

FITTING: A Portal to Fit Potential Energy Functionals to *ab initio* Points

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Abstract. The design and the implementation in a Grid environment of an Internet portal devoted to best fitting potential energy functionals to *ab initio* data for few body systems is discussed. The case study of a generalized LEPS functional suited to fit reactive three body systems is discussed with an application to the NO₂ system.

Keywords: webportal, fitting, *ab initio* calculations, potential energy surfaces, multiscale simulations.

1 Introduction

Thanks to recent progress in computing technologies and network infrastructures it has become possible to assemble realistic accurate molecular simulators on the Grid. This has allowed us to develop a Grid Enabled Molecular Simulator (GEMS) [1,2,3,4] by exploiting the potentialities of the Grid infrastructure of EGEE [5]. The usual preliminary step of molecular approaches to chemical problems is the construction of a suitable potential energy surface (PES) out of the already available theoretical and experimental information on the electronic structure of the system considered. In the first prototype production implementation of GEMS, GEMS.0 [6], it is assumed that available information on the electronic structure of the system considered is formulated as a LEPS [7] PES. Unfortunately, extended use in dynamics studies have singled out the scarce flexibility of the LEPS functional in describing potential energy surfaces having bent (non collinear) minimum energy paths to reaction.

To progress beyond the limits of GEMS.0 an obvious choice was, therefore, not only to derive the value of the LEPS parameters from *ab initio* estimates of the electronic energies but also to add further flexibility to the LEPS functional form. For the former goal an Internet portal, SUPSIM, has been assembled as already discussed in the literature [8]. In the present paper we discuss the latter goal of making more general the LEPS functional. The paper deals in section 2 with a generalization of the functional representation of the LEPS and in section 3 with the assemblage of an Internet portal, called FITTING, devoted to the fitting of the LEPS to *ab initio* data. Finally, in section 4 the case study of the N + O₂ system is discussed.

2 A Generalization of the LEPS Potential

Most often molecular potentials are expressed as a sum of the various terms of a many body expansion [9,10]. In the case of three-atom systems such a sum is made by three one-body, three two-body and one three-body terms as follows:

$$\begin{aligned}
 V(r_{AB}, r_{BC}, r_{AC}) = & V_A^{(1)} + V_B^{(1)} + V_C^{(1)} + \\
 & V_{AB}^{(2)}(r_{AB}) + V_{BC}^{(2)}(r_{BC}) + V_{AC}^{(2)}(r_{AC}) + \\
 & V_{ABC}^{(3)}(r_{AB}, r_{BC}, r_{AC})
 \end{aligned} \tag{1}$$

where the $V^{(1)}$ terms are the one-body ones (taken to be zero for atoms in ground state) while $V^{(2)}$ and $V^{(3)}$ terms are the two- and three-body ones and are usually expressed as polynomials in the related internuclear distances r_{AB} , r_{BC} and r_{AC} . These polynomials are damped by proper exponential-like functions of the related internuclear distances in order to vanish at infinity. More recently, use has been also made of Bond Order (BO) variables [11,12]. The n_{ij} BO variable is related to the internuclear distance r_{ij} of the ij diatom as follows:

$$n_{ij} = \exp[-\beta_{ij}(r_{ij} - r_{eij})] \tag{2}$$

In Eq. 2 β_{ij} and r_{eij} are adjustable parameters (together with D_{ij}) of the best fit procedure trying to reproduce theoretical and experimental information of the ij diatomic molecule using the model potential

$$V_{ij}^{(2)}(r_{ij}) = D_{ij}P(n_{ij}) \tag{3}$$

where $P(n_{ij})$ is a polynomial in n_{ij} . The LEPS functional can be also written as a sum of two and three body BO terms. The usual LEPS can be written, in fact, as

