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Non linear adjustments with external conditions

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Abstract A new non linear adjustment algorithm is proposed that includes the possibility to satisfy conditions involving non linear analytical functions of the adjustment parameters. It is based on the Levenberg-Marquardt algorithm and makes use of Lagrange multipliers to fulfill external conditions. As an application, the method is used to derive a modified Morse potential to represent the potential energy function of the $^2\Pi_{1/2}$ ground state of nitric oxide (NO), while having both an acceptable description of the equilibrium bond length, the vibrational overtone spectrum to up to the 6th overtone, the energy and the dispersion coefficient at dissociation NO $\rightarrow$ N + O.

1 Introduction

The Levenberg-Marquardt algorithm [1,2] is a widely used numerical algorithm for non linear adjustment procedures. In chemistry, this algorithm has been used in a variety of applications, such as to obtain effective spectroscopic parameters from high resolution spectroscopy [3], rate constants in kinetics [4,5], equilibrium constants in thermodynamics [6], and to model high dimensional potential energy [7,8] or dipole

The author has used the Levenberg-Marquardt algorithm for many years and happens to share the same name with the late Dr. Donald W. Marquardt, to whom he dedicates the present work posthumously.

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moment hypersurfaces [9] (this list being far from complete, see also [10,11] for recent reviews).

In these applications, the relationship between variables x and y, given by a series of related data x_i and y_i $(i = 1, \ldots, N)$ is modeled by an analytical expression $y = f(x; \boldsymbol{p})$, where $\boldsymbol{p}$ is a parameter vector to be determined by optimization of a merit function, such as

$$\chi^2(\boldsymbol{p}) = \sum_{n=1}^{N} \left(\frac{y_n - f(x_n, \boldsymbol{p})}{\sigma_n} \right)^2, \tag{1}$$

where the "weights" σ_n may be interpreted as statistical standard deviations of the "measured" values y_n. During the optimization procedure, the parameter vector $\boldsymbol{p}$ is varied by short increments $\boldsymbol{\Delta p}$ such as to minimize the merit function. In order to simplify notation, x is taken to be a one dimensional quantity, here, but in general x can be a higher dimensional vector; y is generally one dimensional.

It is often adequate to consider constrained procedures, in which the parameter vector $\boldsymbol{p}$ is varied only within a subspace of the full parameter space. If that subspace is a linear space, it is rather easy to perform a linear transformation in parameter space and reduce it to the number of parameters that can be varied unconstrainedly. However, very often constraints are non linear functions of the parameters and a more elaborate treatment becomes necessary.

In the present approach we make use of Lagrange multipliers to include external constraints. Let $C_1(\boldsymbol{p}), \ldots, C_M(\boldsymbol{p})$ be M (non linear) functions defining additional constraints on the parameters to be adjusted. Then, the new merit function to be optimized is

$$\tilde{\chi}^2(\boldsymbol{p}) = \chi^2(\boldsymbol{p}) + \sum_{m=1}^{M} \mu_m C_m(\boldsymbol{p}), \tag{2}$$

where μ_m are the Lagrange multipliers. We propose a new and efficient algorithm for the optimization of the changed merit function $\tilde{\chi}$ of Eq. (2). To our knowledge, the problem of non linear adjustments under the consideration of additional constraints has not yet been treated in this form and in connection with the Levenberg-Marquardt algorithm. Previous work [12,13] used the Levenberg-Marquardt algorithm to determine Lagrange multipliers in constrained optimization tasks. The present approach allows for the first time, to our knowledge, to directly derive optimal parameter sets without explicit calculation of the Lagrange multipliers.

2 Theory

2.1 The Levenberg-Marquardt algorithm: a recall

The Levenberg-Marquardt algorithm proposes using the following equations for the determination of the parameter step vector $\boldsymbol{\Delta p}$:

1. If p is far away from its optimal value, then the best variation should be proportional to the opposite of the gradient of the merit function at p:

$$\Delta p = c_\infty \beta(p), \tag{3}$$

   where $\beta(p) = -\nabla\chi^2(p)$ and c_∞ is an adequate proportionality factor.

