Fitting of $3D$ Reaction Surface of Three-Atomic System in the Natural Collision Coordinates

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The objective of present investigation to prove the possibility of representation the $3D$ interaction between particles in various reacting three-body systems by analytical function with a set of adjusting parameters in natural collision coordinates. Realization of this idea imply the procedure of fitting of $3D$ numerical data by $3D$ analytical function or more precisely, calculation of adjusting parameters in mentioned analytical function. In the work is used Levenberg-Marquardt algorithm on the basis of which the numerical method is developed. The possibility of implementation of $3D$ fitting with the big accuracy, on the example of reaction $H + H_2$ is shown.

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I. FORMULATION OF THE PROBLEM

Recently as was shown by authors [1] the three-body quantum reactive scattering problem in the curvilinear Natural Collision Coordinates (NCC) system may be reduced to the inelastic single-arrangement problem. Mathematically the problem consists of solution of first-order ordinary differential equation's system. For numerical investigations of this system it is necessary to define full interaction potential between particles in the NCC system (u, v, θ). Here u is a coordinate along the curve of coordinate of reaction $\Im_{if}$, which connects together (in) and (out) scattering asymptotic subspaces, v is a normal to the curve $\Im_{if}$ coordinate, along which the full wave-function is localized, θ is a scattering angle. Recall that usually the reaction potential is constructed by means of $ab-initio$ quantum calculations, after which this numerical data are used for fitting and reconstructing of the analytical form of interaction potential in terms of scaled Jacobi coordinates (q_0, q_1, θ). Now the $3D$ analytical forms are well known for many reaction potentials $V(q_0, q_1, \theta)$. For definition of reaction potential in the NCC system, the coordinate transformations $(q_0, q_1, \theta) \to (u, v, \theta)$ in the expression of potential $V(q_0, q_1, \theta)$ are carried out. We can organize the one-to-one mapping between coordinate systems $(q_0, q_1, \theta) \Leftrightarrow (u, v, \theta)$ in some subspace of intrinsic $3D$ configuration down form the curve $\Im_{if}$. Following the work [2], we can define the curve $\Im_{if}$, which connects (in) and (out) asymptotic channels in plane (q_0, q_1):

$$q_0^c = \frac{a}{(q_1^c - q_{eq}^-)} + bq_1^c + q_{eq}^+, \qquad q_{eq}^- < q_1^c < +\infty, \quad (1)$$

where a and b are some constants. In eq. (1) q_{eq}^- and q_{eq}^+ are the mass-scaled equilibrium bond length of molecules in (in) and (out) channels correspondingly. Note that the variable q_1^c is defined on a part of axis $\bar{q}_1 \in (q_{eq}^-, +\infty)$ and can have only positive values.

Now we can write the inverse transformations from (q_0, q_1) to (u, v):

$$\begin{aligned} q_0(u, v) &= q_0^c(u) - v \sin\phi(u), \\ q_1(u, v) &= q_1^c(u) + v \cos\phi(u), \end{aligned} \quad (2)$$

where the angle $\phi(u)$ is determined from the requirement that the coordinate system (u, v) should be orthogonal:

$$\left.\frac{dq_0^c}{dq_1^c}\right|_{\Im_{ij}} = \cot\phi(u), \qquad \lim_{u \to +\infty} \cot\phi(u) = \left\{\frac{m_A m_C}{m_B M}\right\}^{1/2}, \quad (3)$$

where m_A, m_B and m_C are masses of scattering particles, M is its sum.

The coordinate u describes the translational motion of three-body system between reactant and product channels and is changed along the curve $\Im_{if}$ measured from an initial point u_0. It in particularly can be determined by equation:

$$u = u_0 - \frac{a}{(q_1^c - q_{eq}^-)} + b(q_1^c - q_{eq}^-). \quad (4)$$

Under the numerical modelling of the system of differential equations near the subspace borders a computation error appears. This problem we can solve by fitting a numerical data in the NCC system. In the limits of NCC system, the full interaction potential may be represented in the following kind:

$$V(q_0, q_1, \theta) \equiv U(u, v, \theta) \doteq \sum_j^m U_j(u, v) P_j(\cos\theta), \quad (5)$$

