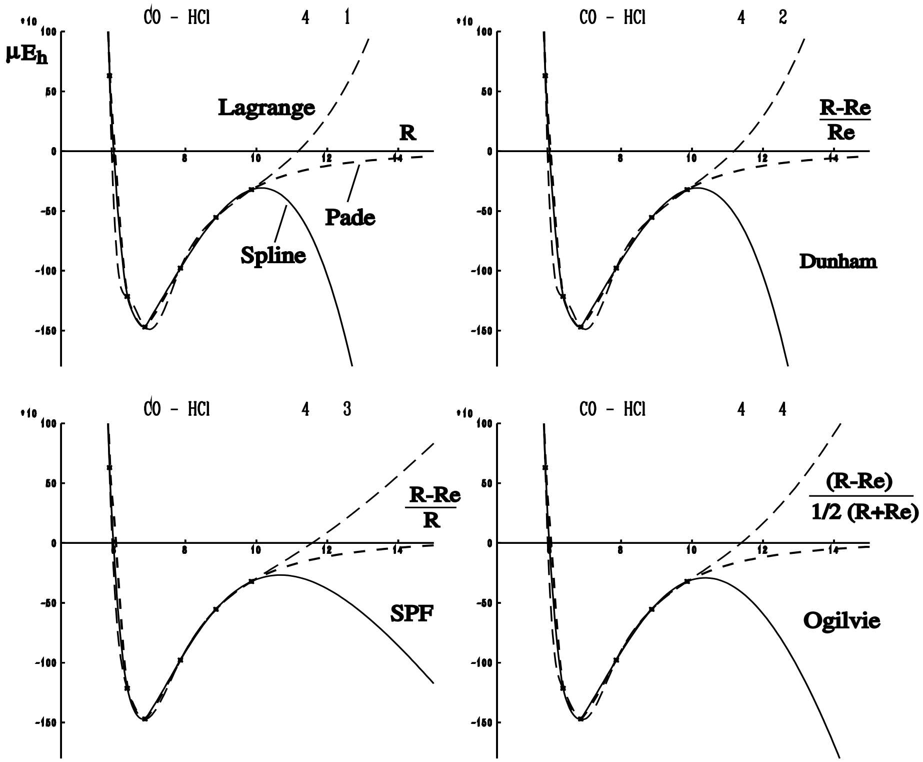


Figure 13: CO – HCl R-dependence of the less attractive CO – HCl approach ($R =$ distance between the two middle points (!) of CO and HCl). Seven energy points (□) are calculated on the CEPA-level [425] and fitted using different expansion variables with different four point interpolation schemes. No energy point used at $R = 15$ a$_o$.

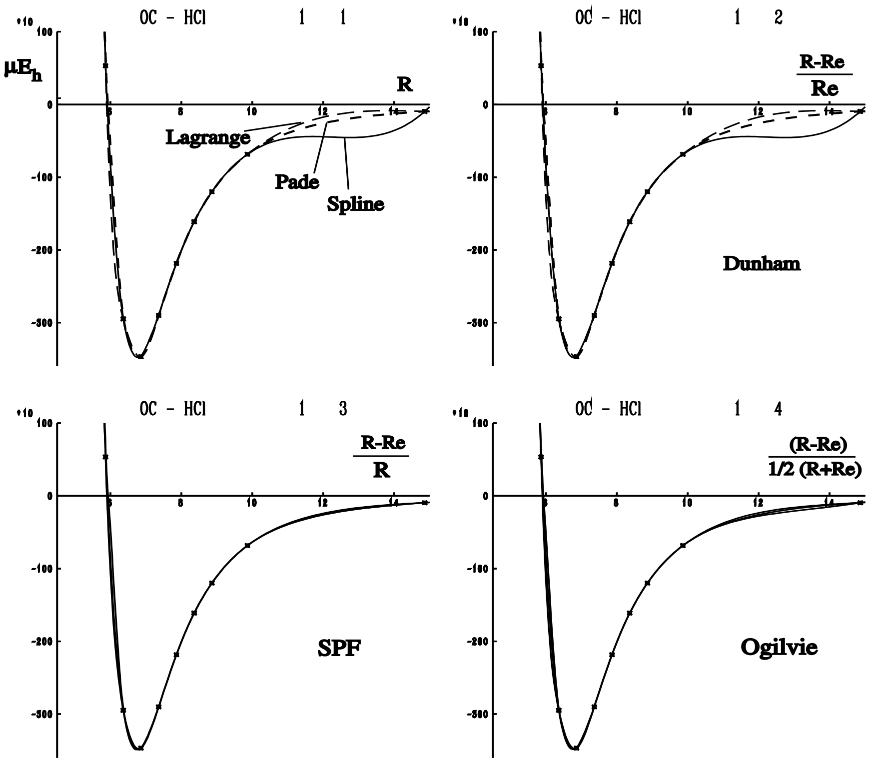


Figure 14: CO – HCl: R-dependence of the most attractive OC – HCl approach ($R =$ distance between the two middle points (!) of OC and HCl). Nine energy points ($\square$) are calculated on the CEPA-level [425] and fitted using different expansion variables with different four point interpolation schemes. Distances in a$_o$ and energies in μH.

(2) two and three dimensional spline fits:

- He + H_2^+: Sathyamurthy and Raff [89]

- spline fitted potential energy values and derivatives are compared with the original DIM values
- influence of different grid sizes on the results of quasiclassical trajectory calculations (e. g. spatial scattering distributions, distribution of final H_2^+ rotational energy for inelastic collisions, etc.)
- detailed analysis (dynamics) shows differences for the two surfaces

- detailed comparison of power series expansions and rational functions: LiH_2^+ [24]
- many body expansions: SO_2 [110, 111, 112]

detailed analysis for NeH$_2^+$ [123, 124, 125, 126]

Ne $+$ H$_2^+$ $\rightarrow$ NeH$_2^+$ $\rightarrow$ NeH$^+$ $+$ H

fit of the calculated energy points (CEPA-quality) to three different many body approaches:

- Joseph and Sathyamurthy [114] (Fit 1: Eqn. (19), introduced by Sorbie and Murrell [109])
- Schinke [113] (Fit 2: Eqn. (20))
- Aguado and Paniagua [115] (Fit 3: Eqn. (21))

- root mean square errors of the diatomic fits are given in Table 2
- standard deviations for totally 225 points (N$_{pts}$) are given in Table 3

Table 2: Root mean square errors of diatomic fits. Energies in eV

	Fits 1,2	Fit 3
Diatomic fit - HH	3.66E(-5)	3.16E(-3)
Diatomic fit - NeH	8.60E(-5)	4.58E(-4)

Table 3: NeH_2^+ Fits: Surface Deviations in eV^a

		Fit 1		Fit 2		Fit 3	
$\Theta(deg)$	N_{pts}	ΔV_{rms}	ΔV_{max}	ΔV_{rms}	ΔV_{max}	ΔV_{rms}	ΔV_{max}
All	225	0.0271	0.189	0.0294	0.221	0.0193	0.138
180	56	0.0204	0.067	0.0208	0.081	0.0120	0.030
150	33	0.0183	0.049	0.0185	0.050	0.0085	0.024
120	32	0.0216	0.076	0.0271	0.074	0.0134	0.042
90	39	0.0156	0.046	0.0190	0.063	0.0103	0.027
60	28	0.0268	0.065	0.0316	0.069	0.0224	0.089
30	33	0.0518	0.189	0.0550	0.221	0.0392	0.138

some details:

- 108 calculated points from an earlier work [124], additional calculations at 117 geometries
- choice of geometries was dictated by a number of considerations:

(1) a series of points on the repulsive wall were chosen to ensure correct behavior in this region

(2) points were chosen around the entrance and exit channels so that the correct asymptotic form would be followed

(3) a choice was made to cover both sides of the saddle points of the reaction surface

(4) because of the problem of extraneous minima and maxima in areas where there are insufficient data for the Sorbie-Murrell form, further points on the bent surfaces were chosen to adequately cover the entrance and exit channels

(5) similar problem with the Aguado and Paniagua functional form, additional strategically placed points on the 30° surface

- contour plots of all three different fits are very similar

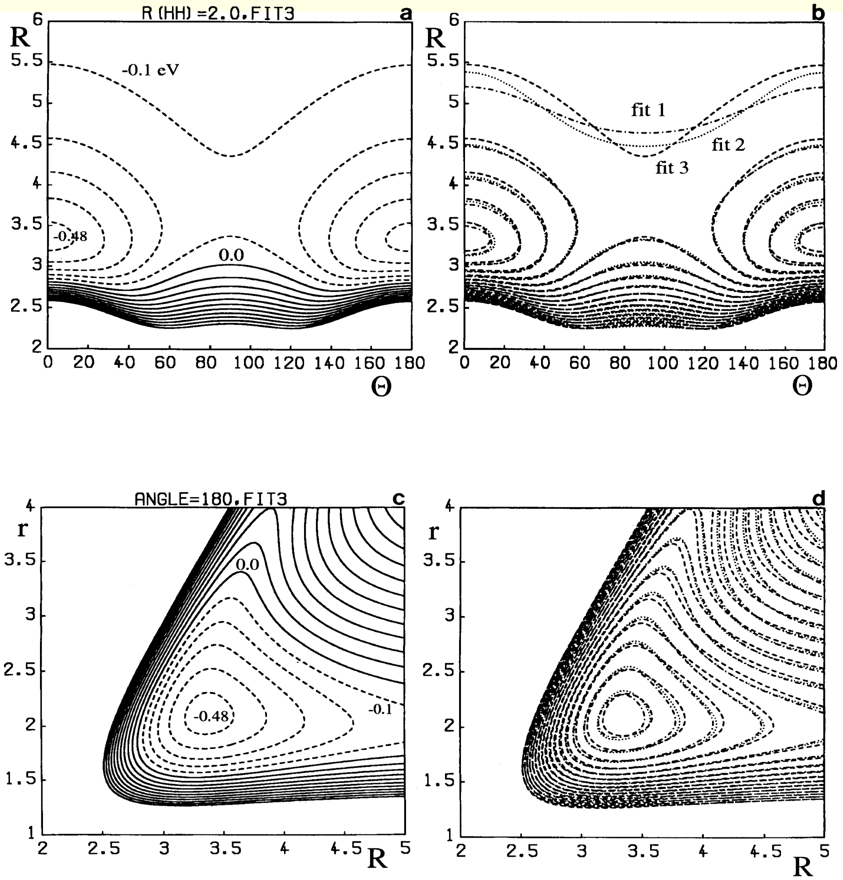


Figure 15: NeH_2^+ : Contour plot of the potential energy surface in Jacobi coordinates [126]. (a) Plot for fit 3 with $r(\mathrm{H}_2) = 2.0$ a$_o$ fixed. (b) Comparison of the 3 fits for the coordinates R and θ. (c) Plot for fit 3 with $\theta = 180^o$ fixed. (d) Comparison of the 3 fits for the coordinates r and R. R is the distance between Ne and the center of mass of H_2^+, θ is the angle between R and the diatomic bond r of H_2^+. Contours are given in steps of 0.1 eV. Jaquet, R.: Theor. Chim. Acta. **88** (1994) 217

- very small differences for collinear Ne-H-H configurations

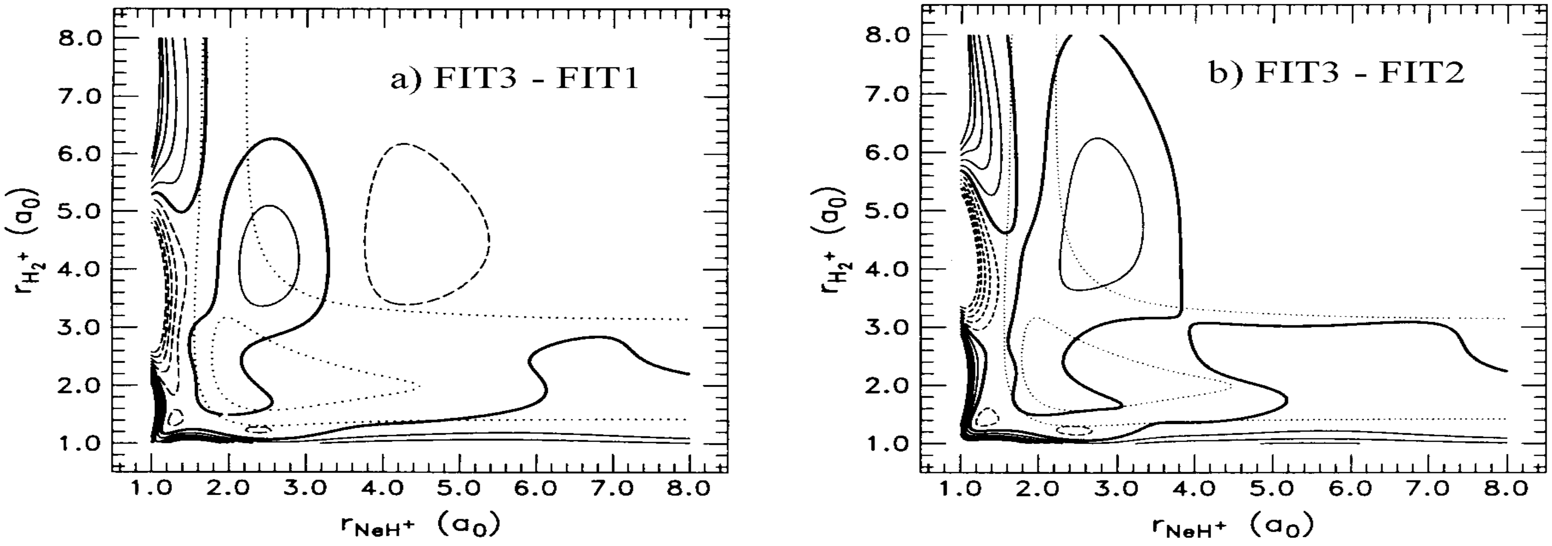


Figure 16: A contour diagram of the difference between the PHHJ-1,2,3 potentials for collinear Ne-H-H configurations [426]. (Kress, J.D., Walker, R.B., Hayes, E.F., Pendergast, P.: J. Chem. Phys. **100** (1994) 2728.)

- detailed information of the three different fits and the minimum energy paths [125]
- differences in the fits are seen more clearly when these PESs are used in dynamics calculations:

\- bound state calculations for the rovibrational levels of NeH_2^+ and its isotopomeres

\- quantum scattering studies of long lived resonances for the reaction
$\mathrm{Ne} + \mathrm{H}_2^+ \rightarrow \mathrm{NeH}^+ + \mathrm{H}$ [426]

\- quasiclassical and approximate quantum mechanical (R-IOSA) studies of the intramolecular isotope effects in proton transfer:
$\mathrm{Ne} + \mathrm{HD}^+ \rightarrow \mathrm{NeH}^+ \; (\mathrm{NeD}^+) + \mathrm{D} \; (\mathrm{H})$ [427]

- bound state calculations reveal the differences in the three fits

\- Table 4: differences in the calculated frequencies of $\approx$ 50 cm^{-1}

\- scattering calculations: 50 $\mathrm{cm}^{-1} \approx$ 0.006 eV; small error: better than the accuracy of the fit - BCRLM reaction probabilities [426]: average height of the strongly osc. reaction probability $\mathrm{P}_{2\rightarrow 0}^{0}$: 0.05 (Fit 1) — 0.15 (Fit 3)

Table 4: Rovibrational levels [cm^{-1}] for NeH$_2^+$($J = 0, j =$ even) for fit 1,2,3; relative to the vibrational ground state energy (Ne + H$_2^+$ dissociation limit). ν_r = H$_2^+$ stretching mode, ν_b= Ne – H$_2^+$ bending mode and ν_s= Ne – H$_2^+$ stretching mode.