2. If p is close to its optimal value, then the best variation should be the solution of the problem:

$$A(p) \cdot \Delta p = \beta(p), \tag{4}$$

   where $A(p)$ is the curvature matrix with matrix elements

$$A_{kl}(p) = \sum_{n=1}^{N} \frac{1}{\sigma_n^2} \frac{\partial f(x_n; p)}{\partial p_k} \frac{\partial f(x_n; p)}{\partial p_l} \tag{5}$$

Eq. (4) may be derived from a similar equation, in which the curvature matrix is replaced by the Hessian matrix with matrix elements $H_{ij} = \frac{\partial^2 \chi^2}{2\partial p_i \partial p_j}$. The reason for using the curvature matrix in Eq. (4) is that, in the iterative algorithm for the determination of the optimized parameter set described below, the cross derivatives $\frac{\partial^2 f}{\partial p_i \partial p_j}$ may generally be neglected with respect to those terms appearing in the curvature matrix, because of a statistical cancellation of terms containing positive and negative deviations $(y_n - f(x_n; p))$.

In practice such a procedure may be implemented as follows (see, for instance, [14]):

1. A is replaced by A_λ, where

$$(A_\lambda)_{kl} = \begin{cases} A_{kl} & \text{if } k \neq l \\ A_{kk}(1 + \lambda) & \text{if } k = l. \end{cases} \tag{6}$$

2. Give an initial guess for p and λ.
3. Compute $\chi^2(p)$, $\beta(p)$ and $A(p)$.
4. Solve for Δp in

$$A_\lambda(p) \cdot \Delta p = \beta(p), \tag{7}$$

   generally via computation of $A_\lambda^{-1}(p)$, and evaluate $\chi^2(p + \Delta p)$.
   If $\chi^2(p + \Delta p) \geq \chi^2(p)$, increase λ by a constant factor and go back to 3.
   If $\chi^2(p + \Delta p) < \chi^2(p)$, decrease λ by the same constant factor, replace p by $p + \Delta p$ and go back to 3.
5. Interrupt the iteration in any of the following cases:
   (a) If $\Delta\chi^2 = \chi^2(p + \Delta p) - \chi^2(p) < 0$ and $\Delta\chi^2 > -\epsilon$, where $\epsilon > 0$ is a convergence threshold.
   (b) If $\lambda > \lambda_{max}$, where λ_{max} is a threshold for λ.

(c) If $N_{\text{cycle}} > N_{\text{max cycle}}$, where N_{cycle} is the iteration cycle number and $N_{\text{max cycle}}$ is the maximal iteration cycle number.

The choice of an appropriate initial value for λ and the value of the constant variation factor of λ depends on the initial guess for $\boldsymbol{p}$. Convenient initial values are quite generally on the order of 0.001 with variation factors on the order of 10. Note that the algorithm is expected to deliver a trustfully converged result only if the first interruption criterion 5a applies.

2.2 Inclusion of additional constraints

We wish to use an iterative procedure similar to that described in the previous section. Given M analytical expressions $C_1(\boldsymbol{p}), \ldots, C_M(\boldsymbol{p})$, we need to consider the merit function $\tilde{\chi}^2(\boldsymbol{p})$ as defined in Eq. (2). Thus we need to evaluate curvature matrices $\tilde{A}_\lambda$ and negative gradients $\tilde{\boldsymbol{\beta}}$ which theoretically include a priori unknown Lagrange multipliers $\mu_1, \ldots, \mu_M$.

Without loss of generality, we may always rewrite all conditions such as to yield

$$C_n(\boldsymbol{p}) \equiv 0 \quad \text{for} \quad n = 1, \ldots, M, \tag{8}$$

at the optimal parameter set.