$$\begin{aligned}
 V(r_{AB}, r_{BC}, r_{AC}) = & {}^1E_{AB} + {}^1E_{BC} + {}^1E_{AC} - J_{AB} - J_{BC} - J_{AC} \\
 & - \sqrt{J_{AB}^2 + J_{BC}^2 + J_{AC}^2 - J_{AB}J_{BC} - J_{AB}J_{AC} - J_{BC}J_{AC}}
 \end{aligned} \tag{4}$$

where the J_{ij} terms are formulated as:

$$J_{ij} = \frac{1}{2}({}^1E_{ij} - a_{ij}{}^3E_i) \tag{5}$$

with a_{ij} being an adjustable parameter (often expressed as $(1 - S_{ij})/(1 + S_{ij})$, where S_{ij} is the Sato parameter) and 1E and 3E being second order BO polynomials of the Morse

$${}^1E_{ij} = D_{ij}n_{ij}(n_{ij} - 2) \tag{6}$$

and antiMorse

$${}^3E_{ij} = \frac{D_{ij}}{2}n_{ij}(n_{ij} + 2) \tag{7}$$

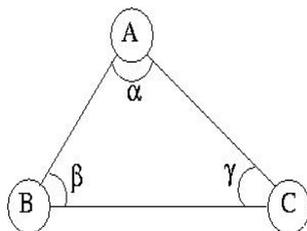


Fig. 1. A pictorial view of an atom-diatom system

type, respectively. Because of the choice of truncating the polynomial of Eq. 3 to the second order, β_{ij} , r_{eij} and D_{ij} correspond to the force constant, the equilibrium distance and the dissociation energy of the ij diatom, respectively. The two-body terms correspond therefore to the three ${}^1E_{ij}$ Morse potentials. The three body component $V^{(3)}$ of the potential is then worked out by subtracting the three diatomic terms to the *ab initio* data. The resulting values of the three body term are then fitted by optimizing the value of the a_{ij} parameters which are taken to be constant in the usual LEPS functional. In our generalization, as proposed some years ago by Takayanagi and Sato [13] and by Brown et al. [14], the Sato variables S_{ij} are made depend on the angle opposed to the bond considered (respectively γ , α and β as sketched in Fig. 1) to bear a kind of three body connotation. Accordingly, the a_{ij} coefficients of eq. 5 can be formulated as depending from the angle opposite to the ij diatom as follows:

$$a_{ab} = c_{\gamma 1} + c_{\gamma 2} \cos \gamma + c_{\gamma 3} \cos^2 \gamma + c_{\gamma 4} \cos^3 \gamma + c_{\gamma 5} \cos^4 \gamma \quad (8)$$

$$a_{bc} = c_{\alpha 1} + c_{\alpha 2} \cos \alpha + c_{\alpha 3} \cos^2 \alpha + c_{\alpha 4} \cos^3 \alpha + c_{\alpha 5} \cos^4 \alpha \quad (9)$$

$$a_{ac} = c_{\beta 1} + c_{\beta 2} \cos \beta + c_{\beta 3} \cos^2 \beta + c_{\beta 4} \cos^3 \beta + c_{\beta 5} \cos^4 \beta \quad (10)$$

3 The Internet Portal Structure

To handle the fitting procedure in an efficient way we developed a web interface (called FITTING) acting as an Internet portal and ensuring the advantages typical of a Grid based environment. This choice was motivated by the wish of being independent from the operating system available on the user side and therefore being able to modify and upgrade the software without the participation of the user. Other motivations were the user friendliness and the ubiquitous usability of the web graphical interfaces. For this purpose we created a cross-browser site using only server-side technologies. Accordingly, the end-user can utilize the FITTING web GUI (Graphical User Interface) by making use only of a W3-Compliant web browser [15]. The related Web Environment was implemented using the following elements:

1. A dynamic web server, based on the Apache Web [16] server containing the PHP4 module [17].
2. An RDBMS (MySQL [18] in our case) that handles the user data and supports the authentication phase.

The Portal was developed and tested using GPL Software and FreeSoftware (namely the Apache Web Server 1.3.32 and MySQL 4.1.3 powered by FreeBSD 5.4).

