New Potential Energy Function for Four-Atom Reactions. Application to OH + H_2

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LAGROBO is a model for fitting analytical potential energy surfaces (PES) in which the potential function is expressed as a many-process expansion of rotating bond order (ROBO) potentials. The model is developed in bond order (BO) coordinates and shows several advantages. In particular, it can be used to make PESs for chemical reactions for which only limited ab initio information is available. Furthermore, it ensures a smooth potential surface and can describe all the different arrangement channels in a many-atom system. So far the LAGROBO model has been applied to three-atom systems. We report the formulation of the model for four-atom reactions. As an example, an analytical PES for the OH + H_2 system has been assembled.

1. Introduction

In the quantum mechanical treatment of molecular collisions, the electronic and nuclear parts of the Schrödinger equation are solved separately via the Born−Oppenheimer approximation. First, the electronic part is solved for a representative sample of geometrical configurations of the nuclei in space. The electronic potential energies so obtained are subsequently interpolated by a function depending on the coordinates that describe the relative positions of the nuclei. Such a function is called the Born−Oppenheimer potential energy surface (PES). Finally, the nuclear Schrödinger equation is solved, using the PES, to derive the quantities that characterize the molecular collision. Therefore, the construction of a reliable PES that accurately maps the solutions of the electronic Schrödinger equation is one of the three key steps in the theoretical study of elementary chemical processes.

Recently a new approach has been developed, called direct dynamics,[1] in which the use of a PES is replaced by directly computing the electronic potential energies as they are needed, so that the task of fitting a PES is removed. However, this approach presents some disadvantages. Often, calculated potential energies must be skilfully corrected before being used since ab initio calculations tend to give biased results for systems with more than a few electrons. Also, calculating the potential energy (and its derivatives, for quasiclassical trajectory calculations) from a closed function is computationally much cheaper than carrying out electronic structure calculations. Thus, it is generally more convenient to carry out accurate, high-quality ab initio calculations only once and fit the potential to a function rather than perform such calculations over and over, necessarily with a cheaper and less accurate method. For these reasons it is expected that the need of fitting PESs will remain in the future, in particular when dealing with heavy atoms.

The choice of functions to fit PESs is not an easy task. Any suitable function must gather several important characteristics. For example, it must correctly reproduce the properties of the whole system and of all of its fragments, it must behave reasonably in configurations for which there is no information about the potential energy, it must respect the symmetry of the system if such is the case, and it must connect smoothly the strong interaction region with the reagents and products regions. Also, it is very desirable that the function is not only suitable for one particular system, but has general applicability. Due to these constraints, the number of functions for fitting PESs for three-atom systems is limited. Among the methods used we can recall spline interpolation,[2] Shepard interpolation,[3,4] distributed approximating functionals (DAF),[5] London−Eyring−Polanyi−Sato (LEPS),[6] diatomics-in-molecules (DIM),[7] rotated potentials,[8] many-body expansions (MBE),[9] double many-body expansions (DMBE),[10] reproducing kernel Hilbert spaces (RKHS),[11] and reaction path functions.[12]

Recently a new PES model has been introduced for three-atom reactions, called LAGROBO (largest angle generalization of rotating bond order).[13] This model is based on a many-process approach and is developed using bond order (BO) coordinates.[14] The LAGROBO model has been successfully applied to several different three-body reactions: N + N_2 and H + H_2,[15] O(^{1} D) + HCl,[16] Li + FH,[13] O(^{1} D) + CF_3 Br,[17] and O(^{1} D) + HBr.[18]

When the PES for a four-atom system has to be constructed, the difficulty in finding a suitable function increases dramatically because of the larger dimensionality of the system (six coordinates are required instead of three for three-atom systems). Only the many-body expansion approach has been successful to some extent in fitting PESs for four-atom systems.[9] However, the many-body expansion is much more difficult to apply in the four-atom case than in the three-atom case.

In this article we report on the extension of the LAGROBO model to make it suitable for fitting PESs for four-atom systems while keeping the advantages that the model shows in the three-atom case. The extended LAGROBO model has been applied in the first instance to construct a PES for the benchmark reaction OH + H_2 → H_2O + H.