For the negative gradient we write

$$\tilde{\boldsymbol{\beta}}(\boldsymbol{p}) = \boldsymbol{\beta}(\boldsymbol{p}) - \sum_{n=1}^{M} \mu_n \nabla C_n(\boldsymbol{p}). \tag{9}$$

For the curvature matrix, let

$$\tilde{A}_\lambda = A_\lambda. \tag{10}$$

In this equation we indeed neglect the cross derivatives $\frac{\partial^2 C_n}{\partial p_i \partial p_j} (n = 1, \ldots, M)$, in analogy to the original Marquardt algorithm, in which the cross derivatives $\frac{\partial^2 f}{\partial p_i \partial p_j}$ are neglected. In the iterative procedure we now impose that the additional conditions be satisfied at each new iteration step. With Eq. (8) and

$$C_n(\boldsymbol{p} + \boldsymbol{\Delta p}) \approx C_n(\boldsymbol{p}) + \nabla C_n(\boldsymbol{p})^T \cdot \boldsymbol{\Delta p} \tag{11}$$

this implies that

$$C_n(\boldsymbol{p}) \approx -\nabla C_n(\boldsymbol{p})^T \cdot \boldsymbol{\Delta p}, \tag{12}$$

where $\nabla C_n(\boldsymbol{p})^T$ is the transposed vector of $\nabla C_n(\boldsymbol{p})$. For non-linear condition functions, this prescription does not normally lead to full satisfaction of Eq. (8). However,

in the convergence limit Δp becomes continuously smaller and it is expected that Eq. (8) is improved at every step.

As we shall show now, Eq. (12) is suitable to calculate an iteration of Lagrange multipliers. Because $\Delta p = A_\lambda^{-1}(p)\tilde{\beta}(p)$, this equation implies

$$- C_n(p) = \nabla C_n(p)^T A_\lambda^{-1}(p)\tilde{\beta}(p) \tag{13}$$

$$= \nabla C_n(p)^T A_\lambda^{-1}(p)\beta(p) - \sum_{m=1}^{M} \mu_m \nabla C_n(p)^T A_\lambda^{-1}(p)\nabla C_m(p). \tag{14}$$

Thus, if μ is the trial vector of Lagrange multipliers, it may be obtained as the solution of a set of linear equations

$$\underline{\underline{\Gamma}}(p)\underline{\mu} = \underline{\tilde{C}}(p), \tag{15}$$

at a given parameter set vector p.

The new procedure may be implemented as follows:

1. Give an initial guess for p and λ.
2. Compute $\chi^2(p)$, $\beta(p)$, $A_\lambda(p)$, $A_\lambda^{-1}(p)$; the latter will normally also be used in step 4 below. Evaluate all conditions $C_n(p)$ and their derivatives $\partial C_n(p)/\partial p_i$, and compute the expressions

$$\Gamma_{nm}(p) = \nabla C_n(p)^T A_\lambda^{-1}(p)\nabla C_m(p) \tag{16}$$
$$\tilde{C}_n = C_n(p) + \nabla C_n(p)^T A_\lambda^{-1}(p)\beta(p). \tag{17}$$

3. Determine trial Lagrange multipliers by solving the set of linear equations

$$\sum_{m=1}^{M} \Gamma_{nm}(p)\mu_m = \tilde{C}_n(p). \tag{18}$$

4. Get $\tilde{\beta}(p) = \beta(p) - \sum_m \mu_m \nabla C_n(p)$, solve for Δp in

$$A_\lambda(p) \cdot \Delta p = \tilde{\beta}(p) \tag{19}$$

   and evaluate $\chi^2(p + \Delta p)$.
   If $\chi^2(p + \Delta p) \geq \chi^2(p)$, increase λ by a constant factor and go back to 2.
   If $\chi^2(p + \Delta p) < \chi^2(p)$, decrease λ by the same constant factor, replace p by $p + \Delta p$ and go back to 2.
5. Interrupt the iteration in any of the following cases:
   (a) If $\Delta\chi^2 = \chi^2(p + \Delta p) - \chi^2(p) < 0$ and $\Delta\chi^2 > -\epsilon$, where $\epsilon > 0$ is a convergence threshold.
   (b) If $\lambda > \lambda_{max}$, where λ_{max} is a threshold for λ.
   (c) If $N_{cycle} > N_{max\ cycle}$, where N_{cycle} is the iteration cycle number and $N_{max\ cycle}$ is the maximal iteration cycle number.