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where $P_j(x)$ is Legendre polynomial and $m < +\infty$. Taking into account the orthogonal property of Legendre polynomials $\int_{-1}^{+1} P_j(x)P_{j'}(x)dx = \frac{2}{2j+1}\delta_{jj'}$ we can find: The full interaction potential between particles may be represented in the following kind:

$$V(q_0, q_1, \theta) \equiv U(u, v, \theta) \doteq \sum_{j}^{m} U_j(u, v) P_j(\cos\theta), \qquad (6)$$

where $P_j(x)$ is Legendre polynomial and $m < +\infty$. Taking into account the orthogonal property of Legendre polynomials $\int_{-1}^{+1} P_j(x)P_{j'}(x)dx = \frac{2}{2j+1}\delta_{jj'}$ we can find:

$$U_j = (j + 1/2) \int_0^{\pi} U(u, v, \theta) P_j(\cos\theta) \sin\theta d\theta, \qquad (7)$$

It is obvious that if the $V(q_0, q_1, \theta)$ are known in the kind of an analytical function or are specified in the form of an numerical array, we can generate $2D$ numerical arrays (databases) and look for its analytical approximation. Based on our experience, it is convenient to present these functions in form:

$$U_j(u, v) = \Big(\sum_{k=0}^{2} A_j^{(k)}(u) v^k \Big) e^{-2\alpha_j(u)v} - B_j(u) e^{-\beta_j(u)v}, \qquad (8)$$

where the functions $A_j^{(k)}(u)$ and $B_j(u)$ provide smooth transition from the bound state ***(AC)*** in the (in) channel to the bound state ***(AB)*** in the (out) channel, ***A***, ***B*** and ***C*** describe the reacting particles. Analyzing the geometrical and topological features of the different energetic surfaces of reactions shows that we can use the following analytical form for these functions:

$$F_j(u) = F_j^{(0)} + \frac{F_j^{(1)} - F_j^{(0)}}{1 + e^{-2\gamma_j u}} + \frac{F_j^{(2)} \gamma_j^2}{(e^{\gamma_j u} + e^{-\gamma_j u})^2}, \qquad (9)$$

where $F_j^{(0)}$, $F_j^{(1)}$, $F_j^{(2)}$, and γ_j are some adjusting parameters and $F_j(u) = (A_j^k(u),\ B_j(u),\ \alpha_j(u),\ \beta_j(u))$.

Thus now the main problem is the elaboration of numerical method for computation of adjusting parameters which would give its a possibility to carry out approximation of a numerical array with the given accuracy.

II. *CHI*-SQUARE FITTING METHOD

There are various methods for fixing adjusting parameters in expressions (7)-(8), the relaxation method, the Newton method, and the modified Newton method [3, 4] et etc. All the mentioned methods are based on the procedure of inverse Jacobian matrix computation with respect to the adjusting parameters. However the direct calculation of the Hessian by means of minimization methods is impossible. For a solution of considered problem in this paper we use nonlinear minimization method.

The minimization methods permit the iterative evaluation of a function and of its gradients. The second essential difference from all previous methods is that all the above methods are based on the linear search or linear minimization. The methods in issue are based on nonlinear procedures with the use of least-squares formalism. The calculation procedure of the gradient and Hessian in the Levenberg-Marquardt method is described in [5].

The j component of decomposition in the expression of full $3D$ reaction potential (3) under the consideration can be represented as:

$$U_j = U_j(\mathbf{u}, \mathbf{v}, \mathbf{C}), \qquad (10)$$

where $\mathbf{C}$ is the vector of adjusting parameters having the dimensions M. The mean-square deviation of the function χ^2 can be determined the following way:

$$\chi_j^2(\mathbf{u}, \mathbf{v}) = \sum_{i=1}^{N} \left[\frac{U_j(u_i, v_i) - U_j(u_i, v_i, \mathbf{C})}{\sigma_i} \right]^2, \qquad (11)$$

(in literature method is called the "chi-square") σ_i-described standard deviation.