2. The ROBO Model for Four-Atom Systems

Like in the three-atom case,[13] the LAGROBO model of the PES for four-atom reactions is expressed as a many-process expansion of rotating bond order (ROBO) reaction channel potentials. This section is devoted to illustrate the formulation of the ROBO potentials for four-atom systems. The many-process expansion will be treated in section 3.

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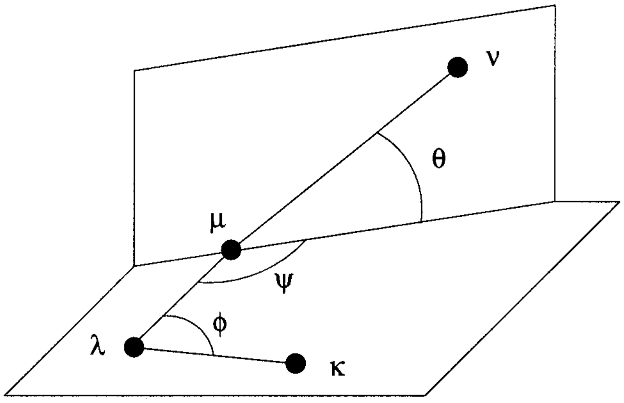

Figure 1. Definition of the $r_{\kappa\lambda}$, $r_{\lambda\mu}$, $r_{\mu\nu}$, ϕ, ψ, and θ coordinates in a four-atom system.

Let A, B, C, and D be the atoms of the system. The ROBO function gives the potential energy along a rearrangement channel such as, for example, A + BCD $\rightleftharpoons$ AB + CB $\rightleftharpoons$ ABC + D. In the remaining part of this section, for the sake of generality, we will use the labels κ, λ, μ, and ν to designate any possible permutation of the atoms A, B, C, and D in the rearrangement channel described by the ROBO potential energy function.

2.1. Coordinates. To describe the configuration of four atoms in space, six coordinates are required. The coordinates used in the formulation of the ROBO function dealing with the $\kappa + \lambda\mu\nu \rightleftharpoons \kappa\lambda + \mu\nu \rightleftharpoons \kappa\lambda\mu + \nu$ process are directly related to the internuclear distances $r_{\kappa\lambda}$, $r_{\lambda\mu}$, and $r_{\mu\nu}$ and to the angles ϕ, ψ, and θ, where ϕ is the angle between $r_{\kappa\lambda}$ and $r_{\lambda\mu}$; ψ is the angle between $r_{\lambda\mu}$ and the projection of $r_{\mu\nu}$ on the plane defined by the atoms κ, λ, and μ; θ is the angle between that same plane and $r_{\mu\nu}$ (see Figure 1). The angle between $r_{\lambda\mu}$ and $r_{\mu\nu}$ is called ϵ. The ranges of the angles are $0 \le \phi \le \pi$, $0 \le \psi \le 2\pi$, $0 \le \theta \le \pi/2$, and $0 \le \epsilon \le \pi$. The out-of-plane angle θ ranges between 0 and $\pi/2$ instead of $-\pi/2$ and $\pi/2$ because of the symmetry of the potential energy field with respect to the $\kappa\lambda\mu$ plane. Therefore, any configuration with negative θ can be mirrored to its respective symmetric configuration with positive θ.

The formulation of the ROBO function is developed in bond order (BO) coordinates. The concept of BO was first introduced by Pauling in 1947.[20] The definition of the BO coordinate n_{ij} for the *ij* diatom is:

$$n_{ij} = \exp[-\beta_{ij}(r_{ij} - r_{\mathrm{eq}ij})] \tag{1}$$

where r_{ij} is the internuclear distance and $r_{\mathrm{eq}ij}$ is the equilibrium internuclear distance. β_{ij} is a parameter related to the bond strength of the diatom, defined as:[21]

$$\beta_{ij} = \omega_{\mathrm{e}ij}\left(\frac{\pi\mu_{ij}}{D_{ij}}\right)^{1/2}$$