3 Application

As an example of an application, we derive an analytical potential energy function for the $^2\Pi_{1/2}$ ground state of nitric oxide ($^{14}N^{16}O$). The analytical form, to be described below, is adjusted to adiabatic energy data calculated ab initio at the MRCI level of theory using an aug-cc-pVQZ basis within the MOLPRO program [15]. A simple (7,6) CAS space was used and the two degenerate Π components were calculated and then used to set up the rank 4 spin-orbit matrix of the full Breit-Pauli operator. The reported energies correspond to the lowest pair of eigenvalues from this matrix. For the present application, we consider equal weight of $1\,cm^{-1}$ to all ab initio data.

20 energy points obtained in this way are then modeled with the following analytical function:

$$V^{(the)}(r) = V_e \left(e^{-2a(r)(r-r_e)} - 2\,e^{-a(r)(r-r_e)} \right)$$
$$+ V_0 + (V_\infty - V_0)e^{-(r_6/r)^6} \tag{20}$$

where

$$a(r) = a_0 \left(1 - b_s \arctan \left(\frac{r_s^2}{r^2} - 2\,\frac{r_s}{r} \right) \right) \tag{21}$$

is an appropriate "anharmonicity" function. Equation (20) is a generalization of the well known Morse potential [16]. Similar functions were used quite successfully in the modeling of the potential energy hypersurfaces for methane [9], ammonia [17] and the CO/Cu(100) adsorption system [18]. The $\exp(-(r_6/r)^6)$ factor was introduced in [7]; it "switches" the last energy term from V_0 at $r \sim r_e$ to V_∞ for $r \to \infty$. Note that the expression from Eq. (20) reduces to the conventional Morse potential when $b_s = 0$ and $V_\infty = V_0$. When $V_\infty > V_0$, however, and contrary to the conventional Morse potential, this form allows to obtain the physically correct $\sim C_6/r^6$ behavior of the interaction energy between neutral particles [19] with a weak interaction coefficient

$$C_6 = (V_\infty - V_0)\,r_6^2. \tag{22}$$

Normally, $r_6 > 2r_e$, and consequently the last term of the model potential has effectively very little influence on the shape of the potential close to r_e.

Results of several fits are collected in Table 1. The column "original Morse potential" gives parameter values from a fit of the original Morse potential. The root-mean-square deviation ("rms")

$$\Delta V_{rms} = \sqrt{\frac{1}{N} \sum_{n=1}^{N} (V_n - V(r_n))^2} \tag{23}$$

Table 1 Parameters obtained from the adjustment of the analytical function Eq. (20) to *ab initio* data as described in the text