Fit			1	2	3
E$_{000}$			-2070.231	-2112.907	-2108.450
ν_r	ν_b	ν_s			
0	0	0	0.0	0.0	0.0
0	0	1	849.5	858.6	810.7
0	2	0	1198.0	1228.4	1189.4
0	0	2	1566.6	1587.3	1513.6
1	0	0^a	1726.6	1740.3	1747.6
0	2	2	1884.7	1919.4	1863.6
0	4	1	2104.8	2146.5	2108.1
0	0	3	2171.8	2203.8	2139.5
			2366.8	2422.1	2394.1
			2456.6	2492.6	2534.5
			2578.1	2610.8	2582.8
			2698.8	2744.3	2700.8
			2744.7	2795.0	2776.2

Fit of H_3^+ (overview: [428])

different fits:
- power series (for rovibrational calculations [99, 101, 205])
- many body expansions(for scattering calculations [280, 282])

PES for calculating the lowest rovibrational states (can also be used for higher energies):

- power series expansion in symmetry adapted deformation coordinates S_a, S_x and S_y (proposed by Meyer, Botschwina, Burton (MBB) [101])
- seems to be the optimal choice

MBB points are labeled by three integers n_a, n_x, n_y, related to the coordinates S_a, S_x, S_y $[a_0]$

$$S_a = \quad 0.15\; n_a = \quad (\tilde{R}_{12} + \tilde{R}_{23} + \tilde{R}_{31})/\sqrt{3} \tag{90}$$

$$S_x = \quad 0.15\; n_x = \quad (2\tilde{R}_{12} - \tilde{R}_{23} - \tilde{R}_{31})/\sqrt{6} = S_e \cos\phi \tag{91}$$

$$S_y = \quad 0.15\; n_y = \quad (\tilde{R}_{23} - \tilde{R}_{31})/\sqrt{2} = S_e \sin\phi \tag{92}$$

$\tilde{R}_{kl}$ are related to the actual bond distances R_{kl} as

$$\tilde{R}_{kl} = \left[1 - \exp\left\{-\beta\left(R_{kl}/R_{ref} - 1\right)\right\}\right]/\beta \tag{93}$$

$$= (R_{kl} - R_{ref})/R_{ref} + O\left\{\left[\left(R_{kl} - R_{ref}\right)/R_{ref}\right]^2\right\}$$

$\beta = 1.30$ (MBB)

- small displacements from the equilibrium:

- the S_a, S_x, S_y are proportional to symmetry deformation coordinates, which are automatically normal coordinates
- at the level of the harmonic approximation there is complete decoupling; only those points matter where two of the labels n_a, n_x, n_y vanish, at least if $R_{ref} = R_e$
- displacements from the equilibrium geometry are described by the MBB coordinates in the most symmetric way - main advantage of MBB coordinates: power series expansion of the PES converges rapidly
- MBB: rms-error: 1 cm^{-1} $(N = 7$; weighted least-square fit)

$$V = \sum_{n,m,k} V_{nmk} S_a^n S_e^{2m+3k} \cos(3k\phi), \; n + 2m + 3k \leq N \tag{94}$$

- expansion in internal coordinates $(R_{12},\ R_{23},\ R_{31})$: not all possible combinations of these coordinates are physically meaningful

- the R_{kl} must obey the triangular inequality; for linear arrangements the triangular inequality becomes an equality(limit of the physically allowed domain)
- MBB coordinates (as well as the MBB selection of points) are well adapted to a study of the vibrations of H_3^+
- scattering of H_2 and H^+, autodissociation of highly vibrationally excited H_3^+: expansion in Jacobi coordinates is presumably preferable

Burton et al. [99]:

- analysis for Dunham, SPF and Ogilvie type variables in the internuclear distance

- power series expansion in the sixth order (23 parameters) for 78 energy points

- χ^2 residual parameters are 60, 1.4 and 2.2 μH

- high order coefficients of the Dunham and Ogilvie expansions are large and swamp the harmonic and cubic terms

- energy contour plot (Fig. 17): vibration symmetry coordinates, big differences for the three types of expansions

- singular value decomposition (SVD): to rule out numerical problems related to linear dependencies for the SPF and Ogilvie expansion

– drastic reduction of the size of the coefficients of higher order – variance χ was only insignificantly changed

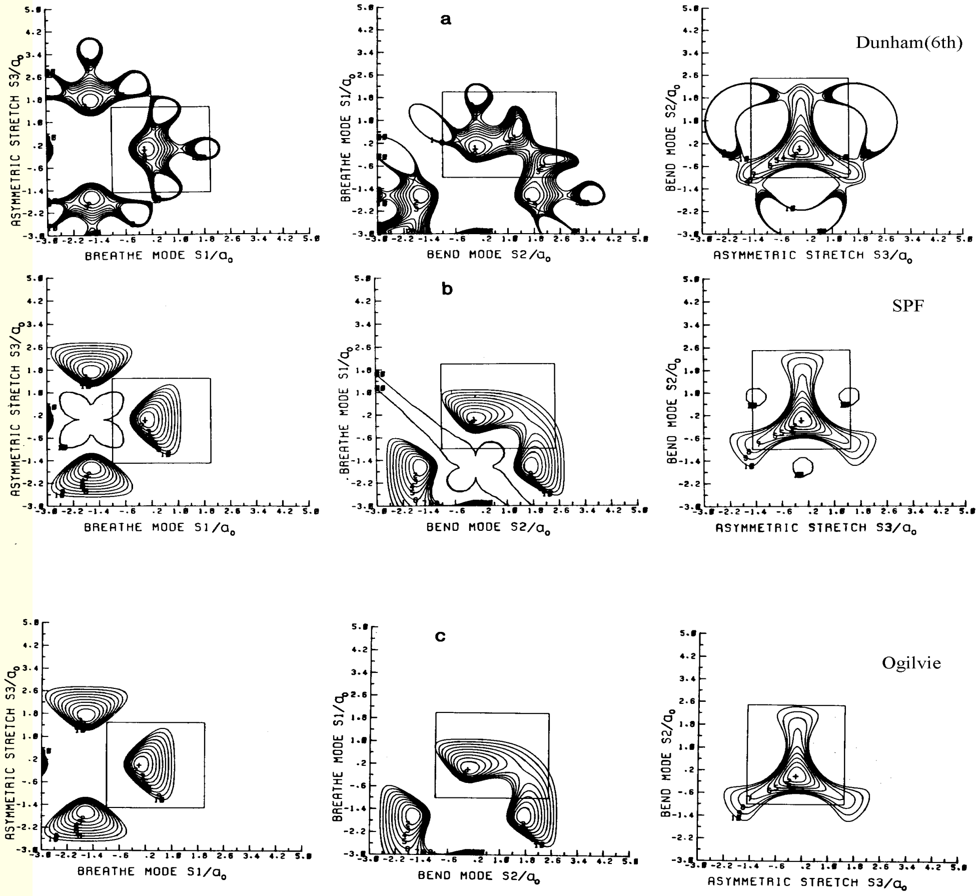


Figure 17: H_3^+: Comparison of the energy contour plots as a function of the vibration symmetry coordinates; (a) Dunham sixth order force field, (b) SPF sixth order force field and, (c) Ogilvie sixth order force field. The fits are based upon 78 PNO-CI ab initio data points. Burton, P.G., von Nagy-Felsobuki, E.I., Doherty, G.,Hamilton, M.: Mol. Phys. **55** (1985) 527

- Röhse et al. [205]:

- 69 energy points; CISD-R12 method; 7-th order fit (using MBB coordinates and SVD) with a weighted standard deviation of 0.6 μH
- error compared to experiment of ± 1 cm^{-1}: for the lowest frequencies of H_3^+ and its isotopomeres depending on which nuclear mass was chosen in the dynamics calculation (BO-level !)

- Cencek et al. [351, 352]:

- fits for 7-th up to the 10-th order expansions, MBB-coordinates - absolute accuracy of the electronic energy (BO): 0.01 cm^{-1}
- contour plots did not show whether or not near the potential energy minimum extraneous minima or maxima are produced
- rovibrational term values and frequencies reveal no internal problems
- adiabatic and relativistic corrections had been included
- different isotopomers of H_3^+: deviations between a few tenth and a hundredth of a wavenumber (without any empirical corrections)
- 10-th order fit slightly better than 9-th order fit; both are different from the results of the 7-th order fit

- reactive H_3 ($H + H_2$): ground state PES; detailed investigated system
- many fits: [256, 258, 296]; influence on scattering calculations: [258, 353, 429, 430]

Further examples: $O(^3P) + H_2$ [290, 291], $OH + H_2$ [51, 140, 335, 336], $F+H_2$ [431, 432, 433], H_3^+: [283, 284]

review: bimolecular reactions involving four or more atoms, using mostly fitted ab initio potentials: [8].

6 Formulae for Lagrange-, Hermite-, spline- interpolations and other solution techniques

Interpolating functions

(a) Lagrange interpolation formula [29] (polynomial degree: $m-1$):
subinterval; m energy points f_j (positions r_j) are exactly reproduced by

$$\text{1D}: \qquad E(r) = \sum_{j=1}^{m} f_j \frac{\prod_{i\neq j}^{m}(r_i - r)}{\prod_{i\neq j}^{m}(r_i - r_j)}, \qquad \text{nD}: \qquad E(\vec{r}) = \sum_{j=1}^{m} f_j \frac{\prod_{i\neq j}^{m}|\vec{r}_i - \vec{r}|}{\prod_{i\neq j}^{m}|\vec{r}_i - \vec{r}_j|} \tag{95}$$

- formulation may be useful on computers with array processors (calculation of vector norms) different formulation: nD

$$E(\mathbf{r}) = \sum_{\mathbf{j=1}}^{\mathbf{m}} \mathbf{f_j} \frac{\sum_{\mathbf{k=1}}^{\mathbf{n}} \prod_{\mathbf{i \neq j}}^{\mathbf{m}} (\mathbf{r_{ik}} - \mathbf{r_k})}{\sum_{\mathbf{k=1}}^{\mathbf{n}} \prod_{\mathbf{i \neq j}}^{\mathbf{m}} (\mathbf{r_{ik}} - \mathbf{r_{jk}})} \tag{96}$$

alternative: use of a recursion formula [80]
(b) rational interpolation: only energy points are given

$$E(\vec{r}) = \frac{P_\mu(\vec{r})}{Q_\nu(\vec{r})} \tag{97}$$

$P_\mu =$ polynomial (degree μ), $Q_\nu =$ polynomial (degree ν)
- recursion relation: given points will be reproduced exactly [80]; poles can be described

(c) Hermite interpolation (polynomial degree: $2m-1$):

subinterval: m energy points f_j and derivatives g_j (positions r_j) are given

1D:

$$E(r) = \sum_{j=1}^{m} \left\{ f_j \left(1 - 2 \sum_{p \neq j}^{m} \frac{(r_j - r)}{(r_p - r_j)} \right) - g_j (r_j - r) \right\} \frac{\prod_{i \neq j}^{m} (r_i - r)^2}{\prod_{i \neq j}^{m} (r_i - r_j)^2} \quad (98)$$

nD:

$$E(\vec{r}) = \sum_{j=1}^{m} \left\{ f_j \left[1 - 2 \sum_{k'=1}^{n} \frac{\displaystyle\sum_{p \neq j}^{m} \prod_{\substack{i \neq j \\ i \neq p}}^{m} (r_{ik'} - r_{jk'})}{\displaystyle\sum_{k=1}^{n} \prod_{i \neq j}^{m} (r_{ik} - r_{jk})} \right] \right\}$$

$$\times \left(\frac{\displaystyle\sum_{k=1}^{m} \prod_{i \neq j}^{m} (r_{ik} - r_k)}{\displaystyle\sum_{k=1}^{n} \prod_{i \neq j}^{m} (r_{ik} - r_{jk})} \right)^2 + \sum_{j=1}^{m} \sum_{k=1}^{n} g_{jk} G_{jk}(\vec{r}) \tag{99}$$

with

$$G_{jk}(\vec{r}) = -(r_{jk} - r_k)\frac{\prod_{i\neq j}^{m}(r_{ik} - r_k)^2}{\prod_{i\neq j}^{m}(r_{ik} - r_{jk})^2} \tag{100}$$

- "osculating" polynomials can be obtained, which reproduce exactly energy points f_j and 1st derivatives g_j (respectively partial derivatives g_{jk})

(d) cubic spline-interpolation [83, 434]:
subinterval: only N energy points f_j (positions r_j) are given

1D:

$$E(r) = E_i(r) = a_i + b_i(r - r_i) + c_i(r - r_i)^2 + d_i(r - r_i)^3 \qquad (101)$$

for $r_i \le r < r_{i+1}$ in $[r_1, r_N]$, i=1,2,...,N-1

(1) $a_i = f_i,$ $h_i = r_{i+1} - r_i,$ i=1,2,...,N-1
(2) from the continuity of $E''(r)$ at inner nodes follows

$$d_{i-1} = \frac{c_i - c_{i-1}}{3h_{i-1}} \qquad (102)$$

(for natural splines: $c_1 = c_N = 0$), $i = 2, 3, .., N - 1$

(3) from the continuity of $E(r)$ at inner nodes follows

$$b_{i-1} = \frac{a_i - a_{i-1}}{h_{i-1}} - \frac{2c_{i-1} + c_i}{3} h_{i-1}, \qquad i = 2, 3, \ldots N \tag{103}$$

(4) continuity of $E'(x)$ at inner nodes leads to

$$c_{i-1}h_{i-1} + 2(h_{i-1} + h_i)c_i + c_{i+1}h_i = 3\left(\frac{a_{i+1} - a_i}{h_i} - \frac{a_i - a_{i-1}}{h_{i-1}}\right), \quad i = 2, 3, \ldots, N-1 \tag{104}$$

(solution of a tridiagonal system of equations)
alternative: recursive formula of Mezey: [29]
further subjects: see [82, 83, 434, 435, 436, 437]

“compensation”-splines [82, 438]: N energy points f_j with error σ_j

$$\sum_{i=1}^{N}\left[\frac{f_i - E(r_i)}{\sigma_i}\right]^2 + \lambda\int_{r_1}^{r_N}[E''(r)]^2 dr = Min \tag{105}$$

(λ: Lagrange multiplier)

Bicubic splines (Ansatz of tensor products) [82], basis splines (B-splines) [434], x-splines [439], Hermite-splines [82], cardinal splines [440], Bezier-splines [82] (no monotonical ordering of the grid points), L-splines [88], Bernstein-Bezier-representations [29] *(e) Akima interpolation* [84, 85, 441, 442]

- variant of the cubic spline: avoids strong “elongations” of the interpolating function between the grid points
- good for sudden changes in the potential, does not depend too strongly on the choice of the grid as in case of the natural splines

(f) Power series (polynomial) expansion
simple Ansatz:

$$y = c_1 + c_2 x + ... c_N x^{N-1} \tag{106}$$

For N points y_i one has to solve a system of linear equations:

$$\begin{bmatrix} 1 & x_1 & x_1^2 & \cdots & x_1^{N-1} \\ \vdots & \vdots & \vdots & & \vdots \\ 1 & x_N^1 & x_N^2 & \cdots & x_N^{N-1} \end{bmatrix} \begin{bmatrix} c_1 \\ \vdots \\ c_N \end{bmatrix} = \begin{bmatrix} y_1 \\ \vdots \\ y_N \end{bmatrix} \tag{107}$$

- different variants to solve the above equation [80]

“Least-squares error” minimization procedure: “more data than parameters”

- different variants of solving least-squares problems [30, 71, 80, 81]

(a) least-squares method (linear/nonlinear)
(b) “χ^2” weighted least-squares method
with commonly used algorithms [30] like Gauss-Newton [15], Levenberg-Marquardt [80, 443], SVD [80, 444], steepest descent [15], iteratively re/weighted [445] steps

for N data points $\{x_i, y_i\}, i = 1, \ldots N$ and M adjustable parameters $\{a_j\}, j = 1, \ldots M, M \leq N$

$$y(x) = y(x; a_1, \cdots a_M) \tag{108}$$

$$\text{minimization of } \{a_j\}: \quad \text{Min}\left\{Q = \sum_{i=1}^{N}[y_i - y(x_i; a_1, \cdots a_M)]^2\right\} \tag{109}$$

$$\text{or} \qquad \text{Min}\left\{\chi^2 = \sum_{i=1}^{N}\left(\frac{[y_i - y(x_i; a_1, \cdots a_M)]}{\sigma_i}\right)^2\right\} \tag{110}$$

- each point (x_i, y_i) has its own known standard deviation or "measurement error" σ_i

● formula can be derived from the maximization of the probability of the data set from the product of probabilities of each point (Gaussian normal distribution of the error)

$$P \propto \prod_{i=1}^{N} \{ e^{-\frac{1}{2}(\frac{y_i - y(x_i)}{\sigma})^2} \Delta y \} \qquad \text{(“maximum likelihood estimation”)} \tag{111}$$

standard deviations σ of these normal distributions are the same for all points:

$$\sigma = \sqrt{\sum_{i=1}^{N} [y_i - y(x_i)]^2/(N-M)} \tag{112}$$

the following equations have to be solved:

$$0 = \sum_{i=1}^{N} \left(\frac{y_i - y(x_i)}{\sigma_i^2} \right) \left(\frac{\partial y(x_i; \cdots a_k \cdots)}{\partial a_k} \right), \qquad k = 1, \ldots M \tag{113}$$

- in general, there are M nonlinear equations

Special case: “linear regression”

$$y(x) = \sum_{k=1}^{M} a_k X_k(x) \tag{114}$$

$X_k(x)$: basis functions, a_k: parameters to be calculated

minimization of χ^2 leads to normal equations (linear equation system):

$$\sum_{j=1}^{M} \alpha_{kj} a_j = \beta_k, \quad \text{or equivalently} \quad \mathbf{A}\mathbf{a} = \mathbf{b} \tag{115}$$

$$\alpha_{kj} = \sum_{i=1}^{N} \frac{X_j(x_i) X_k(x_i)}{\sigma_i^2}, \quad \beta_k = \sum_{i=1}^{N} \frac{y_i X_k(x_i)}{\sigma_i} \tag{116}$$

Solution of a_j:

$$a_j = \sum_{k=1}^{M} [\alpha]^{-1}_{jk} \beta_k = \sum_{k=1}^{M} C_{jk} \Big[\sum_{i=1}^{N} \frac{y_i X_k(x_i)}{\sigma_i^2} \Big] \tag{117}$$

Variance of a_j:

$$\sigma^2(a_j) = \sum_{i=1}^{N} \sigma_i^2 \left(\frac{\partial\, a_j}{\partial\, y_i} \right)^2 \quad \text{with} \quad \frac{\partial\, a_j}{\partial\, y_i} = \sum_{k=1}^{M} C_{jk} X_k(x_i) \,/\, \sigma_i^2 \tag{118}$$

$$\sigma^2(a_j) = \sum_{k=1}^{M} \sum_{l=1}^{M} C_{jk} C_{jl} \left[\sum_{i=1}^{N} \frac{X_k(x_i) X_l(x_i)}{\sigma_i^2} \right] = C_{jj} \tag{119}$$

$C_{jk} = [\alpha]^{-1}_{jk}$ is the covariance between a_j and a_k.