The gradient of function χ_j^2 is:

$$\frac{\partial \chi_j^2}{\partial C_k} = -2 \sum_{i=1}^{N} \frac{\left[U_j^i - U_j(u_i, v_i, \mathbf{C})\right]}{\sigma_i^2} \frac{\partial U_j(u_i, v_i, \mathbf{C})}{\partial C_k}, \qquad (12)$$

where $U_j^i \equiv U_j(u_i, v_i)$.

The second derivative is computed as follows:

$$\frac{\partial^2 \chi_j^2}{\partial C_k \partial C_l} = 2 \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \Big[\frac{U_j(u_i, v_i, \mathbf{C})}{\partial C_k} \cdot \frac{U_j(u_i, v_i, \mathbf{C})}{\partial C_l} - \left[U_j^i - U_j(u_i, v_i, \mathbf{C})\right] \frac{\partial^2 U_j(u_i, v_i, \mathbf{C})}{\partial C_k \partial C_l} \Big]. \qquad (13)$$

Here we introduce some designations:

$$\alpha_k = \frac{1}{2} \frac{\partial \chi_j^2}{\partial C_k}, \qquad \beta_{kl} = \frac{1}{2} \frac{\partial^2 \chi_j^2}{\partial C_k \partial C_l}, \qquad (14)$$

From (14) we obtain the relation:

$$\alpha_k = \sum_{l=1}^{M} \beta_{kl} \delta C_l, \qquad (15)$$

where C_l satisfy a system of linear equations:

$$\delta C_l = constant \cdot \alpha_l, \qquad (16)$$

The second partial derivatives are computed by formula:

$$\beta_{kl} = \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \left[\frac{\partial U(u_i, v_i, \mathbf{C})}{\partial C_k} \frac{\partial U(u_i, v_i, \mathbf{C})}{\partial C_l} \right]. \qquad (17)$$

So, here all necessary formulas for closed computation of adjusting parameters in $3D$ model potential (4)-(9) are presented. The adjusting parameters in our previous article [6] which about a reaction surface of collinear collision, have been computed using the Levenberg-Marquardt's nonlinear optimization method [5].

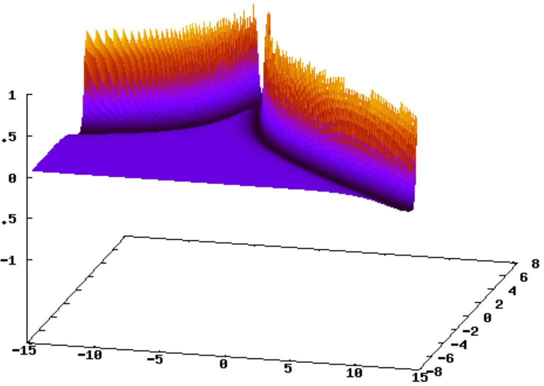

FIG. 1: Reaction surface of collinear collision $H+H_2$ by using quantum-chemical *ab initio* calculations.

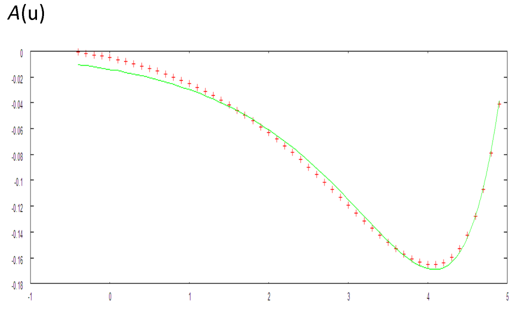

FIG. 2: The behavior of modified Echart function for a reaction surface of collinear collision.