where ω_{eij} is the harmonic constant, μ_{ij} is the reduced mass, and D_{ij} is the dissociation energy of the diatom. The BO coordinate takes the values n_{ij}=0 when the atoms are infinitely separated ($r_{ij} = \infty$) and $n_{ij} = \exp(\beta r_{\mathrm{eq}ij})$ when the atoms collapse ($r_{ij} = 0$). Thus, the infinite domain of existence of the physical coordinates is mapped into a finite domain of the BO coordinates. The equilibrium distance in BO coordinates is $n_{ij} = 1$ for any *ij* diatom. The Morse potential, which is a good approximation to the potential of a diatomic molecule, becomes a simple second degree polynomial when expressed in BO coordinates:

$$V(n_{ij}) = D_{ij}(n_{ij}^2 - 2n_{ij}) \tag{2}$$

For the four-atom system $\kappa\lambda\mu\nu$ the internuclear distances $r_{\kappa\lambda}$, $r_{\lambda\mu}$, and $r_{\mu\nu}$ can be expressed as BO coordinates $n_{\kappa\lambda}$, $n_{\lambda\mu}$, and $n_{\mu\nu}$, provided that the β and r_{eq} parameters of each diatom are known. The BO coordinates can be subsequently transformed into the spherical BO coordinates ρ, α, and σ as follows:

$$\begin{gathered}\rho = (n_{\kappa\lambda}^2 + n_{\lambda\mu}^2 + n_{\mu\nu}^2)^{1/2} \\ \alpha = \arctan\left(\frac{n_{\mu\nu}}{n_{\kappa\lambda}}\right) \\ \sigma = \arccos\left(\frac{n_{\lambda\mu}}{\rho}\right)\end{gathered} \tag{3}$$

The ϕ, ψ, and θ angles are scaled,

$$\begin{gathered}\phi' = 2\pi - 2\phi \\ \psi' = 2\psi - 2\pi \\ \theta' = 4\theta\end{gathered}$$

and likewise transformed into spherical coordinates:

$$\begin{gathered}\tau = (\phi'^2 + \psi'^2 + \theta'^2)^{1/2} \\ \delta = \arctan\left(\frac{\psi'}{\theta'}\right) \\ \gamma = \left(\frac{\phi'}{\tau}\right)\end{gathered} \tag{4}$$

The formulation of the ROBO function is developed using the set of coordinates (ρ,α,σ,τ,δ,γ). The domains of existence of these coordinates are

$$\begin{gathered}0 \le \rho \le \exp[(2\beta_{\kappa\lambda}r_{\mathrm{eq}\kappa\lambda}) + \exp(2\beta_{\lambda\mu}r_{\mathrm{eq}\lambda\mu}) + (2\beta_{\mu\nu}r_{\mathrm{eq}\mu\nu})]^{1/2} \\ 0 \le \alpha \le \pi/2 \\ 0 \le \sigma \le \pi/2 \\ 0 \le \tau \le 2\pi\sqrt{3} \\ 0 \le \delta \le \pi/2 \\ 0 \le \gamma \le \pi/2\end{gathered}$$

The ρ, α, and σ coordinates are related to the size of the four-atom system: ρ describes the overall size of the system, whereas α and σ describe the relative sizes of the $r_{\kappa\lambda}$, $r_{\lambda\mu}$, and $r_{\mu\nu}$ internuclear distances. If $\rho = 0$, for any value of the remaining coordinates, the atoms are infinitely separated from one another and there is no interaction energy. The larger ρ is, the closer the atoms are, and if ρ reaches its maximum value, the four atoms collapse at the same point. The τ, δ, and γ coordinates relate to the orientation of the atoms. If $\tau = 0$ the four atoms are in collinear configuration, whatever the values of the other coordinates. As τ gets larger the configuration is increasingly out of collinearity. The δ and γ coordinates reflect the relative magnitude of ϕ, ψ, and θ for bent configurations.

2.2. Formulation. The ROBO potential for the $\kappa + \lambda\mu\nu \rightleftharpoons \kappa\lambda + \mu\nu \rightleftharpoons \kappa\lambda\mu + \nu$ process is formulated as a radial function multiplied by an angular function plus an interaction term.