Caution: in case of the direct solution of the normal equations one has to deal with rounding errors for the Gauss-Jordan- or Cholesky-procedure [80]

Alternative: QR-decomposition or even better SVD ("singular value decomposition") [80, 444]

general problem associated with multi-dimensional least-squares problems:

- the parameters are correlated [30, 446] - it is desirable to constrain the least-squares problem to a subspace of the full parameter space [16, 447]

Singular value decomposition

- linear dependencies of the basis functions or combinations of basis functions

- will result in numerical problems with the solution of systems of linear equations
- least-squares procedures: equations can be overdetermined (data) and additionally underdetermined (functional Ansatz, basis)

search for $\mathbf{a}$ (eq. 115) that minimizes:

$$\chi^2 = |\mathbf{A}\ \mathbf{a} - \mathbf{b}|^2 \tag{120}$$

A and **b** are given as

$$A_{ij} = \frac{X_j(x_i)}{\sigma_i}, \quad b_i = \frac{y_i}{\sigma_i} \tag{121}$$

choose the following Ansatz:

$$y(x) = \sum_{k=1}^{M} a_k X_k(x) \tag{122}$$

$$\chi^2 = \sum_{i=1}^{N} \Big[\frac{y_i - \sum_{k=1}^{M} a_k X_k(x_i)}{\sigma_i} \Big]^2 \tag{123}$$

$\mathbf{A}$ $(M \times N)$ will be (following SVD) separated in three matrices [448]:

$$\mathbf{A} = \mathbf{U}\ \mathbf{W}\ \mathbf{V}^T \tag{124}$$

- $\mathbf{U}(M \times N)$, $\mathbf{V}(N \times N)$: orthogonal matrices
- $\mathbf{W}(N \times N)$: diagonal matrix $(w_i \geq 0)$

formal solution of the problem (work from right to left):

$$\mathbf{a} = \mathbf{A}^{-1}\mathbf{b} = \mathbf{V}\left[\mathrm{diag}\left(\frac{1}{w_j}\right)\right](\mathbf{U}^T\mathbf{b}) \tag{125}$$

- for a non-singular matrix $\mathbf{A}$: project one vector space onto another vector space of equal dimension

for a singular matrix $\mathbf{A}$:
- projection will be done on a vector space of smaller dimension
- concepts of nullspace and range are important
- subspace of $\mathbf{a}$ (nullspace) is mapped to zero, $\mathbf{A}\ \mathbf{a} = 0$
- subspace of $\mathbf{b}$ that can be reached by $\mathbf{A}$ (by mapping of $\mathbf{a}$) is called the range of $\mathbf{A}$ - columns of $\mathbf{U}$ with the index j, to which $w_j \neq 0$ belongs, describe orthonormal basis vectors, which span the range
- columns of $\mathbf{V}$ with the index j, to which $w_j = 0$ belongs, describe orthonormal basis vectors for the nullspace

solution of the least-squares problems:

$$\mathbf{a} = \sum_{i=1}^{M} \Big(\frac{\mathbf{U}_{(i)}\,\mathbf{b}}{w_i} \Big) \mathbf{V}_{(i)} \pm \frac{1}{w_1}\mathbf{V}_{(1)} \pm \frac{1}{w_2}\mathbf{V}_{(2)} \pm \cdots \tag{126}$$

$$\sigma^2(a_j) = \sum_{i=1}^{M} \frac{1}{w_i^2} [\,\mathbf{V}_{(i)}\,]_j^2 = \sum_{i=1}^{M} \Big(\frac{V_{ji}}{w_i} \Big)^2 \tag{127}$$

- $\mathbf{V}_{(i)}$ (i denotes the columns of $\mathbf{V}$) defines the principal axis of an error ellipsoid of $\mathbf{a}$

- if $1/w_i$ is singular or very large, one sets $1/w_i$ to zero.

Nonlinear Ansatz

function to be fitted:

$$y(x) = y(x; a_1 \cdots a_m) \tag{128}$$

- depends nonlinearly on the set of m unknown parameters a_k

define a χ^2 function:

$$\chi^2 = \sum_{i=1}^{N} \left(\frac{y_i - y(x; a_1 \cdots a_m)}{\sigma_i} \right)^2 \tag{129}$$

- determine best-fit parameters by minimization which has to proceed iteratively
- iterative minimization of χ^2 starts with current trial parameters $\mathbf{a}_{cur}$

approximation near the minimum (quadratic form)

$$\chi^2(\mathbf{a}) \approx \gamma - \mathbf{d}\ \mathbf{a} + \frac{1}{2}\,\mathbf{a}\ \mathbf{D}\ \mathbf{a} \tag{130}$$

$\mathbf{d}$: gradient of χ^2, $\mathbf{D}$: 2nd derivative (“Hessian”) of χ^2

good approximation: jump to the optimal value

$$\mathbf{a}_{min} = \mathbf{a}_{cur} + \mathbf{D}^{-1}[-\nabla\chi^2(\mathbf{a}_{cur})] \tag{131}$$

poor local approximation (130): use the steepest descent approach

$$\mathbf{a}_{next} = \mathbf{a}_{cur} - \text{const}\ \times \nabla\chi^2(\mathbf{a}_{cur}) \tag{132}$$

$$[\nabla\chi^2]_k = \frac{\partial\chi^2}{\partial a_k} = -2\sum_{i=1}^{N}\frac{y_i - y(x_i;\mathbf{a})}{\sigma_i^2}\frac{\partial y(x_i;\mathbf{a})}{\partial a_k}, \quad k = 1, 2, \ldots, M \quad (133)$$

$$\frac{\partial^2\chi^2}{\partial a_k \partial a_l} = 2\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\left[\frac{\partial y(x_i;\mathbf{a})}{\partial a_k}\frac{\partial y(x_i;\mathbf{a})}{\partial a_l} - (y_i - y(x_i;\mathbf{a}))\frac{\partial^2 y(x_i;\mathbf{a})}{\partial a_l \partial a_k}\right] \quad (134)$$

constant: small enough not to overshoot the downhill direction

second derivatives: $\frac{\partial^2 y(x_i;\mathbf{a})}{\partial a_l \partial a_k}$
- can be destabilizing depending on the functional Ansatz or the available data points, so that they can be neglected!
- minor (or even larger) manipulations of (134) have no effect on the final result of $\mathbf{a}$, but only on the route of iteration

- Levenberg-Marquardt-procedure: varies smoothly between the inverse-Hessian method and the steepest descent method [80]

- Denis et al. [449] developed a code (NL2SOL) that keeps the second derivative term (“full Newton type” method) and is reputed to be more robust than the Levenberg-Marquardt procedure [80]

Minimization / Maximization of functions: general procedures

search for global and local minima with respect to optim. parameters [80]:
(a) there is no “best” optimization procedure
(b) for local minima one has to use different starting parameters, whereas for global minima the use of “simulated annealing” methods [450, 80] is advisable
(c) there is the possibility of restricted and unrestricted optimization
(d) there are different optimization procedures depending on the “quality” of the input: (1) only functional values (energy) or (2) functional values and derivatives are given
(e) if only energies are given: use “Downhill Simplex”-method, Powell-, Brent-method [80]
(f) if energies and 1st derivatives are given: use conjugate gradients (Fletcher-Reeves, Polak-Ribiere), “quasi Newton”-method (Davidon-Fletcher-Powell), Broyden-Fletcher-Goldfarb-Shanno algorithm [71]

References

[1] Shaik, S.S., Schlegel, H.B., Wolfe, S.: Theoretical aspects of physical organic chemistry, chap. 2, Wiley, New York, 1992

[2] LeRoy, R.J. in: Semiclassical methods in molecular scattering and spectroscopy, Child, M.S. (Ed.), Reidel, London, 1980

[3] Jørgensen, P., Simons, J.: Geometrical derivatives of energy surfaces and molecular properties, Reidel, Dordrecht, 1986

[4] Yamaguchi, Y., Osamura, Y., Goddard, J.D., Schaefer, III, H.F.: A new dimension to quantum chemistry: Analytical derivative methods in ab initio molecular electronic structure theory, Oxford Univ. Press, Oxford, 1994

[5] Tennyson, J.: Comp. Phys. Rep. **4** (1986) 1

[6] Bacic, Z., Light, J.C.: Ann. Rev. Phys. Chem. **40** (1989) 469

[7] Hutson, J.M.: Comput. Phys. Commun. **84** (1994) 1

[8] Bowman, J.M., Schatz, G.C.: Ann. Rev. Phys. Chem. **46** (1995) 169

[9] Schatz, G.C.: J. Phys. Chem. **100** (1995) 12839

[10] Jaquet, R., Kumpf, A., Heinen, M.: J. Chem. Soc. Faraday Trans. **93** (1997) 1027 and Ref. 1-17 therein on time-dependent and time-independent approaches for quantum scattering treatment of elementary reactions

[11] Issue on Quantum reactive scattering, J. Chem. Soc. Faraday Trans. **93** (1997), no. 5

[12] Zhang, J.Z.H., Dai, J.Q., Zhu, W.: J. Phys. Chem. **101** (1997) 2764

[13] Hedberg, L., Mills, I.M.: J. Mol. Spectr. **160** (1993) 117

[14] Dennis, J.E. in: Nonlinear Optimisation, Powell, M.J.D. (Ed.), Academic Press, London, 1982

[15] Bevington, P.R., Robinson, D.K.: Data reduction and error analysis for the physical sciences, McGraw-Hill, London, 1992

[16] Gill, P.E., Murray, W., Wright, M.H.: Practical Optimization, Academic Press, London, 1981

[17] Kuntz, P.J. in: Dynamics of Molecular Collisions, Miller, WH. (Ed.), part B, chap. 2, Plenum, New York, 1976

[18] Wright, J.S., Gray, S.K.: J. Chem. Phys. **69** (1978) 67

[19] Connor, J.N.L.: Comput. Phys. Commun. **17** (1979) 117

[20] Sathyamurthy, N.: Comp. Phys. Rep. **3** (1985) 1

[21] Carter, S.: Comp. Phys. Rep. **3** (1986) 209

[22] Schatz, G.C.: Rev. Mod. Phys. **61** (1989) 669

[23] Searles, D.J., von Nagy-Felsobuki, E.I. in: Vibrational spectra and structure, Durig, J.R. (Ed.), **l9**, Elsevier, Amsterdam, 1991

[24] Searles, D.J., von Nagy-Felsobuki, E.I.: Phys. Rev. A. **43** (1991) 3365

[25] Searles, D.J, von Nagy-Felsobuki, E.I.: Ab initio variational calculations of molecular vibrational rotational spectra, Lecture Notes in Chemistry, **61**, Springer, Berlin, 1993

[26] Varandas, A.J.C.: Adv. Chem. Phys. **74** (1988) 255

[27] Varandas, A.J.C. in: Trends in atomic and molecular physics, Yanez, M. (Ed.), Universidad Autonomade Madrid, Madrid, 1990

[28] Varandas, A.J.C., Voronin, A.I.: Mol. Phys. **85** (1995) 497

[29] Mezey, P.G.: Potential energy hypersurfaces, Elsevier, Amsterdam, 1987

[30] Law, M.M., Hutson, J.M.: Comput. Phys. Commun. **102** (1997) 252

[31] Murrell, J.N., Carter, S., Farantos, S.C., Huxley, P., Varandas, A.J.C.: Molecular potential energy functions, Wiley, Brisbane, 1984

[32] Hirst, D.M.: Potential energy surfaces: Molecular structure and reaction dynamics, Taylor and Francis, London, 1985

[33] Madsen, D., Pearman, R., Gruebele, M.: J. Chem. Phys. **106** (1997) 5874

[34] Schlegel, H.B.: Adv. Chem. Phys. **67** (1987) 249

[35] Popelier, P.L.A., Stone, A.J., Wales, D.J.: Faraday Disc. Chem. Soc. **97** (1994) 243

[36] Wales, D.J., Stone, A.J., Popelier, P.L.A.: Chem. Phys. Lett. **240** (1995) 89

[37] Morokuma, K., Kato, S. in: [38], p. 243

[38] Truhlar, D.G.: Potential energy surfaces and dynamics calculations, Plenum, New York, 1981

[39] Dunning, T.H., Harding, L.B. in: Theory of Chemical Reaction Dynamics, Baer, M. (Ed.), p. 1, CRC Press, Boca Raton, 1985

[40] Kuntz, P.J. in: Theory of Chemical Reaction Dynamics, Baer, M. (Ed.), p. 1, CRC Press, Boca Raton, 1985

[41] Schatz, G.C.: J. Phys. Chem. **99** (1995) 516

[42] Sathyamurthy, N.: Chem. Phys. **62** (1981) 1

[43] McKee, M.L., Page, M. in: Reviews in Computational Chemistry, Lipkowitz, K.B., Boyd, D.B. (Eds.), **4** (1993) 35, VCH, Weinheim

[44] Quapp, W., Imig, O., Heidrich, D. in: The Reaction Path in, Chemistry: Current Approaches and Perspectives, Heidrich, D. (Ed.), p. 95, 137, Kluwer, Dordrecht, 1995

[45] Truhlar, D.G. in: The Reaction Path in Chemistry: Current Approaches and Perspectives, Heidrich, D. (Ed.), p. 229, Kluwer, Dordrecht, 1995

[46] Chang, J., Brown, N.J., D'Mello, M., Wyatt., R.E., Rabitz, H.: J. Chem. Phys. **97** (1992) 6240

[47] Bowman, J.M., Bittman, J.S., Harding, L.S.: J. Chem. Phys. **85** (1986) 9119

[48] Jensen, H.J.A., Jøergensen, P., Helgaker, T.: J. Chem. Phys. **85** (1986) 3917

[49] Baldridge, K.K., Gordon, M.S., Steckler, R., Truhlar, D.G.: J. Phys. Chem. **93** (1989) 5107

[50] Steckler, R., Truhler, D.G.: J. Chem. Phys. **93** (1990) 6570

[51] Nguyen, K.A., Rossi, I., Truhlar, D.G.: J. Chem. Phys. **103** (1995) 5522

[52] Berry, R.S.: Chem. Rev. **93** (1993) 2379

[53] Berry, R.S.: J. Phys. Chem. **98** (1994) 6910

[54] Berry, R.S.: Int. J. Quant. Chem. **58** (1996) 657

[55] Freeman, D.L., Doll, J.D.: Ann. Rev. Phys. Chem. **47** (1996) 43

[56] Faraday discussion, Potential energy surfaces: Faraday Disc. Chem. Soc. **62** (1977)

[57] Lawley, K.P. (Ed.): Potential energy surfaces, Adv. Chem. Phys. **XLII**, Wiley, 1980

[58] Faraday discussion, Van der Waals molecules: Faraday Disc. Chem. Soc. **73** (1982)

[59] Truhlar, D.G., Steckler, R., Gordon, M.S.: Chem. Rev. **87** (1987) 217

[60] Jasien, P.G., Shepard, R.: Int. J. Quant. Chem. Symp. **22** (1988) 183

[61] Ho, T.S., Rabitz, H.: J. Phys. Chem. **97** (1993) 13447

[62] Ernesti, A., Hutson, J.M., Wright, N.J.: Fashioning a Model: Optimization methods in chemical physics, CCP6, Durham, 1998

[63] Law, M.M., Hutson, J.M., Ernesti, A.: Fitting potential energy surfaces, CCP6, Durham, 1993

[64] Mills, I.M. in: Recent Experimental and Computational Chemistry, Fausto, R. (Ed.), Kluwer, London, 1993

[65] Faraday discussion, Structure and dynamics of van der Waals complexes: Faraday Disc. Chem. Soc. **97** (1994)

[66] Western, C.M.: Chem. Soc. Rev. **24** (1995) 299

[67] Stone, A.J.: The theory of intermolecular forces, Oxford Univ. Press, Oxford, 1996

[68] Moszynski, R., Wormer, P.E.S., Jeziorski, B., van der Avoird, A.: J. Chem. Phys. **103** (1995) 8058; J. Chem. Phys. **107** (1997) 672

[69] Moszynski, R., Heijmen, T.G.A., Wormer, P.E.S., van der Avoird, A.: Advan. Quant. Chem. **28** (1997) 119

[70] Laane, J.: Ann. Rev. Phys. Chem. **45** (1994) 179

[71] Gans, P.: Data fitting in the chemical sciences, Wiley, Chichester, 1992

[72] European Community Workshop: Calculations of PESs, Rosmus, P. (Ref.), Champagne, France, 1995

[73] Bowen, J.P., Allinger, N.L. in: Reviews in Computational Chemistry, Lipkowitz, K.B, Boyd, D.B. (Eds.), **2** (1991) 81, VCH, New York

[74] Kast, S.M., Brickmann, J., Berry, R.S. in: Conceptual Trends in Quantum Chemistry, Kryachko, E.S, Calais, J.L. (Eds.), **3**, Kluwer, Dordrecht, 1997

[75] Deumens, E., Diz, A., Longo, R., Öhrn, Y.: Rev. Mod. Phys. **66** (1994) 917

[76] Öhrn, Y., Oreiro, J., Deumens, E.: Int. J. Quant. Chem. **58** (1996) 583

[77] Car, R., Parinello, M.: Phys. Rev. Lett. **55** (1985) 2471

[78] Tuckerman, M.E., Ungar, P.J., von Rosenvinge, T., Klein, M.: J. Phys. Chem. **100** (1996) 12878

[79] Forsythe, G.E., Malcolm, M.A., Moler, C.B.: Computer methods, for mathematical computations, Prentice-Hall, New York, 1977

[80] Press, W.H., Teukolsky, S.A., Vetterling, W.T., Flannery, B.P.: Numerical Recipes: The Art of Scientific Computing, Cambridge Univ. Press, Cambridge, 1992

[81] Daniel, C., Wood, F.S.: Fitting equations to data, Wiley, New York, 1980

[82] Engeln-Müllges, G., Reutter, F.: Numerische Mathematik für Ingenieure, BI, Zürich, 1987

[83] Bronstein, I.N., Semendjajew, K.A., Musiol, G., Mühlig, H.: Taschenbuch der Mathematik, Teubner, Stuttgart, 1993

[84] Akima, H.: Commun. Assoc. Comput. Mach. **17** (1974) 18; **17** (1974) 26

[85] Akima, H.: ACM transactions on Mathematical Software **4** (1978) 148; **4** (1978) 160; **5** (1979) 242

[86] Upadhayay, S.K., Sathyamurthy, N.: Chem. Phys. Lett. **92** (1982) 631

[87] Malik, D.J., Eccles, J., Secrest, D.: J. Comput. Phys. **38** (1980) 157

[88] Tornow, V.: Comput. Phys. Commun. **28** (1982) 61

[89] Sathyamurthy, N., Raff, L.M.: J. Chem. Phys. **63** (1975) 464

[90] Gray, S.K., Wright, J.S.: J. Chem. Phys. **66** (1977) 2867

[91] Gray, S.K., Wright, J.S.: J. Chem. Phys. **68** (1978) 2002

[92] Dunham, J.L.: Phys. Rev. **41** 713;721

[93] Simons, G., Parr, RG., Finlan, J.M.: J. Chem. Phys. **59** (1973) 3229

[94] Ogilvie, J.F.: Proc. R. Soc. London Ser. A **378** (1981) 287

[95] Thakkar, A.J.: J. Chem. Phys. **62** (1975) 1693

[96] Huffaker, J.N.: J. Chem. Phys. **64** (1976) 3175

[97] Beckel, C.L., Engelke, R.: J. Chem. Phys. **49** (1968) 5199

[98] Beckel, C.L.: J. Chem. Phys. **65** (1976) 4319

[99] Burton, P.G., von Nagy-Felsobuki, E.I., Doherty, G., Hamilton, M.: Mol. Phys. **55** (1985) 527