	Reference value	Original Morse potential	Modified Morse potential	Constrained mod. Morse potential I	Constrained mod. Morse potential II
$r_e/\text{Å}$	1.151[a]	1.135	1.153	1.151	1.155
$a_0/\text{Å}^{-1}$	–	2.932	3.481	3.610	3.249
$V_e/hc\,\text{cm}^{-1}$	–	52921	51260	51254	52290
b_S	–	0.000	0.1463	0.1606	0.1189
$r_S/\text{Å}$	–	–	3.787	3.891	3.458
$V_0/hc\,\text{cm}^{-1}$	–	1111	−222.4	−521.6	458.2
$V_\infty/hc\,\text{cm}^{-1}$	–	1111	6.014	571.7	516.5
$r_6/\text{Å}$	–	–	3.000[h]	3.000[h]	3.000[h]
$\Delta V_{rms}/hc\,\text{cm}^{-1}$		1193	12	247	335
$D_e/hc\,\text{cm}^{-1}$	52348[b]	51810	51489	52348	52348
$C_6/\text{Å}^6 hc\,\text{cm}^{-1}$	42550[c]	0.000	1664900	7969000	42550
$\tilde{\nu}_{n \leftarrow 0}/\text{cm}^{-1}$					
$1 \leftarrow 0$	1876.1[d]	1988	1876	1891	1875
$2 \leftarrow 0$	3723.9[e]	3937	3724	3752	3724
$3 \leftarrow 0$	5543.7[e]	5848	5543	5585	5546
$4 \leftarrow 0$	7335.6[f]	7719	7333	7388	7343
$5 \leftarrow 0$	9099.5[f]	9552	9096	9163	9113
$6 \leftarrow 0$	10835[f]	11346	10830	10909	10857
$7 \leftarrow 0$	12547[g]	13101	12536	12626	12575
$\Delta\tilde{\nu}_{rms}/\text{cm}^{-1}$		561	5	55	15

The quantities D_e and C_6 are the dissociation energy on the potential energy function and the C_6 coefficient, respectively; $\tilde{\nu}_{n \leftarrow 0}(n = 1, \ldots)$ are the vibrational fundamental and overtones

[a] From [22]

[b] From [21]; the value of $52348\,\text{cm}^{-1}$ corresponds to D_0, and has been used in the present fit in place of D_e, for which the value $53286\,\text{cm}^{-1}$ can be derived from ref. [21]

[c] From [23]

[d] From [24]

[e] From [25]

[f] From [26]

[g] From [27]

[h] This value was kept fixed during the fits

of the fitted data ($N = 20$) is rather large, in this case, showing that a simple Morse potential is insufficient to give an acceptable quantitative representation of the data. This can also be seen from Fig. 1.

In the following, we compare also the dissociation energy

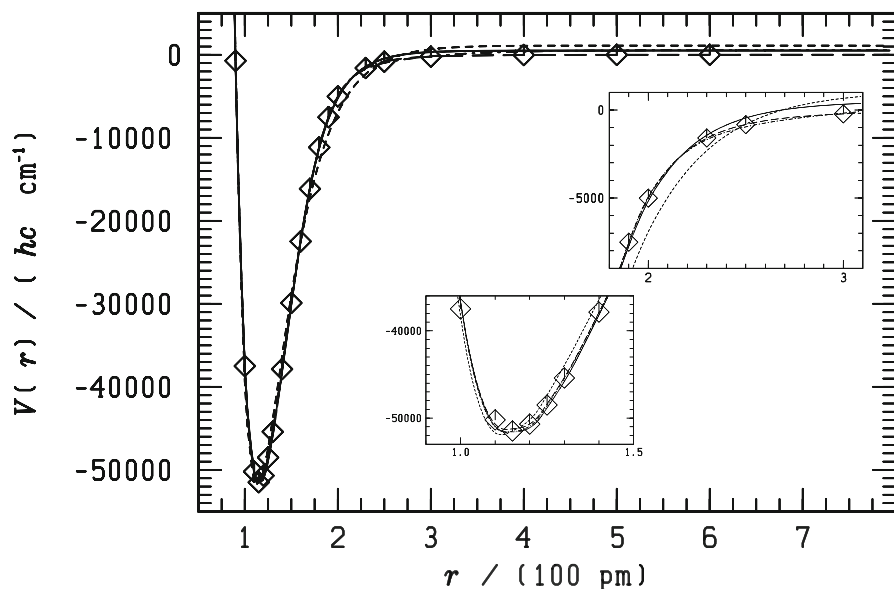$$D_e = V_\infty - V_0 + V_e, \tag{24}$$

Fig. 1 Potential energy functions for the $^2\Pi_{1/2}$ ground state of nitric oxide; r is the NO bond length. The different symbol corresponds to (see also Table 1): *diamond* indicates MRCI energies as described in the text; the value at $r = 600$ pm corresponds to $-129.4980\,E_h$; *dashed lines* original Morse potential; *long dashed lines* modified Morse potential from Eq. (20), unconstrained fit; *dash with dotted lines* modified Morse potential from Eq. (20), constrained fit I (see text); *solid lines* modified Morse potential from Eq. (20), following constrained fit II (see text)