III. FITTING OF 3D REACTION SURFACE $H+H_2$ SYSTEM

The approximation of numerical data with an analytical surface is done by applying several numerical methods, mainly the Levenberg-Marquardt algorithm and Fourier transformation. The first step in this process is analysis of the numerical data and finding an analytical function that visually matches the numerical data. In the case of collinear surface fig. 1 the following scenario has been followed. First, a pre-calculated numerical array of reaction surface points is considered as a set of data points over (u,v) plain. The surface is sliced over the u axis and the graphs of slices are analyzed. In the process of analyzing of slices it was pointed out, that each slice can be approximated using the simple version of generalized Mors potential (see (8)):

$$U_{GM}(u,v)=A(u)\Big[e^{-2\alpha(u)[v-v_0(u)}-2e^{-\alpha(u)[v-v_0(u)}\Big]. \tag{18}$$

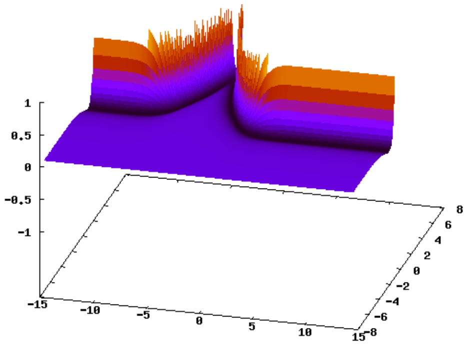

FIG. 3: The reaction surface of collinear collision $H+H_2$ constructed by analytical formula (18) after fixing of adjusting parameters.

For the fitting to be more accurate the following modifications on the numerical surface are applied. First, the surface is analyzed to find the optimal value of $\triangle z$ shift along the z axis (potential energy axis), for which $z\to 0$ when $v\to -\infty$ for any value of u. After that, on each slice, only negative values are considered for fitting (as it was shown by a series of numerical experiments, this gives the most accurate results). It's also worth mentioning, that the points of our interest lye in the ”flute”, and are localized near the ”peak” in fig. 2 (that is, approximately, in the range $u\in[-7,+7]$), that's why the numerical experiment aims to produce the best results in that area. The result of fitting the slices produces a 2D numerical array, that contains values for parameters $A(u)$, and for each value of u. Further, these sets of points are fitted (again using Levenberg-Marquardt algorithm) to the following modified Echart function:

$$A(u)=a+\frac{b-a}{1+e^{\gamma(u-u_0)}}+de^{-\alpha(u-u_0)^2} +\frac{c\gamma^2}{\left(e^{\gamma(u-u_0)}-e^{-\gamma(u-u_0)}\right)^2}, \tag{19}$$

where a,b,c,d,u_0 and γ are some adjusting parameters. Finding an approximated analytical representation of Mors potential parameters gives us an analytical approximation of reaction surface. This analytical representation of surface (fig. 3) gives a value of relative error of not more than 5 percent, at maximum in the region which important for a elementary atom-molecular processes (fig. 4). The analysis of input data shows, that some inaccuracy in it can lead to this error. Hence, further reducing of relative error can be done by further refinement of input data in the first step. The non-collinear problem requires finding an analytical representation of (7) surface (using numerical values of that we already

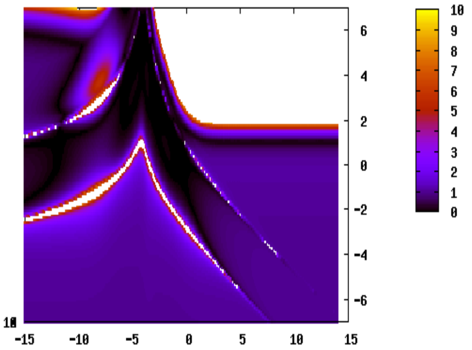

FIG. 4: The relative error between figures 1 and 3.

have), which is later used in (5) formula. As the numerical experience have proved, the values of m that are bigger than 8 give a variance in potential values less than 1 percent, the potential surface for non-collinear reaction can be calculated using above mentioned decomposition by Legendre polynomials with high degree of accuracy taking into account the first 8 Legendre polynomials.

For analytical approximation of numerically calculated U_j surface, again, the surface is sliced along its u axis, and the slices are first analyzed visually. During that process, it was inspected, that some of the slices are "well behaved" while others follow an irregular pattern. For being able to deal with these irregularities, it was decided to approximate the slices using Fourier transformations. The Fourier polynomial of degree 40 showed a good approximation in the surface area of our interest (the peak and its surroundings).

IV. ACKNOWLEDGMENTS

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