[100] Coolidge, A.S., James, H.M., Vernon, E.L.: Phys. Rev. **54** (1938) 726

[101] Meyer, W., Botschwina, P., Burton, P.G.: J. Chem. Phys. **84** (1986) 891

[102] Searles, D.J., Dunne, SJ., von Nagy-Felsobuki, E.I.: Spect. Acta. A **44** (1988) 505

[103] Murrell, J.N., Varandas, A.J.C., Brandao, J.: Theor. Chim. Acta. **71** (1987) 459

[104] Murrell, J.N.: Mol. Phys. **62** (1987) 1403

[105] Downing, J.W., Michl, J., Cizek, J., Paldus, J.: Chem. Phys. Lett. **67** (1979) 377

[106] Bunker, P.R., Knowles, D.B., Schürmann, B., Buenker, R.J.: Chem. Phys. Lett. **139** (1987) 159

[107] Sato, S.: J. Chem. Phys. **23** (1955) 592; 2465

[108] Ellison, F.O.: J. Am. Chem. Soc. **85** (1963) 3540

[109] Sorbie, K.S., Murrell, J.N.: Mol. Phys. **29** (1975) 1387

[110] Farantos, S., Leisegang, EC., Murrell, J.N., Sorbie, K., Texeira-Dias, J.J.C., Varandas, A.J.C.: Mol. Phys. **34** (1977) 947

[111] Carter, S., Mills, I.M., Murrell, J.N., Varandas, A.J.C.: Mol. Phys. **45** (1982) 1053

[112] Murrell, J.N., Craven, W., Vincent, M., Zhu, Z.H.: Mol. Phys. **56** (1985) 839

[113] Schinke, R.: J. Chem. Phys. **80** (1984) 5510

[114] Joseph, T., Sathyamurthy, N.: J. Chem. Phys. **86** (1987) 704

[115] Aguado, A., Paniagua, M.: J. Chem. Phys. **96** (1992) 1265

[116] Garcia, E., Lagana, A.: Mol. Phys. **52** (1984) 1115

[117] Varandas, A.J.C., Murrell, J.N.: Faraday Disc. Chem. Soc. **62** (1977) 92

[118] Nager, C., Jungen, M.: Chem. Phys. **70** (1982) 189

[119] Thareja, S., Sathyamurthy, N.: quoted as Ref. 111 in [20]

[120] Brown, P.J., Hayes, E.F.: J. Chem. Phys. **55** (1971) 922

[121] Kuntz, P.J., Roach, A.C.: J. Chem. Soc. Faraday Trans. 2 **68** (1972) 259

[122] Kuntz, P.J.: Chem. Phys. Lett. **16** (1972) 581

[123] Urban, J., Jaquet, R., Staemmler, V.: Int. J. Quant. Chem. **38** (1990) 339

[124] Urban, J., Klimo, V., Staemmler, V., Jaquet, R.: Z. Phys. D. **21** (1991) 329

[125] Pendergast, P., Heck, J.M., Hayes, E.F., Jaquet, R.: J. Chem. Phys. **98** (1993) 4543

[126] Jaquet, R.: Theor. Chim. Acta. **88** (1994) 217

[127] Varandas, A.J.C., da Silva, J.D.: J. Chem. Soc. Faraday Trans. **88** (1992) 941

[128] Aguado, A., Suárez, C., Paniagua, M.: J. Chem. Phys. **101** (1994) 4004

[129] Saint-Martin, H., Medina-Llanos, C., Ortega-Blake, I.: J. Chem. Phys. **93** (1990) 6448

[130] Moszynski, R., Wormer, P.E.S., Heijmen, T.G.A., van der Avoird, A.: J. Chem. Phys. **108** (1998) 579

[131] Russek, A., Garcia, G.R.: Phys. Rev. A. **26** (1982) 1924

[132] Corchado, J.C., Espinosa-Garcia, J.: J. Phys. Chem. **106** (1997) 4013

[133] Aguado, A., Paniagua, M., Lara, M., Roncero, O.: J. Chem. Phys. **106** (1997) 1013

[134] Álvarez-Collado, J.R., Aguado, A., Paniagua, M.: J. Chem. Phys. **102** (1995) 5725

[135] Sumpter, B.G., Noid, D.W.: Chem. Phys. Lett. **192** (1992) 455

[136] Blank, T.B., Brown, S.D., Calhoun, A.W., Doren, D.J.: J. Chem. Phys. **103** (1995) 4129

[137] Rossi, I., Truhlar, D.G.: Chem. Phys. Lett. **233** (1995) 231

[138] Ischtwan, J., Collins, M.A.: J. Chem. Phys. **100** (1994) 8080

[139] Jordan, M.J.T., Thompson, K.C., Collins, M.A.: J. Chem. Phys. **102** (1995) 5647

[140] Jordan, M.J.T., Thompson, K.C., Collins, M.A.: J. Chem. Phys. **103** (1995) 9669

[141] Ischtwan, J., Schwerdtfeger, P., Peyerimhoff, S.D., Collins, M.A., Helgaker, T., Jørgensen, P., Jensen, H.J.A.: Theor. Chim. Acta. **89** (1994) 157

[142] Corchado, J.C., Espinosa-Garcia, J., Hu, W.P., Rossi, I., Truhlar, D.G.: J. Phys. Chem. **99** (1994) 687

[143] Chuang, Y.Y., Truhlar, D.G.: J. Phys. Chem. **101** (1997) 3808

[144] Downing, J.W., Michl, J. in: Potential Energy Surfaces and Dynamics Calculations, Truhlar, D.G. (Ed.), p. 199, Plenum, New York, 1981

[145] Suhm, M.A.: Chem. Phys. Lett. **214** (1993) 373

[146] Suhm, M.A.: Chem. Phys. Lett. **223** (1994) 474

[147] Ho, T.S., Rabitz, H.: J. Chem. Phys. **104** (1996) 2584

[148] Ho, T.S., Hollebeek, T., Rabitz, H., Harding, L.B., Schatz, G.C.: J. Chem. Phys. **105** (1996) 10472

[149] Hollebeek, T., Ho, TS., Rabitz, H.: J. Chem. Phys. **106** (1997) 7223

[150] Kendall, M.G., Stuart, A.: The Advanced Theory of Statistics, Griffin, London, 1979

[151] Engelke, R.: J. Chem. Phys. **68** (1978) 3514; **70** (1978) 3745

[152] Mattera, L., Salvo, C., Terreni, S., Tommasini, F.: J. Chem. Phys. **72** (1980) 6815; Surf. Sci. **97** (1988) 158

[153] Surkus, A.A., Rakauskas, R.J., Bolotin, A.B.: Chem. Phys. Lett. **105** (1984) 291

[154] Lennard-Jones, J.E.: Proc. Roy. Soc. A. **106** (1924) 463

[155] Hirschfelder, J.O., Curtiss, C.F., Bird, R.B.: Molecular Theory of gases and Liquids, p. 32, Wiley, New York, 1964

[156] Morse, P.M.: Phys. Rev. **34** (1929) 57

[157] Varshni, Y.P.: Rev. Mod. Phys. **29** (1957) 664; **31** (1959) 839

[158] Hepburn, J., Scoles, G., Penco, R.: Chem. Phys. Lett. **36** (1975) 451

[159] Ahlrichs, R., Penco, R., Scoles, G.: Chem. Phys. **19** (1977) 119

[160] Tang, K.T., Toennies, J.P.: J. Chem. Phys. **66** (1977) 1496; **68** (1978) 786 (E); **68** (1978) 5501

[161] Tang, K.T., Toennies, J.P.: Z. Phys. D. **1** (1986) 91

[162] Mansky, E.J., Flannery, M.R.: J. Chem. Phys. **99** (1993) 1962

[163] Meath, W.J., Margoliash, D.J., Jhanwar, B.L., Koide, A., Zeiss, G.D. in: Intermolecular Forces, Pullman, B. (Ed.), p. 101, Reidel, Dordrecht, 1981

[164] Hulbert, H.M., Hirschfelder, J.O.: J. Chem. Phys. **9** (1941) 61

[165] Schubert, J.G., Certain, P.R.: unpublished, cited in: Herbst, E.: Chem. Phys. Lett. **47** (1977) 517

[166] Kafri, O., Berry, M.J.: Faraday Disc. Chem. Soc. **62** (1977) 127

[167] Kafri, O.: Chem. Phys. Lett. **61** (1979) 538

[168] Navati, B.S., Korwar, V.M.: Pramana **20** (1983) 457

[169] Murrell, J.N., Sorbie, K.S.: J. Chem. Soc. Faraday Trans. II **70** (1974) 1552

[170] Ref. 82 – 90 in [20]

[171] Hall, G.G.: Theor. Chim. Acta. **67** (1985) 439

[172] Hall, G.G., Okada, M.: J. Mol. Struct. Theochem. **123** (1985) 179

[173] Swalen, J.D., Ibers, J.A.: J. Chem. Phys. **36** (1962) 1914

[174] Wicke, B.G., Harlis, D.O.: J. Chem. Phys. **64** (1976) 5236

[175] Huffacker, J.N.: J. Chem. Phys. **74** (1981) 1217

[176] Eaker, C.W., Parr, C.A.: J. Chem. Phys. **64** (1976) 1322

[177] Jordan, R.M., Siska, P.E.: J. Chem. Phys. **80** (1984) 5027

[178] Chapman, S., Dupuis, M., Green, S.: Chem. Phys. **78** (1983) 93

[179] Pedersen, L., Porter, R.N.: J. Chem. Phys. **47** (1967) 4751

[180] Berces, T.: React. Kinet. Catal. Lett. **7** (1977) 379

[181] Varandas, A.J.C., Brandao, J.: Mol. Phys. **45** (1982) 857

[182] Duan, X., Scheiner, S.: J. Mol. Spectr. **270** (1992) 173

[183] Jordan, K.D.: Chem. Phys. **9** (1975) 199

[184] Jonas, R., Staemmler, V.: Z, Phys, D **14** (1989) 143

[185] Kolczewski, C., Fink, K., Staemmler, V., Neitsch, L.: J. Chem. Phys. **106** (1997) 7637

[186] Meyer, W., Hariharan, P.C., Kutzelnigg, W.: J. Chem. Phys. **73** (1980) 1880

[187] Parker, G.A., Snow, R.L., Pack, R.T.: Chem. Phys. Lett. **33** (1975) 399

[188] Schagen, I.P.: J. Inst. Math. Appl. **23** (1979) 53; Int. J. Comput. Math. Sec. B **8** (1980) 63

[189] Ewing, T.F., Detrich, J., Conn, R.W.: J. Chem. Phys. **69** (1978) 4662

[190] Loesch, H.J.: Adv. Chem. Phys. **XLIII** (1980) 421

[191] Gordon, R.G., Kim, Y.S.: J. Chem. Phys. **56** (1972) 3122

[192] van Hemert, M.C.: Intermolecular Forces, Pullman, B. (Ed.), p. 161, Reidel, Dordrecht, 1981

[193] Jaquet, R., Staemmler, V.: Chem. Phys. **101** (1986) 243

[194] Dougheny, E., Rabitz, H., Detrich, J., Conn, RW.: J. Chem. Phys. **67** (1977) 4742

[195] Bienich, R.J., Green, S.: Chem. Phys. Lett. **84** (1981) 380

[196] Moszynski, R., Korona, T., Wormer, P.E.S., van der Avoird, A.: J. Chem. Phys. **103** (1995) 321

[197] Heijmen, T.G.A., Moszynski, R., Wormer, P.E.S., van der Avoird, A.: J. Chem. Phys. **107** (1997) 9921

[198] Moszynski, R., Korona, T., Wormer, P.E.S., van der Avoird, A.: J. Phys. Chem. **101** (1997) 4690

[199] Schröder, K., Staemmler, V., Jaquet, R., Smith, M.D., Flower, D.: (1991) J. Phys. B: At. Mol. Opt. Phys. **24** (1991) 2487

[200] Jaquet, R., Staemmler, V., Smith, M.D., Flower, D.R,: J. Phys. B: At. Mol. Opt. Phys. **25** (1992) 285

[201] Huang, S.S., Bieler, C.R., Janda, K.C., Tao, F.M., Klemperer, W., Casavecchia, P., Volpi, G., Halberstadt, N.: J. Chem. Phys. **102** (1995) 8846

[202] Bissonette, C., Chuaqui, C.E., Crowell, KG., LeRoy, R.J.: J. Chem. Phys. **105** (1996) 2639

[203] Bowman, J.M., Gazdy, B., Bentley, J.A., Lee, TJ., Dateo, CE.: J. Chem. Phys. **99** (1993) 308

[204] Lotrich, V.F., Williams, H.L., Szalewicz, K., Jeziorski, B., Moszynski, R., Wormer, P.E.S., van der Avoird, A.: J. Chem. Phys. **103** (1995) 6076

[205] Röhse, R., Kutzelnigg, W., Jaquet, R., Klopper, W.: J. Chem. Phys. **101** (1994) 2231

[206] Kedziora, G.S., Shavitt, I.: J. Chem. Phys. **106** (1997) 8733

[207] Partridge, H., Schwenke, D.W.: J. Chem. Phys. **106** (1997) 4618

[208] Polyansky, O.L., Jensen, P., Tennyson, J.: J. Chem. Phys. **101** (1994) 7651

[209] Polyansky, O.L., Jensen, P., Tennyson, J.: J. Chem. Phys. **105** (1996) 6490

[210] Schneider, F., Jeziorek, D., Kejna, A,, Zurawski, B.: Int. J. Quant. Chem. **28** (1985) 921

[211] Bush, A.M., Wright, T.G., Spirko, V., Jurek, M.: J. Chem. Phys. **106** (1997) 4531

[212] Gianturco, F.A., Kumar, S., Pathak, S.K., Raimondi, M., Sironi, M., Gerratt, J., Cooper, D.L.: Chem. Phys. **215** (1997) 227; 239

[213] Garrison, B.J., Lester, W.A, Jr., Siegbahn, P., Schaefer, III, H.F.: J. Chem. Phys. **63** (1975) 4167

[214] Green, S.: J. Chem. Phys. **64** (1976) 3463

[215] Clary, D.C.: Chem. Phys. **65** (1982) 247

[216] Billing, G.D., Clary, D.C.: Chem. Phys. **80** (1983) 213

[217] Billing, G.D.: Chem. Phys. **76** (1983) 315

[218] Green, S.: J. Chem. Phys. **67** (1977) 715

[219] Flower, D.R., Launay, J.M., Kochanski, E., Prissette, J.: Chem. Phys. **37** (1979) 355

[220] Berns, R.M., van der Avoird, A.: J. Chem. Phys. **72** (1980) 6107

[221] Shukla, C.P., Bachhawat, A.K., Sathyamurthy, N.: Chem. Phys. **70** (1982) 83

[222] Welker, M., Steinebrunner, G., Solca, J., Huber, H.: Chem. Phys. **213** (1996) 253

[223] van der Avoird, A., Brocks, G.: J. Chem. Phys. **87** (1987) 5346

[224] Buckingham, A.D.: Adv. Chem. Phys. **12** (1967) 107

[225] Poulson, L.L.: Chem. Phys. **68** (1968) 29

[226] Schinke, R., Meyer, M., Buck, U., Diercksen, G.H.F.: J. Chem. Phys. **80** (1984) 5518

[227] van der Pol, A., van der Avoird, A., Wormer, P.E.S.: J. Chem. Phys. **92** (1990) 7498

[228] Miller, S.M., Clary, D.C.: J. Chem. Phys. **98** (1993) 1843

[229] van der Avoird, A.: Topics in Curr. Chem. **93** (1980) 1

[230] Schwenke, D.W., Truhlar, D.G.: J. Chem. Phys. **88** (1988) 4800

[231] Billing, G.D., Kolesnick, R.R.: Chem. Phys. Lett. **200** (1992) 382

[232] Varandas, A.J.C., Pais, A.A.C.C. in: Theoretical and computational models for organic chemistry, Formosinho, S.J., Czismadia, I.G., Arnaut, L.G. (Eds.), p. 55, Kluwer, Dordrecht, 1991

[233] Rigby, M., Smith, E.B., Wakeham, W.A., Maitland, G.C.: The forces between molecules, Oxford Univ. Press, Oxford, 1986

[234] Rijks, W., Wormer, P.E.S.: J. Chem. Phys. **90** (1989) 5607

[235] Redmon, M.J., Binkley, J.S.: J. Chem. Phys. **87** (1987) 969

[236] Hancock, G.C., Truhlar, D.G., Dykstra, CE.: J. Chem. Phys. **88** (1988) 1786

[237] Klopper, W., Schutz, M., Lüthi, H.P., Leutwyler, S.: J. Chem. Phys. **103** (1995) 1085

[238] Engkvist, O., Forsberg, N., Schütz, M., Karström, G.. Mol. Phys. **90** (1997) 277

[239] Bersohn, R., Shapiro, M.: J. Chem. Phys. **85** (1986) 1396

[240] Ramaswamy, R.: PhD thesis, Princeton University, 1977

[241] Schaefer, J., Meyer, W.: J. Chem. Phys. **70** (1979) 344

[242] Bunker, P.R., Epa, V.C., Jensen, P., Karpfen, A.: J. Mol. Spectr. **146** (1991) 200

[243] Elrod, M.J., Saykally, R.J.: J. Chem. Phys. **103** (1995) 933

[244] Qiu, Y., Bacic, Z.: J. Chem. Phys. **106** (1997) 2158

[245] Buckingham, A.D., Fowler, P.W., Hutson, J.M.: Chem. Rev. **88** (1988) 963

[246] Smit, P.H., Derissen, J.L., van Duijneveld, F.B.M.: Mol. Phys. **37** (1979) 521