Because of the complexity of the workflow of FITTING, we produced a set of dynamically generated pages according to the following scheme:

1. registration of the user
2. selection of the atoms and the functional form
3. specification of the *ab initio* data
4. specification of additional *ab initio* data
5. generation of the best-fit parameters

These pages take care of managing the execution of the computational procedure by the Web server and help the user to define the input parameters of the fitting calculation through the GUI.



FITTING
on demand

[Register](#)
[Documentation](#)
[FAQ](#)
[Info](#)
[Contact](#)

User info

You are logged as

Username: demo

Email: email@email.com

Account information: demo user account

[\(Logout\)](#)

Select system atoms:

Select the system:

Atom:

Select the functional form:

LEPS (about the LEPS method)

Bond Order [not implemented]

Job info

Job ID: 685308fab5ee7906416e8bebb9f71177

System: none

Function: none

Diatomic file:

Triatomic file:

[\(Clean job\)](#)

Fig. 2. Screenshot of a System configuration page of FITTING

As a first step the user registers through the GUI when first accessing the portal. After the verification of the identity, the user is assigned an account and the associated login and password. At this point the user can access the portal and run the fitting procedure. Because of the multiuser environment adopted, multiple requests to the web server are dealt using the Session support (enabled in PHP by default).

In the second step, the user selects, using the same GUI, the atoms composing the triatomic system considered and the fitting functional form to be used (see Fig. 2). In the third step, the server creates a dynamic web page which prompts the user to supply the name of the file of the *ab initio* data to be used during the

Fig. 3. Screenshot of a System configuration page of FITTING

calculation. In the fourth step, the same page allows the user to insert new *ab initio* data. The page asks the files of diatomic *ab initio* data (from one to three depending on the symmetry of the investigated system), as illustrated in Fig. 3. These files contain the *ab initio* values arranged in a two column format (the first column contains the value of the internuclear distance while the second column contains the corresponding value of the diatomic *ab initio* potential energy). The page prompts also the request for a file containing the *ab initio* triatomic data. This file contains in the first three columns the value of the three internuclear distances and in the fourth column the value of the corresponding triatomic *ab initio* potential energy. It is possible also to introduce other potential energy values to enforce some specific features of the potential or to constrain some input parameters. These choices depend on the functional form adopted for the fitting.

Finally, the best fit is carried out using the LMDER routine of MINPACK [20] which is based on an improved version of the Levenberg-Marquardt method [21] which solves non linear least squares problems. The calculated best-fit values are inserted, together with the already determined diatomic parameters, in the automatically generated source of the corresponding Fortran routine.

4 The N + O₂ Case Study

As already mentioned, in order to test the developed procedure, we considered the N + O₂ system for which a large set of accurate *ab initio* electronic energy values (calculated at both CASSCF and MR-SDCI level) are available from the literature [22]. CASSCF calculations were performed at various fixed values of the N $\dot{O}O$ β attack angle ($\beta = 135^\circ, 110^\circ, 90^\circ, 70^\circ, 45^\circ$). For each value of β , a matrix of geometries corresponding to regularly spaced values of $\rho_\beta = \sqrt{n_{NO}^2 + n_{OO}^2}$

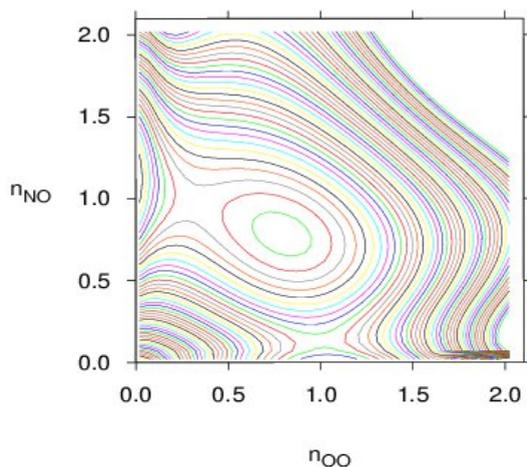


Fig. 4. Isoenergetic contours, plotted as a function of the n_{NO} (y axis) and n_{OO} (x axis) BO variables at $\beta = 135^\circ$. Energy contours are drawn every 3 Kcal/mol.