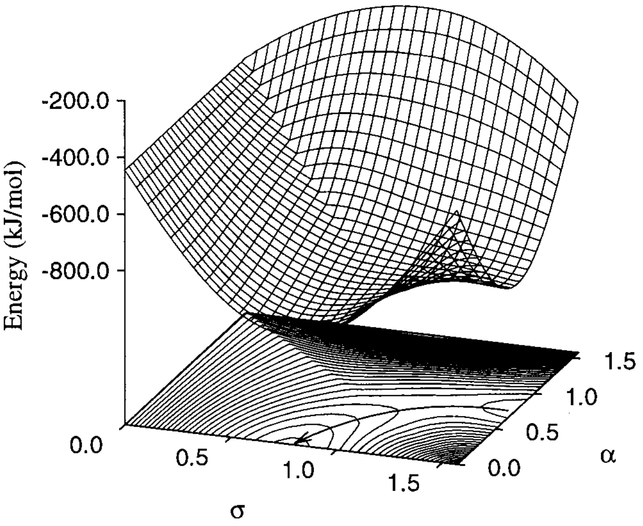

Figure 2. Minimum energy surface $D(\alpha,\sigma;\tau,\delta,\gamma)$ of the OH + H_2 LAGROBO PES plotted against α and σ at fixed values of τ, δ, and γ corresponding to the transition state. The minimum energy path from OH + H_2 to H_2O + H is indicated in the contour map by an arrow.

$$V^{\mathrm{ROBO}}(\rho,\alpha,\sigma,\tau,\delta,\gamma) = F(\rho;\alpha,\sigma,\tau,\delta,\gamma)D(\alpha,\sigma;\tau,\delta,\gamma) + I(n_{\kappa\nu}, \bar{n}) \tag{5}$$

The radial function $F(\rho;\alpha,\sigma,\tau,\delta,\gamma)$ contains the dependence of the ROBO function along the radial coordinate ρ. It also depends parametrically on the other coordinates. Analogous to the Morse potential in BO coordinates (2), the radial function is given as a second-degree polynomial of ρ:

$$F(\rho;\alpha,\sigma,\tau,\delta,\gamma) = -\frac{\rho^2}{\rho_0(\alpha,\sigma;\tau,\delta,\gamma)^2} + \frac{2\rho}{\rho_0(\alpha,\sigma;\tau,\delta,\gamma)} \tag{6}$$

At $\rho = 0$ the radial function takes the value 0 (the zero potential energy of the PES is chosen to be that of the full dissociation configuration $\kappa + \lambda + \mu + \nu$) and it has a maximum at $\rho = \rho_0(\alpha,\sigma;\tau,\delta,\gamma)$, where it takes the value 1. This polynomial has opposite sign to that of the Morse polynomial (2) (i.e., it has a maximum rather than a minimum) because the due negative sign is provided by the angular function by which it is multiplied.

The angular function $D(\alpha,\sigma;\tau,\delta,\gamma)$ depends on the angular coordinates α and σ and, parametrically, on τ, δ, and γ. The angular function is the minimum energy surface along the α and σ coordinates and it is situated at $\rho = \rho_0(\alpha,\sigma;\tau,\delta,\gamma)$ for any fixed orientation determined by τ, δ, and γ. The minimum energy surface links the transition state, in the strong interaction region, and the asymptotic states atom + triatom, atom + atom + diatom, and diatom + diatom. The asymptotic configurations $\kappa\lambda + \mu + \nu$, $\kappa\lambda + \mu\nu$ and $\kappa + \lambda + \mu\nu$ are located at the points ($\alpha = 0$, $\sigma = \pi/2$), ($\alpha = \pi/4$, $\sigma = \pi/2$), and ($\alpha = \pi/2$, $\sigma = \pi/2$), respectively. The configuration $\kappa + \lambda\mu + \nu$ is located at $\sigma = 0$ for any value of α. The $D(\alpha,\sigma;\tau,\delta,\gamma)$ function is plotted in Figure 2 against the α and σ coordinates for τ, δ, and γ fixed. Since the zero potential energy has been chosen to be at the full dissociation configuration the minimum energy surface must have negative value all over the (α,σ) plane.

The $\rho_0(\alpha,\sigma;\tau,\delta,\gamma)$ function gives the value of the radial coordinate at which the minimum energy surface $D(\alpha,\sigma;\tau,\delta,\gamma)$ is located for all the asymptotic configurations and the strong interaction region. The $\rho_0(\alpha,\sigma;\tau,\delta,\gamma)$ function is plotted in Figure 3.