the C_6-coefficient and the values for vibrational band centers $\tilde{\nu}_{n\leftarrow 0}$ (fundamental $n = 1$ and overtones to up to $n = 7$). Theoretical values of the latter are obtained from a numerical solution of the Schrödinger equation for the nuclear motion using a DVR eigensolver reported elsewhere [20]; atomic masses $m_N = 14.00307$ u and m_O = 15.99491 u are used, and the numerical convergence is verified. Experimental and theoretical reference values are given in the first column of Table 1.

We see that the simple Morse potential reproduces reference values too poorly. In the extended version of the Morse potential, the parameter b_s may be varied away from zero, and V_∞ away from V_0; consequently both r_s and r_6 parameters become additional adjustable parameters. The increased flexibility allows, as we see from inspection of Table 1 and Fig. 1, to improve the analytical representation of the potential function considerably, as ΔV_{rms} is decreased by two orders of magnitude. In particular, the rms of deviations to experimental vibrational band centers to up to the 6th overtone,

$$\Delta\tilde{\nu}_{rms} = \sqrt{\frac{1}{7}\sum_{n=1}^{7}\left(\tilde{\nu}_{n\leftarrow 0}^{(exp)} - \tilde{\nu}_{n\leftarrow 0}^{(the)}\right)^2}, \tag{25}$$

is reduced from $561\,\mathrm{cm}^{-1}$, obtained for the original Morse potential, to $5\,\mathrm{cm}^{-1}$. The number of adjustable parameters has hereby been increased from four to eight. We

find that ΔV_{rms} is quite a flat function of the parameter r_6. We prefer thus to fix the value of this parameter to 300 pm. Hence, seven parameters are effectively varied.

The representation of the MRCI energy points with the modified Morse potential allows thus, perhaps fortuitously, for a much better description of the overtone spectrum. However, the dissociation energy obtained from this representation is roughly $10\,\mathrm{kJmol}^{-1}$ ($859\,\mathrm{cm}^{-1}$) lower than predicted from a high level ab initio calculation [21], a deviation 10 times larger than the currently acceptable "chemical accuracy" of $1\,\mathrm{kJmol}^{-1}$.

In a first attempt to improve this energy, we consider $D_{\mathrm{e}} = 52\,348\,hc\,\mathrm{cm}^{-1}$, with D_{e} from Eq. (24) as an additional condition to be satisfied during the adjustment (column "constrained modified Morse potential I" in Table 1). Note that this linear condition among the parameters V_{e}, V_0 and V_{∞} can more simply be implemented by defining, e.g. $V_0 = V_{\mathrm{e}} + V_{\infty} - 52\,348\,hc\,\mathrm{cm}^{-1}$. Here, we used instead the procedure described in Sect. 2.2. As can be seen from the table, parameters change slightly and the dissociation energy can be made to match the reference value. As expected, the rms to the *ab initio* data points increases (from 12 to about $250\,\mathrm{cm}^{-1}$). The quality of the description of the vibrational transitions is quite substantially reduced, too. Also, the C_6 coefficient is two orders of magnitude larger than the reference value.