[247] van der Avoird, A.: J. Chem. Phys. **98** (1993) 5327

[248] Palma, A. in: Dynamical processes in molecular physics, Delgado-Barrio, G. (Ed.), p. 29, IOP, 1991

[249] Zhang, Q., Chenyang, L., Ma, Y., Fish, F., Szczesniak, M.M., Buch, V.: J. Chem. Phys. **96** (1992) 6039

[250] Yang, M., Alexander, M.H., Werner, H.-J., Bemish, R.J.: J. Chem. Phys. **105** (1996) 10462

[251] Pack, R.T., Piper, E., Pfeffer, G.A., Toennies, J.P.: J. Chem. Phys. **80** (1984) 4940

[252] Heijmen, T.G.A., Korona, T., Moszynski, R., Wormer, P.E.S., van der Avoird, +584 A.: J. Chem. Phys. **107** (1997) 902

[253] Moszynski, R., Wormer, P.E.S., van der Avoird, A.: J. Chem. Phys. **102** (1995) 8385

[254] Porter, R.N., Karplus, M.: J. Chem. Phys. **40** (1964) 1105

[255] Siegbahn, P., Liu, B.: J. Chem. Phys. **68** (1978) 2457

[256] Truhlar, D.G., Horowitz, C.J.: J. Chem. Phys. **68** (1978) 2466; **71** (1979) 1514 (E)

[257] Varandas, A.J.C., Brown, FB., Mead, C.A., Truhlar, D.G., Blais, N.C.: J. Chem. Phys. **86** (1987) 6258

[258] Peng, Z.W., Kristyan, S., Kuppermann, A., Wright, J.S.: Phys. Rev. A. **52** (1995) 1005

[259] Porter, R.N., Stevens, R.M., Karplus, M.: J. Chem. Phys. **49** (1968) 5163

[260] Truhlar, D.G., Wyatt, R.E.: Adv. Chem. Phys. **36** (1977) 141

[261] London, F.: Z. Electrochem. **35** (1929) 552

[262] Polanyi, J.C.: J. Quant. Spect. Rad. Trans. **3** (1963) 471

[263] Polanyi, J.C., Schreiber, J.L.: Chem. Phys. Lett. **29** (1974) 319

[264] Gauss, A., Jr.: Chem. Phys. Lett. **52** (1977) 252

[265] Allison, T.C., Lynch, G.C., Truhlar, D.G., Gordon, M.S.: J. Phys. Chem. **100** (1996) 13575; 13588

[266] Last, I., Baer, M.: Int. J. Quant. Chem. **29** (1986) 1067

[267] Kuntz, P.J. in: The Concept of the Chemical Bond, Maksic, ZB. (Ed.), p. 321, Springer, Berlin, 1990

[268] Polak, R., Paidarova, I., Kuntz, P.J.: Int. J. Quant. Chem. **62** (1997) 659

[269] Kendrick, B., Pack, R.T.: J. Chem. Phys. **102** (1995) 1994

[270] Naumkin, F.Y., Knowles, P.J., Murrell, J.N.: Chem. Phys. P**93** (1995) 27

[271] Sathyamurthy, N., Duff, J.W., Stroud, C., Raff, L.M.: J. Chem. Phys. **67** (1977) 3563

[272] Stroud, C., Raff, L.M.: Chem. Phys. **46** (1980) 313

[273] Connor, J.N.L., Jakubetz, W., Manz, J.: Mol. Phys. **29** (1975) 347

[274] Wall, F.T., Porter, R.N.: J. Chem. Phys. **36** (1962) 3256

[275] Truhlar, D.G., Kuppermann, A.: J. Chem. Phys. **52** (1970) 3841; **56** (1972) 2232

[276] Bowman, J.M., Kuppermann, A.: Chem. Phys. Lett. **34** (1975) 523

[277] Jakubetz, W., Connor, J.N.L.: Faraday Disc. Chem. Soc. **62** (1977) 140

[278] Jakubetz, W.: Chem. Phys. **35** (1978) 141

[279] Maierle, C.S., Schatz, G.C., Gordon, M.S., Mccabe, P., Connor, J.N.L.: J. Chem. Soc. Faraday Trans. **93** (1997) 709

[280] Schinke, R, Lester, W.A, Jr.: J. Chem. Phys. **70** (1979) 4893; **72** (1980) 6821 (E)

[281] Redmon, M.J., Schatz, G.C.: Chem. Phys. **54** (1981) 365

[282] Schinke, R., Lester, W.A, Jr.: J. Chem. Phys. **72** (1980) 3754

[283] Schinke, R., Dupuis, M., Lester, W.A, Jr.: J. Chem. Phys. **72** (1980) 3909

[284] Schinke, R.: J. Chem. Phys. **72** (1980) 3916

[285] Carter, S., Murrell, J.N.: Mol. Phys. **41** (1980) 567

[286] Gittins, M.A., Hirst, D.M., Guest, M.F.: Faraday Disc. Chem. Soc. **62** (1977) 7

[287] Herbst, E.: Chem. Phys. Lett. **47** (1977) 517

[288] Joseph, T., Sathyamurthy, N.: J. Chem. Phys. **86** (1987) 704

[289] Murrell, J.N., Farantos, S.M.: Mol. Phys. **34** (1977) 1185

[290] Wagner, A.F., Schatz, G.C., Bowman, J.M.: J. Chem. Phys. **74** (1981) 4960

[291] Schatz, G.C., Wagner, A.F., Walch, S.P., Bowman, J.M.: J. Chem. Phys. **74** (1981) 4984

[292] Salazar, M.R., Simons, J.: J. Chem. Phys. **105** (1996) 10919

[293] de Lara-Castells, M.P., Villarreal, P., Delgado-Barrio, G., Miret-Artés, S., Buonomo, E., Gianturco, F.A.: Chem. Phys. Lett. **242** (1995) 336

[294] Buonomo, E., Gianturco, F.A., de Lara-Castells, M.P., Delgado-Barrio, G., Miret-Artés, S.,Villarreal, P.: J. Chem. Phys. **106** (1997) 1718

[295] Aguado, A., Sanz, V., Paniagua, M.: Int. J. Quant. Chem. **61** (1997) 491

[296] Varandas, A.J.C.: J. Chem. Phys. **70** (1979) 3786

[297] Giese, C.F., Gentry, W.R.: Phys. Rev. A. **10** (1974) 2156

[298] Ichihara, A., Yokoyama, K.: J. Chem. Phys. **103** (1995) 2109

[299] Prosmiti, R., Polyansky, O.L., Tennyson, J.: Chem. Phys. Lett. **273** (1997) 107

[300] Starck, J., Meyer, W.: Chem. Phys. **176** (1993) 83

[301] Aguado, A., Suárez, C., Paniagua, M.: J. Chem. Phys. **98** (1993) 308

[302] Hopper, D.G.: J. Chem. Phys. **80** (1984) 4290

[303] Wormer, P.E.S., de Groot, F.: J. Chem. Phys. **90** (1989) 2344

[304] Kuppermann, A.: J. Phys. Chem. **100** (1996) 2621

[305] Köppel, H.: Z. Phys. Chem. **200** (1997) 3

[306] Klessinger, M.: Angew. Chem. Int. Ed. Engl. **34** (1995) 549

[307] Bernardi, F., Olivucci, M., Robb, M.A.: Chem. Soc. Rev. **25** (1996) 321

[308] Xantheas, S.S., Atchity, G.J., Elbert, S.T., Ruedenberg, K.: J. Chem. Phys. **94** (1991) 8054

[309] Atchity, G.J., Ruedenberg, K.: Theor. Chem. Acc. **96** (1997) 176

[310] Ivanic, J., Atchity, G.J., Ruedenberg, K.: J. Chem. Phys. **107** (1997) 4307

[311] Atchity, G.J., Xantheas, S.S., Ruedenberg, K.: J. Chem. Phys. **95** (1991) 1862

[312] Valtazanos, P., Elbert, S.T., Xantheas, S., Ruedenberg, K.: Theor. Chim. Acta. **78** (1991) 287

[313] Valtazanos, P., Ruedenberg, K.: Theor. Chim. Acta. **78** (1991) 397

[314] Xantheas, S.S., Valtazanos, P., Ruedenberg, K.: Theor. Chim. Acta. **78** (1991) 327

[315] Xantheas, S.S., Elbert, S.T., Ruedenberg, K.: Theor. Chim. Acta. **78** (1991) 365

[316] Atchity, G.J., Ruedenberg, K.: Theor. Chem. Acc. **96** (1997) 205

[317] Atchity, G.J., Ruedenberg, K.: J. Chem. Phys. **99** (1993) 3790

[318] Atchity, G.J., Ruedenberg, K.: Theor. Chem. Acc. **97** (1997) 47

[319] Murrell, J.N., Carter, S., Mills, I.M., Guest, M.F.: Mol. Phys. **42** (1981) 605

[320] Knowles, P.J., Handy, N.C., Carter, S.: Mol. Phys. **49** (1983) 681

[321] Murrell, J.N., Dunne, L.J.: Chem. Phys. Lett. **102** (1983) 155

[322] Varandas, A.J.C. in: Dynamical processes in molecular physics, Delgado-Barrio, G. (Ed.), p. 3, IOP, 1991

[323] Allison, T.C., Mielke, S.L., Schwenke, D.W., Truhlar, D.G.: J. Chem. Soc. Faraday Trans. **93** (1997) 825

[324] Woywod, C., Domcke, W., Sobolewski, A.L., Werner, H.J.: J. Chem. Phys. **100** (1994) 1400

[325] Müller, H., Köppel, H.: Chem. Phys. **183** (1994) 107

[326] Müller, H., Köppel, H., Cederbaum, L.S.: J. Chem. Phys. **101** (1994) 10263

[327] Köppel, H.: Chem. Phys. Lett. **205** (1993) 361

[328] Leonardi, E., Petrongolo, C., Hirsch, G., Buenker, R.J.: J. Chem. Phys. **105** (1996) 9051

[329] Loettgers, A., Untch, A., Keller., H.M., Schinke, R., Werner, H.J., Bauer, C., Rosmus, P.: J. Chem. Phys. **106** (1997) 3186

[330] Keller, H.M., Floethman, H., Dobbyn, A.J., Schinke, R., Werner, H.J., Bauer, C., Rosmus, P.: J. Chem. Phys. **105** (1996) 4983

[331] Engel, V., Staemmler, V., van der Wal, RL., Crim, FF., Sension, R.J., Hudson, B., Andresen, P., Hennig, S., Weide, K., Schinke, E.: J. Chem. Phys. **96** (1992) 3201

[332] Leforestier, C., LeQuere, F., Yamashita, K., Morokuma, K.: J. Chem. Phys. **101** (1994) 3806

[333] Brown, S.S., Cheatum, C.M., Fitzwater, D.A., Crim, F.F.: J. Chem. Phys. **105** (1996) 10911

[334] Schatz, G.C., Elgersma, H.: Chem. Phys. Lett. **73** (1980) 21

[335] Clary, D.C.: J. Chem. Phys. **95** (1991) 7298

[336] Isaacson, A.D.in: The Reaction Path in Chemistry: Current Approaches and Perspectives, Heidrich, D. (Ed.), p. 191, Kluwer, Dordrecht, 1995

[337] Eaker, C.W., Schatz, G.C.: J. Phys. Chem. **89** (1985) 2612

[338] Kudla, K., Schatz, G.C., Wagner, A.F.: J. Chem. Phys. **95** (1991) 1635

[339] Sun, Q., Bowman, J.M.: J. Chem. Phys. **92** (1990) 5201

[340] ter Horst, M.A., Schatz, G.C., Harding, L.B.: J. Chem. Phys. **105** (1996) 588

[341] Takayanagi, T., Schatz, GC.: Chem. Phys. Lett. **265** (1997) 410

[342] Starr, T.L., Williams, D.E.: J. Chem. Phys. **66** (1977) 2054

[343] Schmuttenmaer, C.A., Cohen, R.C., Saykally, R.J.: J. Chem. Phys. **101** (1994) 146

[344] van de Linde, S.R., Hase, W.L.: J. Phys. Chem. **94** (1990) 2778

[345] Clary, D.C., Palma, J.: J. Chem. Phys. **106** (1997) 575

[346] McLaughlin, D.R., Thompson, D.L.: J. Chem. Phys. **59** (1973) 4393

[347] Sathyamurthy, N., Rangaryan, R., Raff, L.M.: J. Chem. Phys. **64** (1976) 4606

[348] Sathyamurthy, N.: Chem. Phys. Lett. **59** (1978) 95

[349] Schor, H., Chapman, S., Green, S., Zare, R.N.: J. Chem. Phys. **69** (1978) 3790; J. Chem. Phys. **83** (1979) 920

[350] NoorBatcha, L., Sathyamurthy, N.: J. Chem. Phys. **76** (1982) 6447

[351] Cencek, W., Rychlewski, J., Jaquet, R., Kutzelnigg, W.: J. Chem. Phys. **108** (1998) 2831

[352] Jaquet, R., Cencek, W., Rychlewski, J., Kutzelnigg, W.: J. Chem. Phys. **108** (1998) 2837

[353] Frishman, A., Hoffman, D.K., Kouri, D.J.: J. Chem. Phys. **107** (1997) 804

[354] Galvan, D.H., Abu-Jafar, M., Sanders, F.C.: J. Chem. Phys. **102** (1995) 4919

[355] Warken, M.: private communication, markus@kirk.chemie.hu-berlin.de

[356] Eggenberger, R., Gerber, S., Huber, H., Welker, M.: Mol. Phys. **82** (1993) 689

[357] Eggenberger, R., Huber, H., Welker, M.: Chem. Phys. **187** (1994) 317

[358] Ermakova, E., Solca, J., Huber, H., Welker, M.: J. Chem. Phys. **102** (1994) 4942

[359] Schindler, H., Vogelsang, R., Staemmler, V., Siddiqi, M.A., Svejda, P.: Mol. Phys. **80** (1993) 1413

[360] Kölmel, C., Ahlrichs, R., Karch, B.: Mol. Phys. **66** (1989) 1015

[361] Sagarik, K.P., Ahlrichs, R., Brode, S.: Mol. Phys. **57** (1986) 1247

[362] Böhm, H.J., Ahlrichs, R.: Mol. Phys. **55** (1985) 1159

[363] Böhm, H.J., Ahlrichs, R., Scharf, P., Schiffer, H.: J. Chem. Phys. **81** (1984) 1389

[364] Clementi, E., Corongui, G., Bahattacharya, D., Feuston, B., Frye, D., Preiskorn, A., Rizzo, A., Xue, X.: Chem. Rev. **91** (1991) 679

[365] Bunker, P.R., Kofranek, M., Lischka, H., Karpfen, A.: J. Chem. Phys. **89** (1988) 3002

[366] Bunker, P.R., Carrington, T.J., Gomez, PC., Marshall, M.D., Kofranek, M., Lischka, H., Karpfen, A.: J. Chem. Phys. **91** (1989) 5154

[367] Quack, M., Suhm, M.A.: Mol. Phys. **69** (1990) 791

[368] Murrell, J.N., Mottram, R.E.: Mol. Phys. **69** (1990) 571

[369] Murrell, J.N., Rodriguez-Ruiz, J.A.: Mol. Phys. **71** (1990) 823

[370] Kaufman, J.J. in: Molecules in Physics, Chemistry and Biology, Maruani, J. (Ed.), **2** (1988) 563, Kluwer, Dordrecht

[371] van der Avoird, A. in: The Concept of the Chemical Bond, Maksic, Z.B. (Ed.), p. 391 Springer, Berlin, 1990

[372] Luty, T., van der Avoird, A., Berns, R.M.: J. Chem. Phys. **73** (1980) 5305

[373] Jacox, M.E., Thompson, W.E.: J. Chem. Phys. **100** (1994) 750

[374] Shalabi, A.S.: Chem. Phys. **156** (1991) 359

[375] Wang, Y., Gunn, J.R.: J. Chem. Phys. **106** (1997) 3248

[376] Garrison, B.J., Srivastava, D.: Ann. Rev. Phys. Chem. **46** (1995) 373

[377] Wiesenekker, G., Kroes, G.J., Baerends, E.J.: J. Chem. Phys. **104** (1996) 7344

[378] Sellers, H.: J. Chem. Phys. **98** (1993) 627

[379] Becker, O.M., Karplus, M.: J. Chem. Phys. **106** (1997) 1495

[380] Battaglia, F., Gianturco, F.A., Casavecchia, P., Pirani, F., Vecchiocattivi, F.: Faraday Disc. Chem. Soc. **73** (1982) 257

[381] Beneventi, L., Casavecchia, P., Volpi, G.G., Wong, C.C.K., McCourt, F.R.W.: J. Chem. Phys. **98** (1993) 7926

[382] Toennies., J.P. in: Physical Chemistry: An Advanced Treatise, Eyring, H., Henderson., D., Jost., W. (Eds.), **6A** (1974) 227, Academic Press, New York

[383] Dinelli, B.M., Polyansky, O.L., Tennyson, J.: J. Chem. Phys. **103** (1995) 10433

[384] Tiemann, E., Ogilvie, J.F.: J. Mol. Spectr. **165** (1994) 377

[385] Moss, R.E.: Mol. Phys. **89** (1996) 195

[386] Ogilvie, J.F.: Ber. Bunsenges. Phys. Chem. **100** (1996) 1906

[387] Ogilvie, J.F.: Chem. Phys. Lett. **267** (1997) 590

[388] Hutson, J.M.: Ann. Rev. Phys. Chem. **41** (1990) 123

[389] Nesbitt, D.J., Child, M.S., Clary, D.C.: J. Chem. Phys. **90** (1989) 4855

[390] Slee, T., LeRoy, R.J., Chuaqui, C.: Mol. Phys. **77** (1992) 111

[391] Slee, T., LeRoy, R.J.: J. Chem. Phys. **99** (1993) 360

[392] LeRoy, R.J., Hutson, J.M.: J. Chem. Phys. **86** (1987) 837

[393] LeRoy, R.J., Bissonnette, C., Wu, T.H., Dham, AK., Meath, W.J.: Faraday Disc. Chem. Soc. **97** (1994) 81

[394] Schnupf, U., Bowman, J.M., Heaven, M.C.: Chem. Phys. Lett. **189** (1992) 487