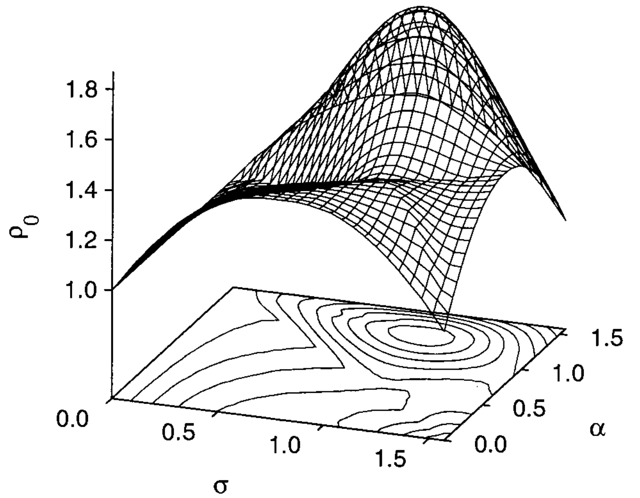

Figure 3. Radial coordinate $\rho_0(\alpha,\sigma;\tau,\delta,\gamma)$ of the OH+H_2 LAGROBO PES plotted against α and σ at fixed values of τ, δ, and γ corresponding to the transition state.

For any value of τ, δ, and γ and for whatever four-atom system, the values of the $D(\alpha,\sigma;\tau,\delta,\gamma)$ and $\rho_0(\alpha,\sigma;\tau,\delta,\gamma)$ functions at the atom + atom + diatom and diatom + diatom configurations are

$$D(\alpha = \text{any}, \sigma = 0; \tau,\delta,\gamma) = -D_{\lambda\mu}$$
$$D(\alpha = 0, \sigma = \pi/2; \tau,\delta,\gamma) = -D_{\kappa\lambda}$$
$$D(\alpha = \pi/4, \sigma = \pi/2; \tau,\delta,\gamma) = -D_{\kappa\lambda} - D_{\mu\nu}$$
$$D(\alpha = \pi/2, \sigma = \pi/2; \tau,\delta,\gamma) = -D_{\mu\nu}$$
$$\rho_0(\alpha = \text{any}, \sigma = 0; \tau,\delta,\gamma) = 1$$
$$\rho_0(\alpha = 0, \sigma = \pi/2; \tau,\delta,\gamma) = 1$$
$$\rho_0(\alpha = \pi/4, \sigma = \pi/2; \tau,\delta,\gamma) = \sqrt{2}$$
$$\rho_0(\alpha = \pi/2, \sigma = \pi/2; \tau,\delta,\gamma) = 1$$

where D_{ij} is the dissociation energy of the *ij* diatom.

For the triatom + atom asymptotic configurations, $\kappa\lambda\mu + \nu$ and $\kappa + \lambda\mu\nu$, the potential energy of the minimum energy surface is given by the functions $D_{\kappa\lambda\mu}(\phi)$ and $D_{\lambda\mu\nu}(\epsilon)$ and the position of the minimum energy surface along the ρ coordinate is given by the functions $\rho_{0\kappa\lambda\mu}(\phi)$ and $\rho_{0\lambda\mu\nu}(\epsilon)$. These functions can be expressed as sixth-degree polynomials of φ and ϵ:

$$\rho_0(\alpha = 0, \sigma = \sigma_{\kappa\lambda\mu};\tau,\delta,\gamma) = \rho_{0,\kappa\lambda\mu}(\phi) = \sum_{i=0}^{6} c_i^{(7)}\phi^i \tag{7}$$

$$\rho_0(\alpha = \pi/2, \sigma = \sigma_{\lambda\mu\nu};\tau,\delta,\gamma) = \rho_{0,\lambda\mu\nu}(\epsilon) = \sum_{i=0}^{6} c_i^{(8)}\epsilon^i \tag{8}$$

$$D(\alpha = 0, \sigma = \sigma_{\kappa\lambda\mu};\tau,\delta,\gamma) = D_{\kappa\lambda\mu}(\phi) = \sum_{i=0}^{6} c_i^{(9)}\phi^i \tag{9}$$

$$D(\alpha = \pi/2, \sigma = \sigma_{\lambda\mu\nu};\tau,\delta,\gamma) = D_{\lambda\mu\nu}(\epsilon) = \sum_{i=0}^{6} c_i^{(10)}\epsilon^i \tag{10}$$