We may then consider the condition $C_6 = 42\,550\,\text{Å}^6 hc\,\mathrm{cm}^{-1}$, with C_6 from Eq. (22) as an additional constraint. We refrain from reproducing the result here. Instead, we consider as an additional, third constraint the condition

$$\tilde{\nu}_{1\leftarrow 0}^{(\exp)} = \omega_{\mathrm{e}} - 2\,\omega_{\mathrm{e}}x_{\mathrm{e}} \tag{26}$$

where

$$\omega_{\mathrm{e}} = \frac{1}{2\pi\,c}\,a(r_{\mathrm{e}})\sqrt{\frac{2\,V_{\mathrm{e}}}{\mu}} \tag{27}$$

$$\omega_{\mathrm{e}}x_{\mathrm{e}} = \frac{\omega_{\mathrm{e}}^2}{4\,V_{\mathrm{e}}} \tag{28}$$

are the usual spectroscopic constants related to the Morse oscillator, $\tilde{\nu}_{1\leftarrow 0}^{(\exp)} = 1876.1\,\mathrm{cm}^{-1}$ is the experimental value for the fundamental transition, and $\mu = m_{\mathrm{N}}\,m_{\mathrm{O}}/(m_{\mathrm{N}} + m_{\mathrm{O}})$. In Eq. (27), $a(r_{\mathrm{e}}) = a_0\left(1 - b_s\,\arctan\left((r_s/r_{\mathrm{e}})^2 - 2\,r_s/r_{\mathrm{e}}\right)\right)$; the condition Eq. (26) is thus highly non-linear and involves five of the seven adjusted parameters.

Given that the original Morse potential is not expected to provide accurately even the fundamental transition, we replace ad hoc $\tilde{\nu}_{1\leftarrow 0}^{(\exp)}$, in Eq. (26), by $\tilde{\nu}_{1\leftarrow 0}^{(\exp)}/1.005$. Together with the conditions on D_{e} (Eq. (24)), and C_6 (Eq. (22)), this set of three additional constraints is considered in an adjustment of the seven parameters, the result of which is given in column "constrained modified Morse potential II". One sees that the overall rms to the *ab initio* data set is larger than for the less constrained or the unconstrained fits. However, the dissociation energy and the C_6 coefficients now match the reference values and the vibrational transitions are quite well described. Note that, effectively, only four parameters have been varied freely in this last fit, since three additional

conditions among the seven adjusted parameters had to be fulfilled simultaneously. It can be expected that a more flexible analytical representation could help to improve further the theoretical description of the vibrational spectrum.

4 Conclusions

Numerical non linear adjustment procedures are used in natural and engineering sciences to optimize processes or models. One widely used numerical method is the Levenberg-Marquardt algorithm [1,2]. The power of this algorithm is the capability of dynamically switching between quadratic (Gauss-Newton) and linear (gradient descent) methods. This feature is based on an ad hoc use of a parameter dependent curvature matrix A_λ; when the parameter λ is small, the adjustment is local and convergence is quadratic, while when λ is large, convergence is linear and the adjustment is global.

In the present paper, and quite in the spirit of the Levenberg-Marquardt idea, an extension of this algorithm is proposed, that allows for the simultaneous fulfillment of additional constraints via the use of Lagrange multipliers. No formal proof is given here, though, that the extension also permits the switching between the quadratic and linear convergence regimes. Also, as for the original algorithm, the extension proposed here does not a priori guarantee convergence, which can be highly problem and model dependent. In particular, the algorithm will fail, if the curvature matrix, A_λ, or the matrix $\underline{\underline{\Gamma}}$ that is needed to obtain trial Lagrange multipliers become singular. However, from the author's own experience, the algorithm is quite robust.

As an example of an application, the derivation of a modified Morse potential is shown to be possible, where parameters are adjusted to an ensemble of energy points calculated *ab initio* of the nitric oxide molecule, while verifying a certain number of additional constraints. Similar applications of this method have lead to successful determinations of analytical potential energy hypersurfaces of polyatomic molecules in the past [7–9,17,18]. It is conceivable that this rather simple method can be applied in other fields of chemistry and science in general.

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