[395] Bowman, J.M., Gazdy, B.: J. Chem. Phys. **95** (1991) 6309

[396] Carter, S., Handy, N.C., Mills, I.M.: Phil. Trans. R. Soc. Lond. A **332** (1990) 309

[397] Carter, S., Handy, N.C., Rosmus, P., Chambaud, G.: Mol. Phys. **71** (1990) 605

[398] Randall, R.W., Cliffe, A.C., Howard, B.J., McKellar, A.R.W.: Mol. Phys. **79** (1993) 1113

[399] Hutson, J.M.: J. Chem. Phys. **89** (1988) 4550

[400] Chang, H.C., Tao, F.M., Klemperer, W., Healey, C., Hutson, J.M.: J. Chem. Phys. **99** (1993) 9337

[401] Cohen, R.C., Saykally, R.J.: J. Chem. Phys. **98** (1993) 6007

[402] Dubernet, M.L., Hutson, J.M.: J. Chem. Phys. **99** (1993) 7477

[403] Ernesti, A., Hutson, J.M.: Faraday Disc. Chem. Soc. **97** (1994) 119

[404] Ernesti, A., Hutson, J.M.: Phys. Rev. A. **51** (1995) 239

[405] Carrington, A., Leach, C.A., Marr, A.J., Shaw, A.M., Viant, M.R., Hutson, J.M., Law, M.M.: J. Chem. Phys. **102** (1990) 2379

[406] Wheatley, R.J., Hutson, J.M.: Mol. Phys. **84** (1995) 879

[407] Roche, C.F., Ernesti, A., Hutson, J.M., Dickinson, A.S.: J. Chem. Phys. **104** (1996) 2156

[408] Hutson, J.M., Ernesti, A., Law, M.M., Roche, CF., Wheatley, R.J.: J. Chem. Phys. **105** (1996) 9130

[409] Hutson, J.M., Atkins, KM.: J. Chem. Phys. **105** (1996) 440

[410] Keil, M., Danielson, LJ., Buck, U., Schleusener, J., Huisken, F., Dingle, T.W.: J. Chem. Phys. **89** (1988) 2866

[411] Keil, M., Danielson, L.J., Dunlop, P.J.: J. Chem. Phys. **94** (1991) 296

[412] Jensen, P.: J. Mol. Spectr. **133** (1989) 438

[413] Cline, J.I., Reid, B.P., Evard, D.D., Sivakumar, N., Halberstadt, N., Janda, K.C.: J. Chem. Phys. **89** (1988) 3535

[414] Waterland, R.J., Lester, M.I., Halberstadt, N.: J. Chem. Phys. **92** (1990) 4261

[415] Halberstadt, N., Beswick, J.A., Rocenro, O., Janda, K.C.: J. Chem. Phys. **96** (1992) 2404; **97** (1992) 341

[416] Roncero, O., Beswick, J.A., Halberstadt, N., Soep, B. in: Dynamics of polyatomic van der Waals complexes, Halberstadt, N., Janda, K.C. (Ed.), NATO Series B Physics **227** (1990) 471, Plenum, New York

[417] Fernley, J.A., Miller, S., Tennyson, J.: J. Mol. Spectr. **150** (1991) 597

[418] Dinelli, B.M., Miller, S., Tennyson, J.: J. Mol. Spectr. **163** (1994) 71,

[419] Paulse, C.D., Tennyson, J.: J. Mol. Spectr. **168** (19994 313

[420] Korsch, H.J., Ernesti, A.: J. Phys. B: At. Mol. Opt. Phys. **25** (1992) 3565

[421] Cohen, R.C., Saykally, R.J.: J. Chem. Phys. **95** (1993) 7891

[422] Mills, I.M.: Faraday Disc. Chem. Soc. **62** (1976) 7

[423] Mills, I.M.: Spec. Period. Rep. **1** (1994) 110

[424] Engelsen, S.B., Fabricius, J., Rasmussen, K.: Acta Chem. Scandin. **48** (1994) 548; **48** (1994) 553

[425] Staemmler, V., Jaquet, R.: Theor. Chim. Acta. **59** (1981) 487

[426] Kress, J.D., Walker, R.B., Hayes, E.F., Pendergast, P.: J. Chem. Phys. **100** (1994) 2728

[427] Gonzalez, M., Blasco, R.M., Gimenez, X., Aguilar, A.: Chem. Phys. **209** (1996) 355

[428] McNab, I.R.: Adv. Chem. Phys. **89** (1994) 1

[429] Takada, S., Ohsaki, A., Nakamura, H.: J. Chem. Phys. **96** (1992) 339

[430] Takada, S., Tsuda, K., Ohsaki, A., Nakamura, H.: Adv. in Mol, Vibrations and Collision Dynamics **2A** (1994) 245

[431] Knowles, P.J., Stark, K., Werner, H.-J.: Chem. Phys. Lett. **185** (1991) 551

[432] Stark, K., Werner, H.-J.: J. Chem. Phys. **104** (1996) 6515

[433] Manolopoulos, D.E.: J. Chem. Soc. Faraday Trans. **93** (1997) 673

[434] de Boor, C.: A Practical Guide to Splines, Springer, Berlin, 1978

[435] Alberg, J.H., Nielson, E.N., Walsh, J.L.: The Theory of Splines and their Applications, Academic Press, New York, 1967

[436] Schumaker, L.L.: Theory and Applications of Spline Functions, Academic Press, New York, 1969

[437] Sand, A., Weintraub, S.: A Book of Splines, Wiley, New York, 1971

[438] Lancaster, P., Salkauska, S.K.: Curve and Surface Fitting, Academic Press, London, 1986

[439] Ramachandran, M.P.: Appl. Math. Lett. **7** (1994) 97

[440] Leforestier, C.: Chem. Phys. Lett. **51** (1977) 132

[441] Akima, H.: J. Assoc. Comput. Mach. **17** (1970) 589; Commun. Assoc. Comput. Mach. **15** (1972) 914

[442] Akima, H.: ACM transactions on Mathematical Software **22** (1996) 357; 362

[443] Marquardt, D.: SIAM J. Appl. Math. **11** (1963) 431

[444] Lawson, C.L., Hanson, R.J.: Solving Least Squares Problems, Prentice, New Jersey, 1974

[445] Dennis, J.E. in: The State of the Art in Numerical Analysis, Jacobs, D. (Ed.), Academic Press, London, 1977

[446] Albritton, D.L., Schmeltekopf, A.L., Zare, R.N. in: Molecular Spectroscopy: Modern Research, Rao, K.N. (Ed.), **2** (1976) 1, Academic Press, London

[447] Bartell, L.S., Romenesko, D.J., Wong, T.C. in: Molecular Structure by Diffraction Methods (Specialist Periodical Reports) **3** (1975) 72, Chemical Society, London

[448] Golub, G.H., VanLoan, C.F.: Matrix Computations, John Hopkins Univ. Press, 1989

[449] Dennis, J.E., Gay, D.M., Welsch, R.E.: ACM transactions on Mathematical Software **7** (1981) 348;369

[450] Kirkpatrick, S.: J. Stat. Phys. **34** (1984) 975

[451] DeTar, D.F.: Computer programs for Chemistry **4**, Academic Press, New York, 1972

[452] Searles, D.J., von Nagy-Felsobuki, E.I.: Comput. Phys. Commun. **67** (1992) 527

[453] Engelsen, S.B., Fabricius, J., Rasmussen, K.: Comp. Chem. **18** (1994) 397

[454] Ermler, W.C., Hsieh, H.C., Harding, L.B.: Comput. Phys. Commun. **51** (1988) 257

Appendix Software (a) GENLSS: Gauss-Newton-method [451], slow convergence

(b) Marquardt-method: ZXSSQ (from IMSL-library), Levenberg-Marquardt [443, 80], nonlinear

(c) Gauss-Newton-method: E04FCF (from NAG-library), slow convergence

(d) Gauss-Newton-, gradient-, Marquardt-method: STEPT (from QCPE)

(e) algorithm for SVD-method [80], nonlinear

(f) software from different contributors like CERN, CPC, HSL, ACM (NL2SOL), QCPE

(g) different programs from "Numerical Recipes" [80], chapters 2, 3, 10 and 15

(h) Fit-PowPad [452] from CPC-library: three dimensional for triatomics with D_{3h}, C_{2v}, C_s - symmetry

(i) I-NoLLS: from Law and Hudson [30], interactive computer program (windows version) for nonlinear least-squares

(j) software of different contributors like CERN, CPC, HSL, ACM (NL2SOL), quantum chemistry program exchange (QCPE): spline, least-squares, etc.

(k) GFF-GOPT: interactive graphical optimization of PE parameters in the consistent force field [453]

(l) polyatomic surface fitting, vibrational-rotational analysis, expectation value and intensity program [454]

(m) ASYM20: harmonic force field calculations: least-squares fitting of PESs to experimental data [13]

List of abbreviations and symbols

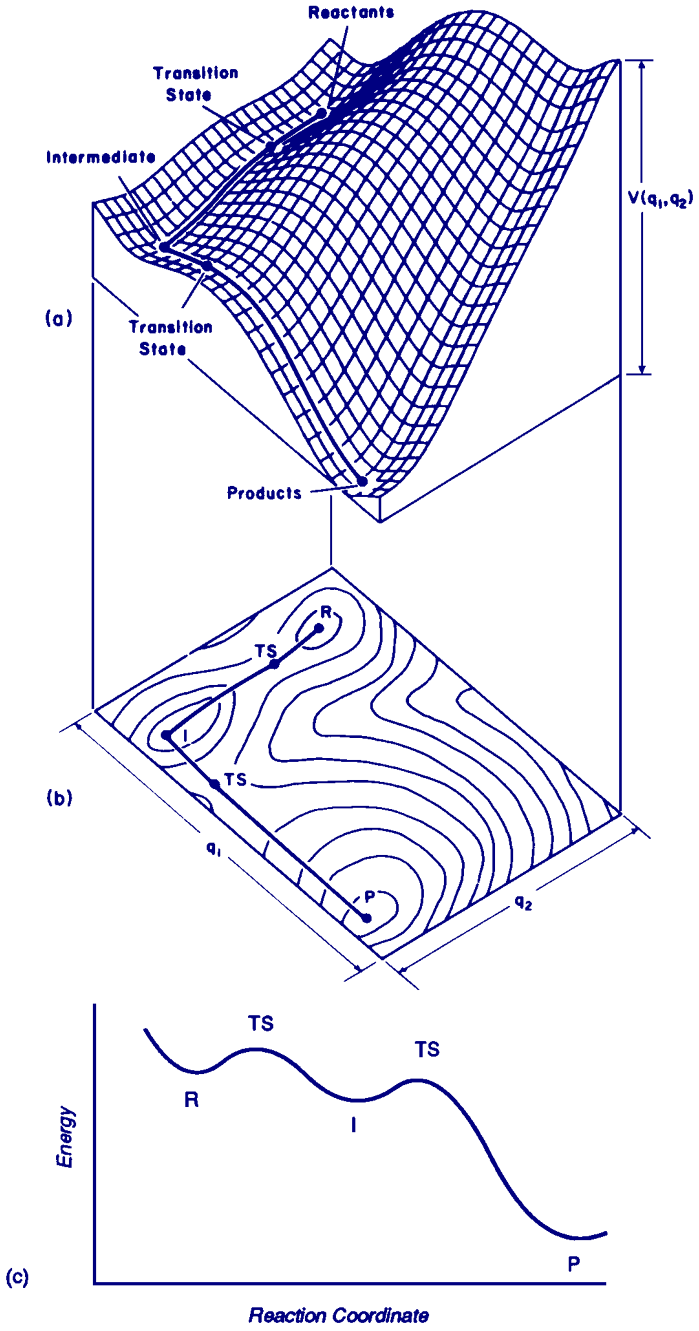
P_λ: Legendre polynomial
P_λ^μ: unnormalized associated Legendre polynomial
R: interatomic distance
θ, ϕ: angles as internal coordinates
V: potential energy
V_λ: V in Legendre polynomials
V_l^m: V expanded in spherical harmonics

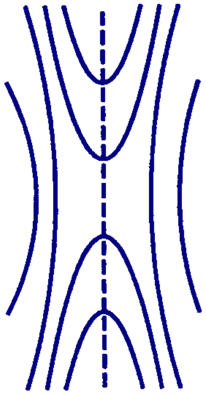
Y_l^m: spherical harmonics
1D, 2D, 3D - one, two, three dimensional
AM1 - semiempirical quantum chemical program (Austin 1)
BCRLM - bending corrected linear model
BF - Body-fixed
BO - Born-Oppenheimer
CEPA - Coupled electron pair approximation
CG - Clebsch-Gordan
DIM - Diatomics-in-molecules
DMBE - double many body expansion
ER - Extended Rydberg
GL - Gauss-Legendre
HFD - Hartree-Fock dispersion
HI - Hermite interpolation
LEPS - London- Eyring- Polanyi- Sato
LJ - Lennard-Jones
LI - Lagrange interpolation
LLS - linear least-squares
LR - Long range
MBB - Meyer - Botschwina - Burton
MEP - Minimum energy path
MM - modified Morse function
NLLS - nonlinear least-squares
PE - potential energy
PES - Potential energy surface
QCPE - Quantum chemistry program exchange

QCT - quasi classical trajectories
QM - quantum mechanical
PNO-CI - configuration interaction with pair natural orbitals
Rg - rare gas
RIOSA - reactive infinite order sudden approximation
RKHS - reproducing kernel Hilbert space
RKR - Rydberg-Klein-Rees
RMCS - Rotated-Morse-curve-spline
rms - root mean square
RR - Rigid rotor
SF - Space-fixed
SI - Spline interpolation
SLTH - Siegbahn-Liu-Truhlar-Howovitz
SM - Sorbie-Murrell
SPF - Simon-Parr-Finlan
SR - Short range
SVD - singular value decomposition
VDW - van der Waals
VSR - Voronoï step representation

Further help

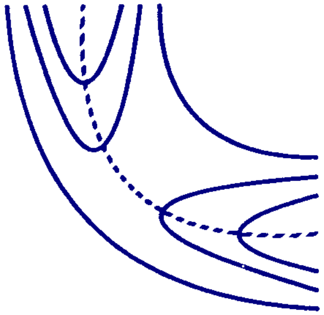
More information about PESs and fitting can be got by searching through the WEB-pages of the relevant journals, e.g. the journals of the American Institute of Physics (AIP) (http:www.aip.org). Another possibility is to use database systems like Current Contents (CC), Journal Articles Database (JADE), Quantum Chemistry Literature Database (QCLDB), etc.


Reactants
Transition State
Intermediate
Transition State
Products
$V(q_1,q_2)$
(a)
R
TS
I
TS
P
q_1
q_2
(b)
TS
TS
R
I
P
Energy
Reaction Coordinate
(c)



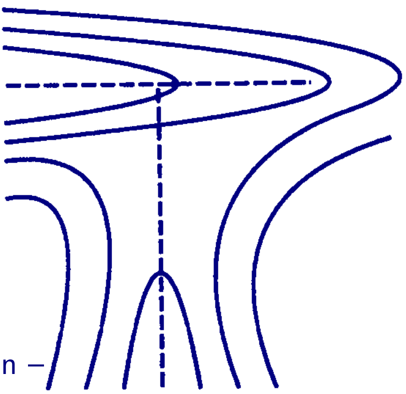
I shaped valley

(*a*)



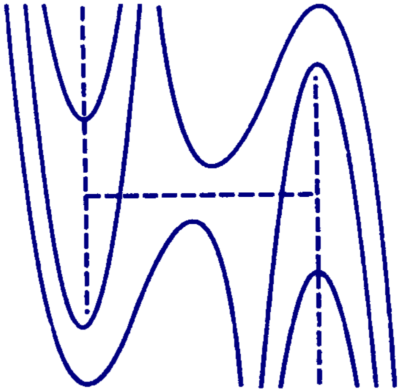
L or V shaped valley

(*b*)