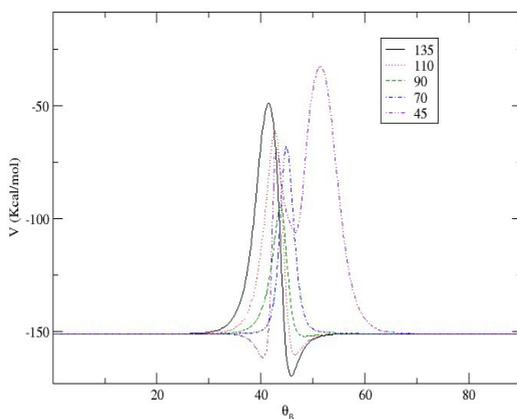


Fig. 5. Minimum energy paths of the generalized LEPS calculated at $\beta = 135^\circ, 110^\circ, 90^\circ, 70^\circ$ and 45° plotted as a function of θ_β

(the radius of the polar version of the BO coordinates) and of the associated $\theta_\beta = \sin^{-1}(n_{NO}/\rho_\beta)$ angle were considered for the *ab initio* calculations. Calculated CASSCF values were scaled to the MR-CI energies at the minimum of the fixed θ_β cut of the *ab initio* values.

Following the above mentioned procedure the asymptotic cuts of the *ab initio* points were fitted first to Morse diatomic potentials and the best-fit values of the parameters were used to compute the three body component of the potential. The computed three body component was then fitted using both three constant

Sato parameters (as in the usual extended LEPS functional) and the fifteen coefficients of our generalized angular dependent LEPS given in eqs. 8-10. Due also to the particular structure of the NO₂ PES we found the extended LEPS based on three constant Sato parameters to be scarcely flexible and to lead to a root mean square deviation of about 3.0 eV. Moreover, the isoenergetic contour plots in general poorly reproduce the *ab initio* values and have a wrong topology.

A much better reproduction of the *ab initio* data was obtained when using the generalized LEPS (the one which has angle dependent Sato parameters) which gave a root mean square deviation half that of the extended LEPS. This result, though still preliminary, can be considered highly satisfactory due to the fact that a non negligible fraction of the deviation is due to the already mentioned particular structure of the NO₂ PES whose two body component is not well reproduced by a Morse functional. The definitely better quality of the fitting carried out using the generalized LEPS functional can also be appreciated by inspecting the isoenergetic contours drawn at different fixed values of β and comparing them with the *ab initio* values. In particular, they not only always reproduce the topology of the fixed angle *ab initio* values (see for example the contours calculated at $\beta=135^\circ$ shown in Fig. 4) but they also reproduce in a quasi quantitative fashion the corresponding minimum energy paths (MEP). MEP plots (see Fig. 5) show, in fact, the large variability of the MEP and the peculiar double barrier structure of the MEP at some values of the approaching angle. Moreover, in agreement with the structure of the *ab initio* data we found also that when moving from large β values to 110° the barrier lowers to rise again in going from $\beta=110^\circ$ to $\beta=70^\circ$.

5 Conclusions

In this paper the use of angle dependent LEPS functionals is proposed out and the development of an Internet portal called FITTING, aimed at inserting its fitting to *ab initio* data as part of the Grid Enabled Molecular Simulator (GEMS) implemented within EGEE, is illustrated. Using FITTING it is now possible to perform *ab initio* simulations starting from the generation of the potential energy values (for which the portal SUPSIM is already available) and continuing with their representation by a proper functional form to be used in dynamical calculations. This completes the workflow of GEMS for establishing a service of validation of LEPS potentials. Future work will be concerned with a further generalization of the angle dependent LEPS for its use as a three body component of force fields used in molecular dynamics.

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