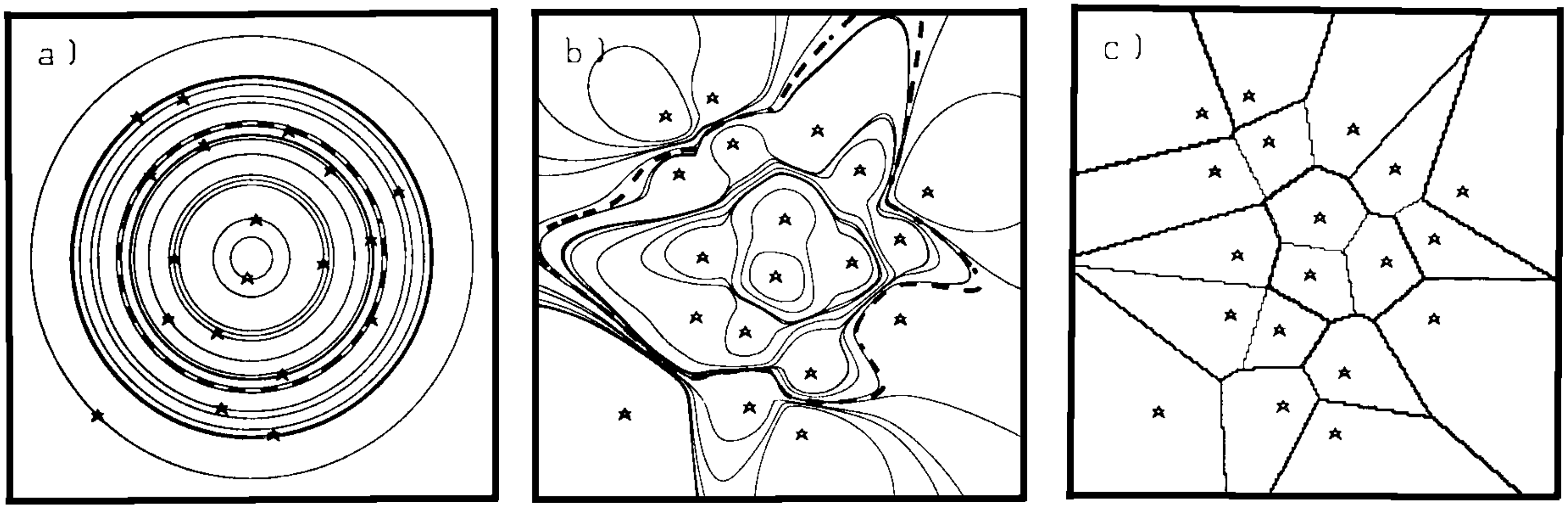
T shaped valley

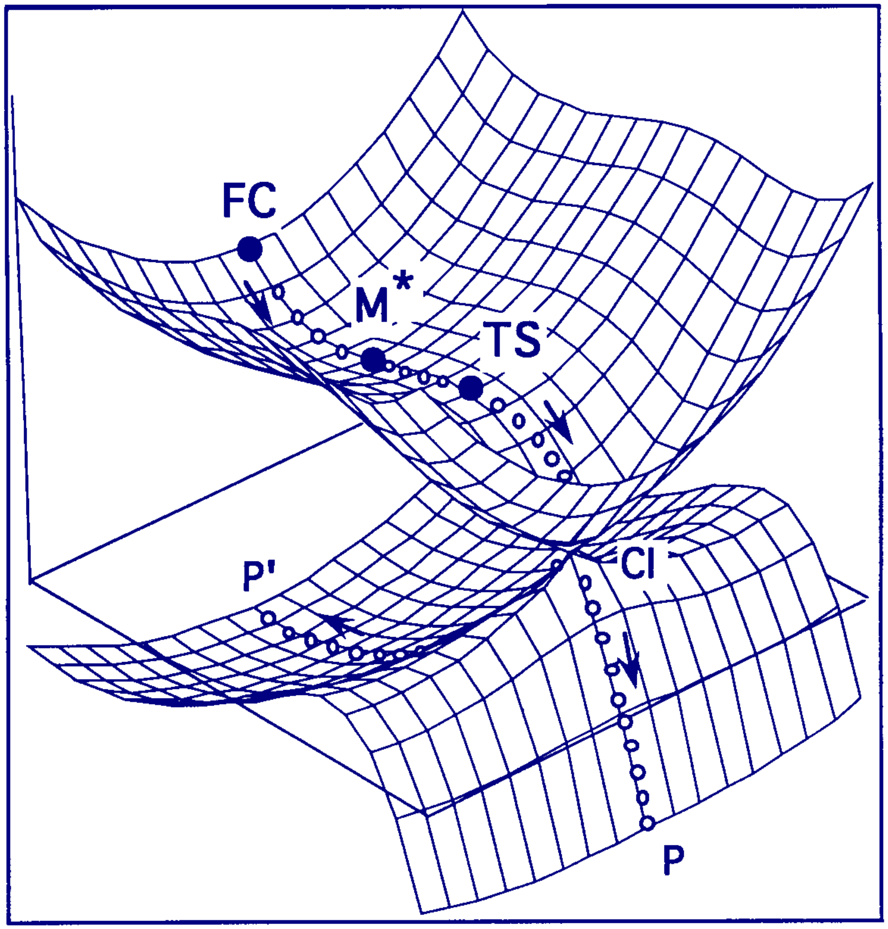
(*c*)

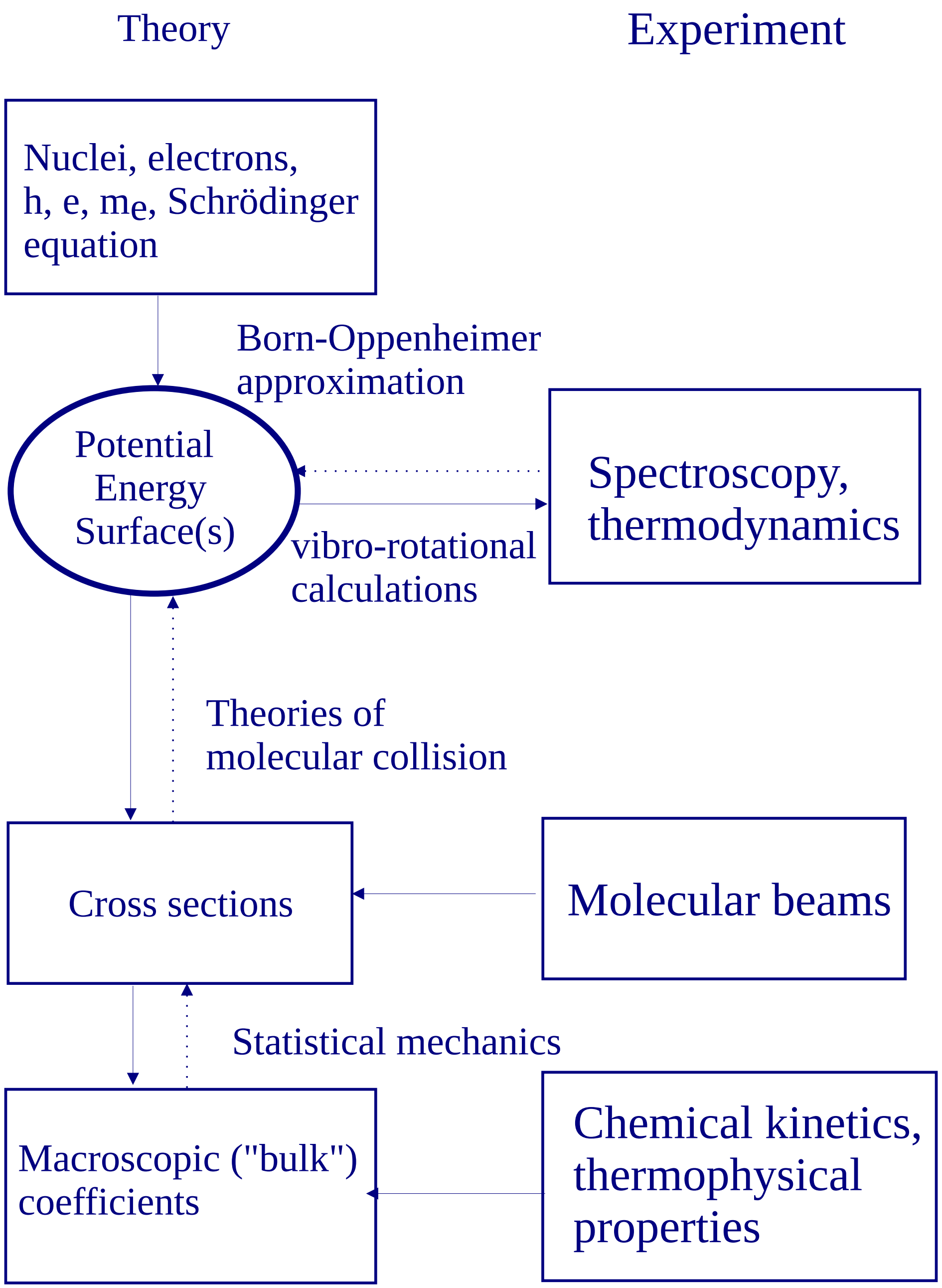


H or X shaped valley

(*d*)


a)
b)
c)


FC
M*
TS
CI
P'
P



Theory

Experiment

Nuclei, electrons, h, e, m_e, Schrödinger equation

Born-Oppenheimer approximation

Potential Energy Surface(s)

vibro-rotational calculations

Spectroscopy, thermodynamics

Theories of molecular collision

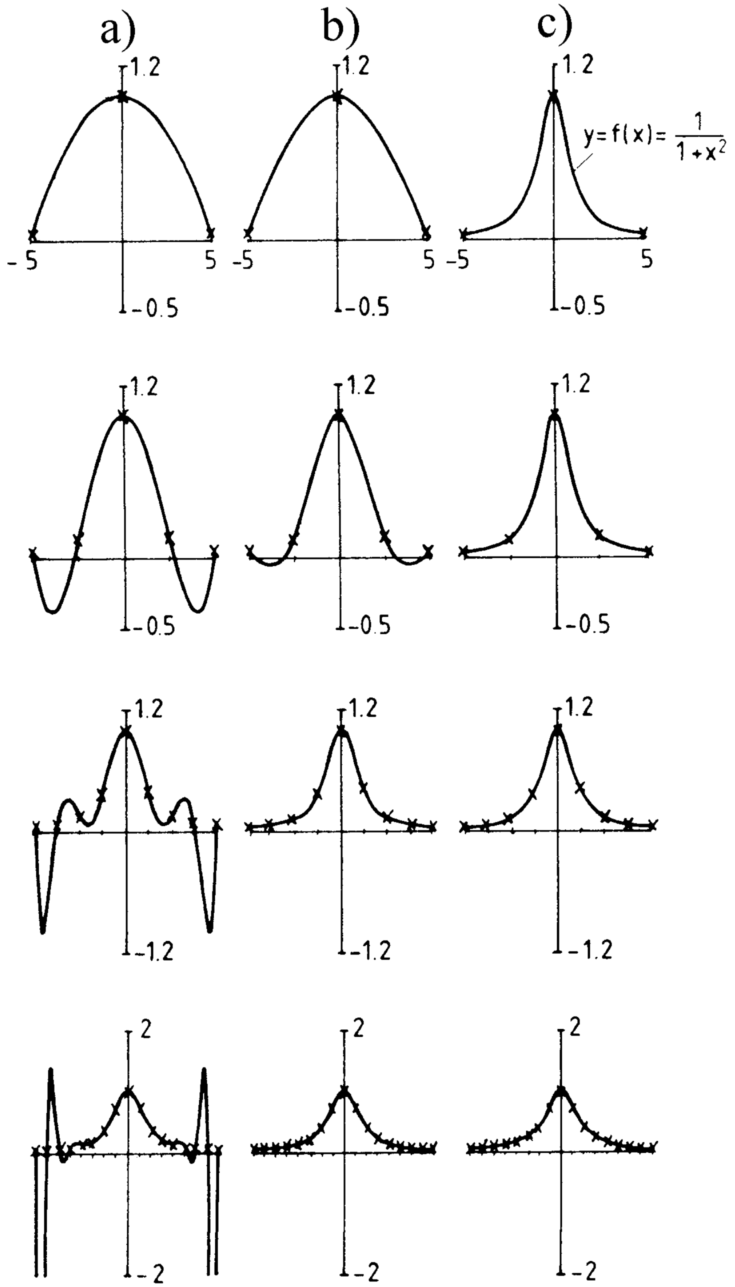
Cross sections

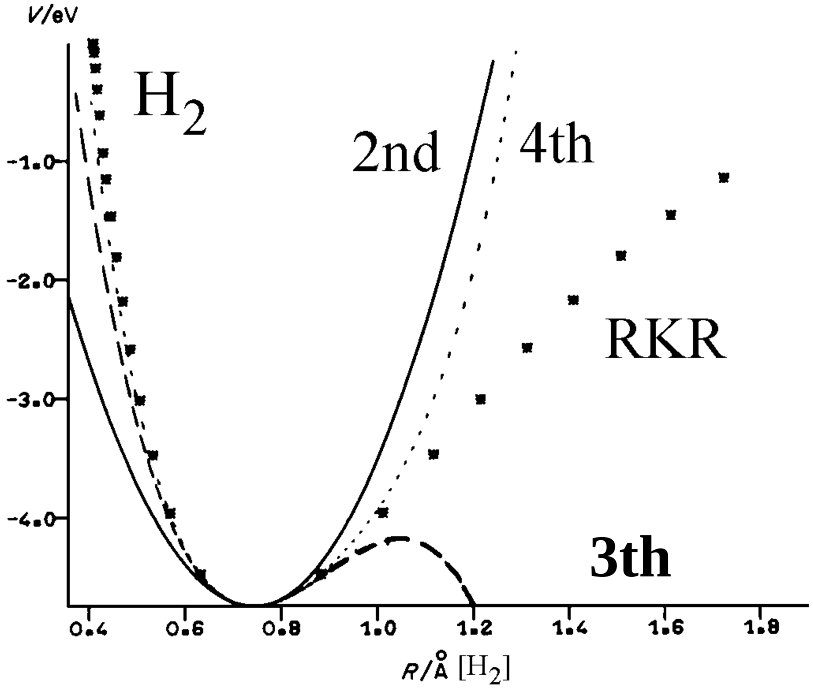
Molecular beams

Statistical mechanics

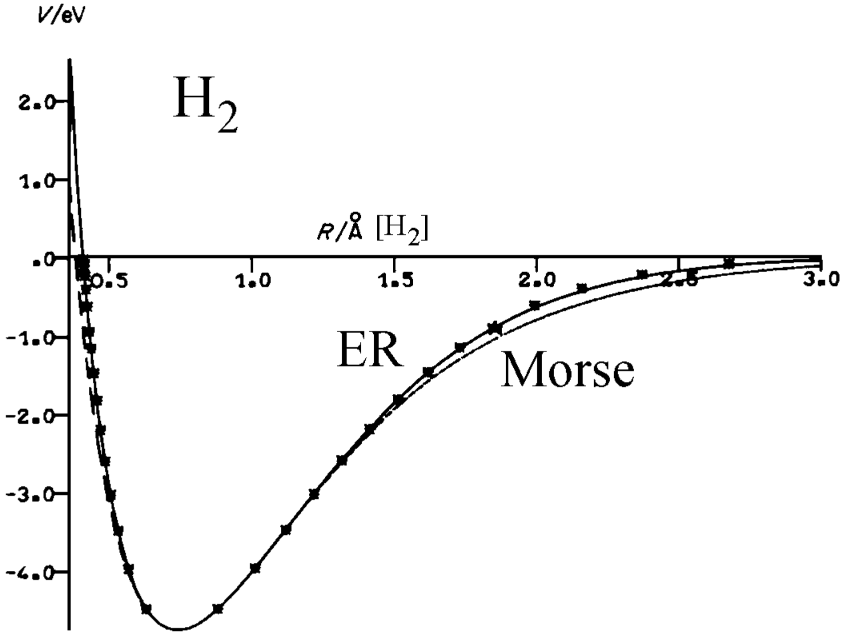
Macroscopic ("bulk") coefficients

Chemical kinetics, thermophysical properties

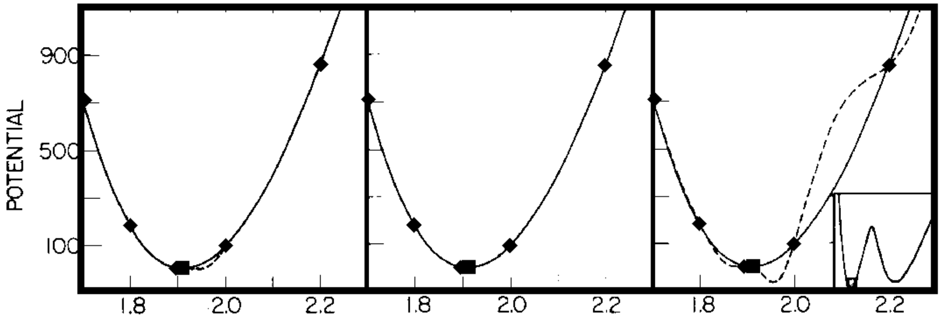

a)
b)
c)
1.2
-0.5
-5
5
$y=f(x)=\frac{1}{1+x^2}$
-1.2
2
-2


V/eV
H2
2nd
4th
RKR
3th
-1.0
-2.0
-3.0
-4.0
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
R/Å [H2]

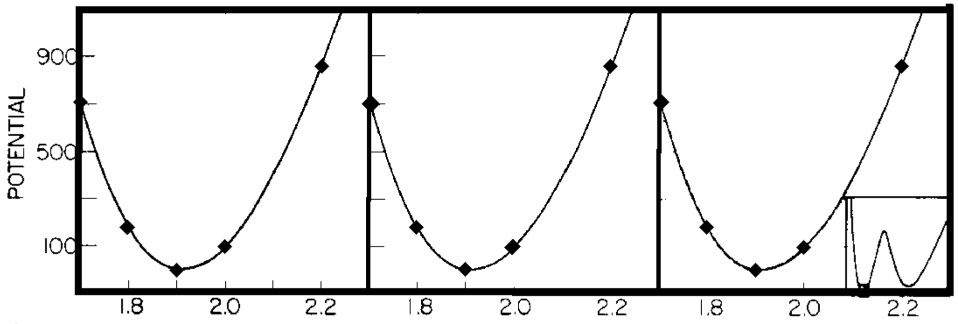
a)


V/eV
H2
2.0
1.0
.0
-1.0
-2.0
-3.0
-4.0
R/Å [H2]
0.5
1.0
1.5
2.0
2.5
3.0
ER
Morse

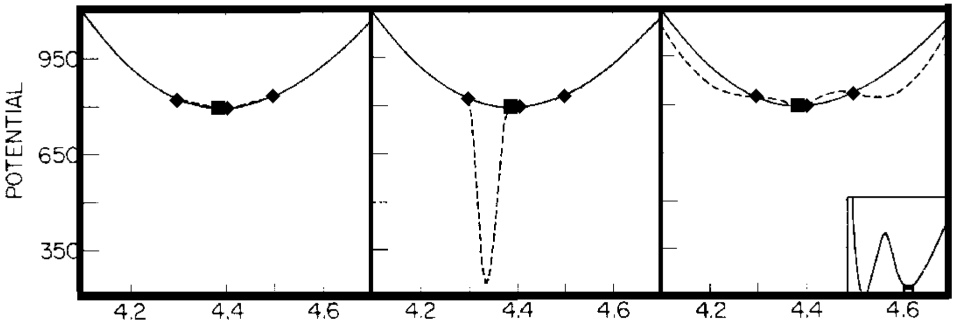
b)


POTENTIAL
900
500
100
1.8
2.0
2.2
1.8
2.0
2.2
1.8
2.0
2.2

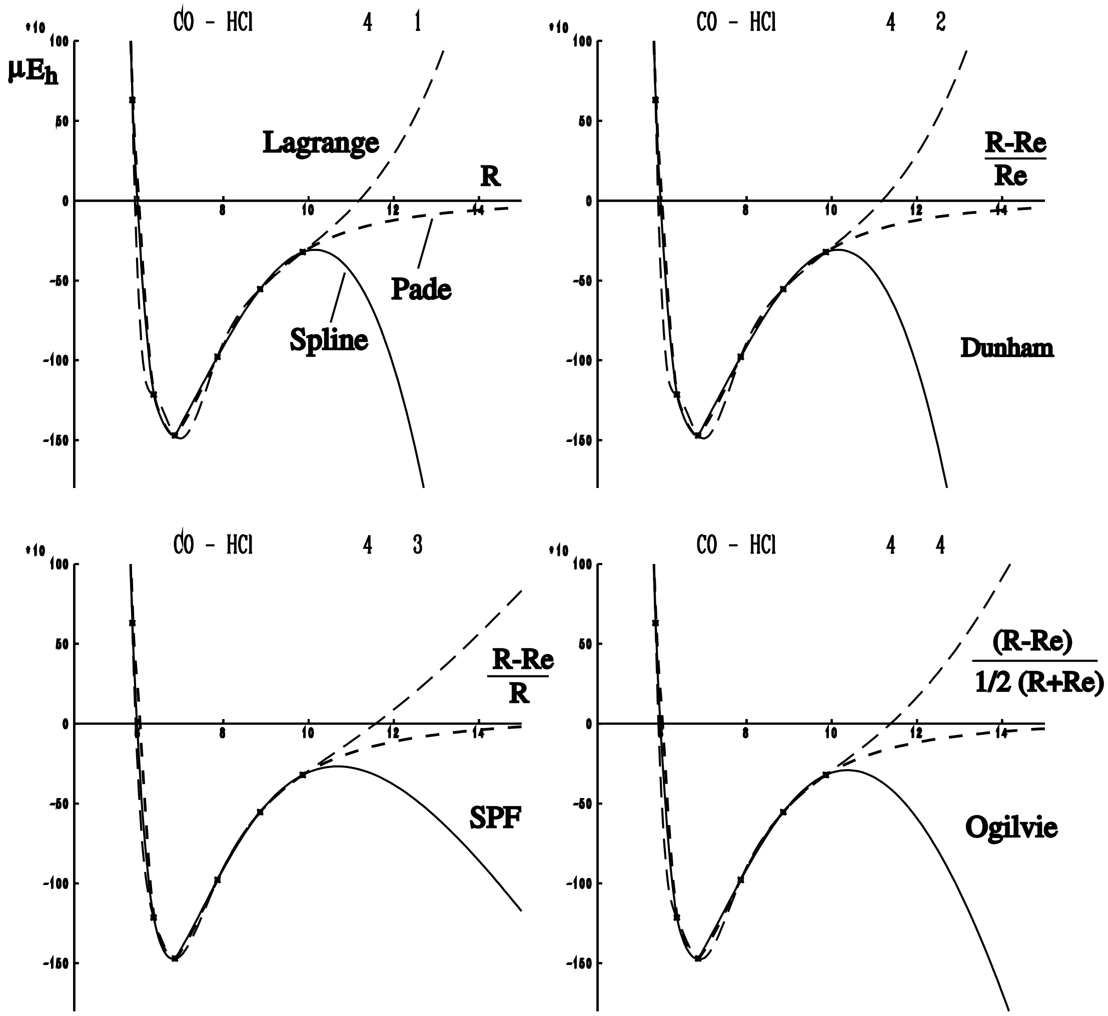
a)

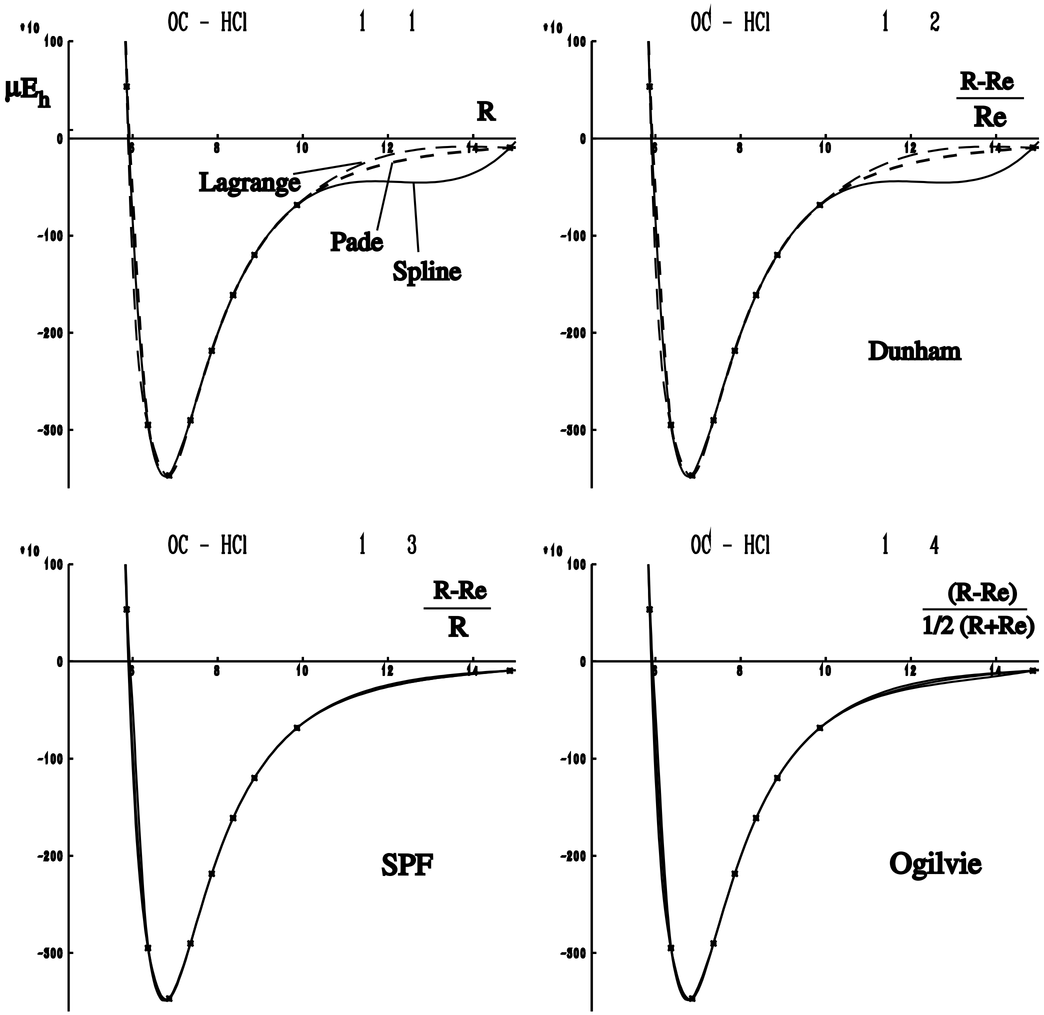

POTENTIAL
900
500
100
1.8
2.0
2.2
1.8
2.0
2.2
1.8
2.0
2.2

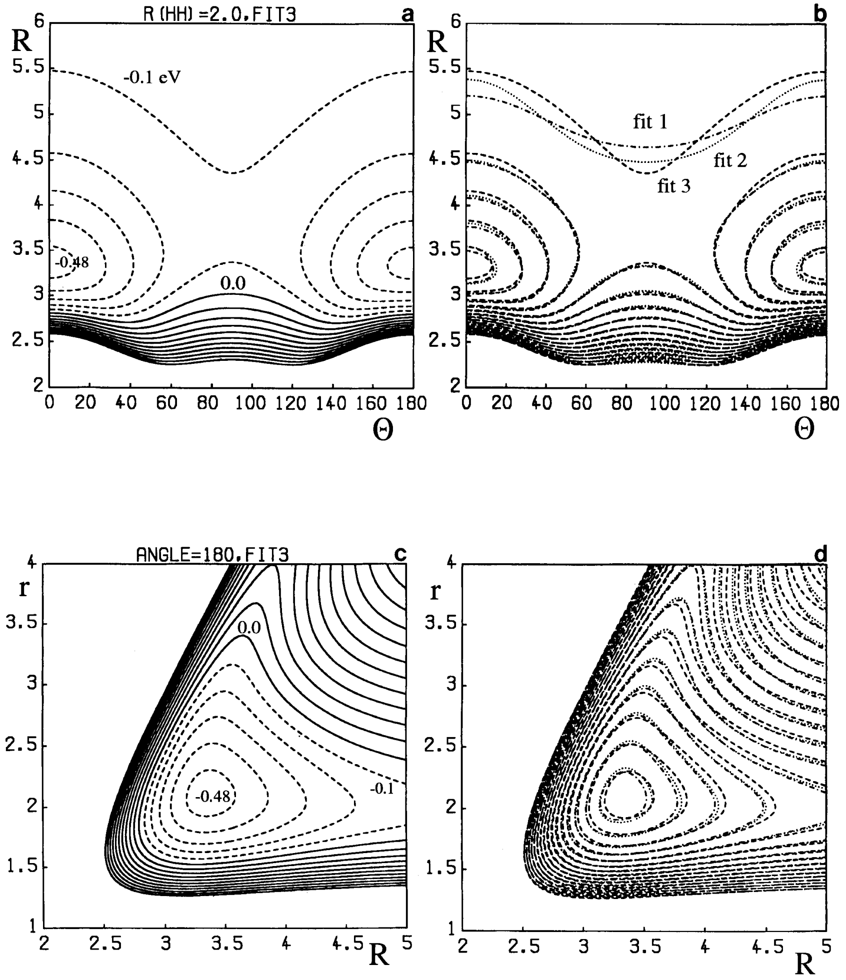
b)

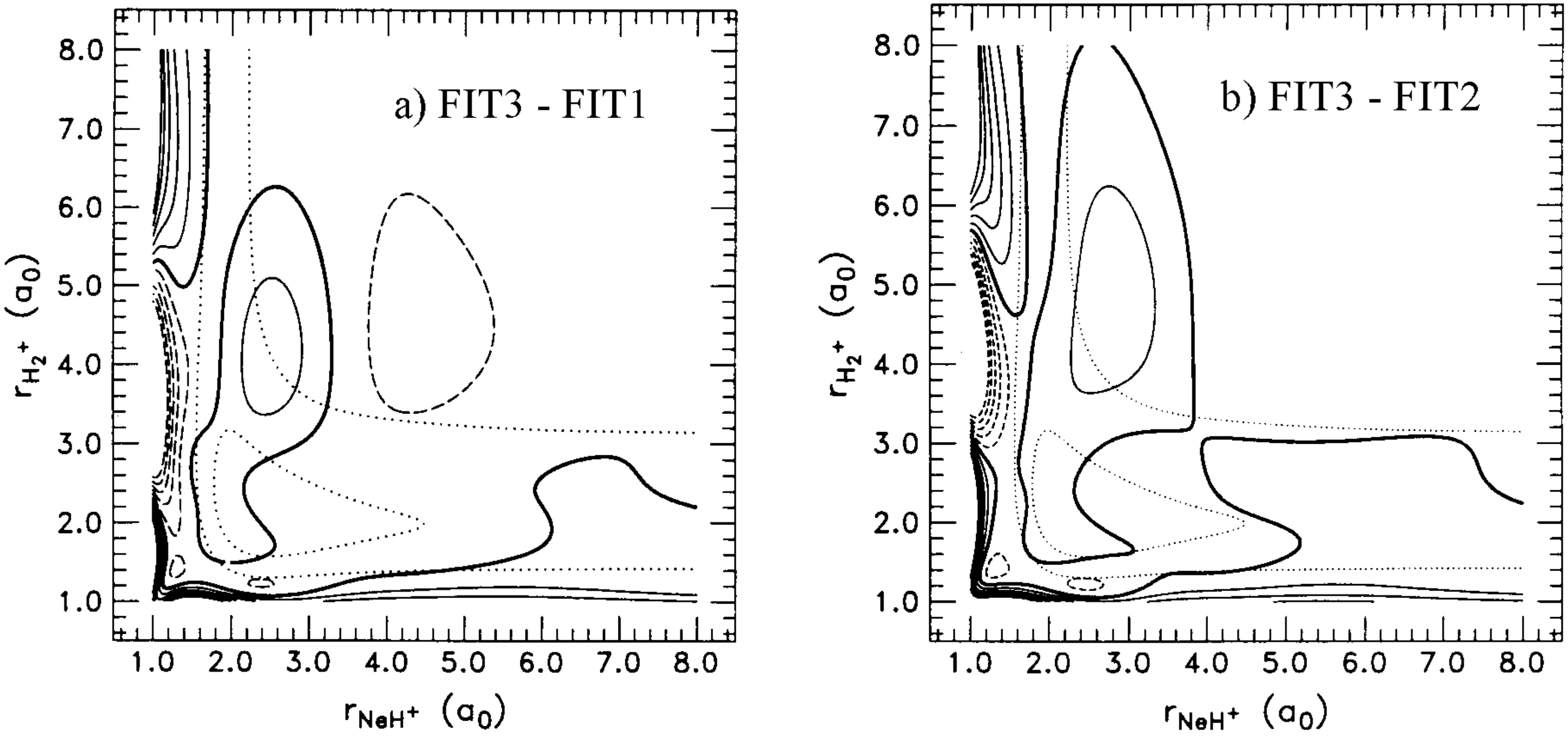

POTENTIAL
950
650
350
4.2
4.4
4.6
4.2
4.4
4.6
4.2
4.4
4.6

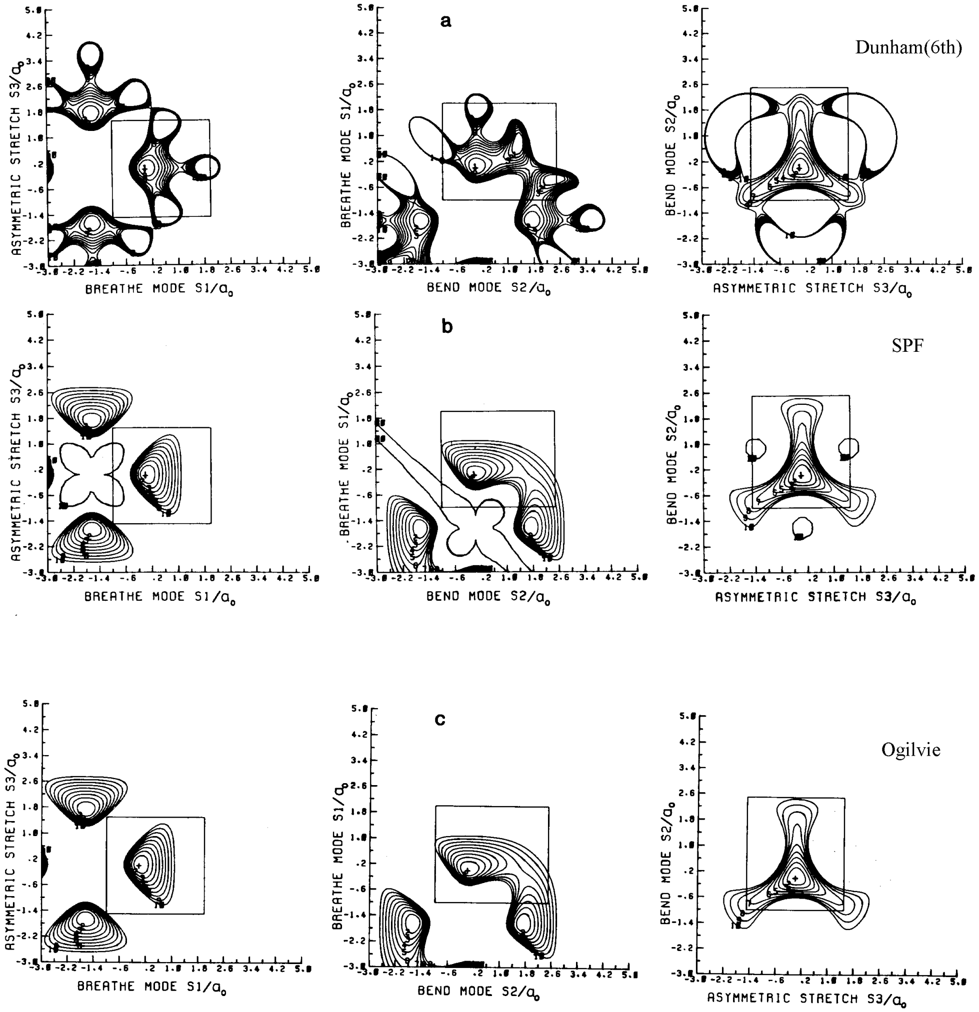
c)


CO - HCl 4 1
*10
μE_h
100
50
0
-50
-100
-150
8
10
12
14
Lagrange
R
Pade
Spline
CO - HCl 4 2
R-Re / Re
Dunham
CO - HCl 4 3
R-Re / R
SPF
CO - HCl 4 4
(R-Re) / 1/2 (R+Re)
Ogilvie


OC - HCl 1 1
*10
100
0
-100
-200
-300
μE_h
R
Lagrange
Pade
Spline
6
8
10
12
14
OC - HCl 1 2
R-Re / Re
Dunham
OC - HCl 1 3
R-Re / R
SPF
OC - HCl 1 4
(R-Re) / 1/2 (R+Re)
Ogilvie


R (HH) =2.0, FIT3
a
R
6
5.5
5
4.5
4
3.5
3
2.5
2
-0.1 eV
-0.48
0.0
0
20
40
60
80
100
120
140
160
180
Θ
b
R
fit 1
fit 2
fit 3
Θ
ANGLE=180, FIT3
c
r
4
3.5
3
2.5
2
1.5
1
0.0
-0.48
-0.1
2
2.5
3
3.5
4
4.5
5
R
d
r
R


a) FIT3 - FIT1
b) FIT3 - FIT2
$r_{H_2^+}$ (a_0)
r_{NeH^+} (a_0)
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


a
Dunham(6th)
b
SPF
c
Ogilvie
ASYMMETRIC STRETCH S3/a0
BREATHE MODE S1/a0
BREATHE MODE S1/a0
BEND MODE S2/a0
BEND MODE S2/a0
ASYMMETRIC STRETCH S3/a0
5.0
4.2
3.4
2.6
1.8
1.0
.2
-.6
-1.4
-2.2
-3.0