The $\kappa\lambda\mu + \nu$ and $\kappa + \lambda\mu\nu$ configurations are located at ($\alpha = 0$, $\sigma = \sigma_{\kappa\lambda\mu}$) and ($\alpha = \pi/2$, $\sigma = \sigma_{\lambda\mu\nu}$), respectively, in the (α,σ) plane. $\sigma_{\kappa\lambda\mu}$ and $\sigma_{\lambda\mu\nu}$ depend also on φ and ϵ, and they can also be expressed as polynomials

$$\sigma_{\kappa\lambda\mu}(\phi) = \sum_{i=0}^{6} c_i^{(11)}\phi^i \tag{11}$$

$$\sigma_{\lambda\mu\nu}(\epsilon) = \sum_{i=0}^{6} c_i^{(12)}\epsilon^i \tag{12}$$

The potential energy and ρ_0, α, and σ of the transition state at any fixed orientation are given by the functions $D_{\mathrm{TS}}(\tau;\delta,\gamma)$, $\rho_{0\mathrm{TS}}(\tau;\delta,\gamma)$, $\sigma_{\mathrm{TS}}(\tau;\delta,\gamma)$, and $\alpha_{\mathrm{TS}}(\tau;\delta,\gamma)$. The dependence of these functions on τ is obtained by interpolating their values at $\tau = 0$, $\tau = \tau_1$, and $\tau = \tau_2$. These functions at $\tau = 0$ (i.e., the values at the collinear configuration) are constants, independent from δ and γ, but at τ_1 and τ_2 they depend on δ and γ. This dependence is expressed as a Fourier series of γ whose coefficients are polynomials of δ:

$$D_{\mathrm{TS},\tau_1}(\gamma;\delta) = \frac{c_0^{(13)}(\delta)}{2} + \sum_{l=2,4,6,8} [c_{l-1}^{(13)}(\delta)\sin(l\gamma) + c_l^{(13)}(\delta)\cos(l\gamma)] \tag{13}$$

$$c_i^{(13)}(\delta) = \sum_{j=0}^{6} c_{ij}^{(14)}\delta^j \qquad i = 0,...,8 \tag{14}$$

$$\rho_{0\mathrm{TS},\tau_1}(\gamma;\delta) = \frac{c_0^{(15)}(\delta)}{2} + \sum_{l=2,4,6,8} [c_{l-1}^{(15)}(\delta)\sin(l\gamma) + c_l^{(15)}(\delta)\cos(l\gamma)] \tag{15}$$

$$c_i^{(15)}(\delta) = \sum_{j=0}^{6} c_{ij}^{(16)}\delta^j \qquad i = 0,...,8 \tag{16}$$

The expressions for $D_{\mathrm{TS},\tau_2}(\gamma,\delta)$ and $\rho_{0\mathrm{TS},\tau_2}(\gamma,\delta)$ are analogous to (13−16). In general, it is convenient to choose τ_1 to be that of the transition state, when it is not collinear, and $\tau_2 = 2\tau_1$.

Finally, the values of $D(\alpha,\sigma;\tau,\delta,\gamma)$ and $\rho_0(\alpha,\sigma;\tau,\delta,\gamma)$ at any point of the (α,σ) plane are not obtained from any function, but by interpolating their values at the six asymptotic configurations (atom + atom + diatom, diatom + diatom, and atom + triatom) and at the transition state, for any set of τ, δ, and γ.

If the internuclear distances $r_{\kappa\lambda}$ and $r_{\mu\nu}$ are large but the distance $r_{\kappa\nu}$ is short enough to prevent the κ−ν interaction from being negligible, it happens that the product FD of (5) is unable to take into account the interaction between atoms κ and ν. Therefore, it is necessary to add a term, the $I(n_{\kappa\nu};\bar{n})$ function, that accounts for that interaction, but that becomes zero when $r_{\kappa\lambda}$ and $r_{\mu\nu}$ are not large. Of course, if $r_{\kappa\nu}$ is large the $I(n_{\kappa\nu};\bar{n})$ function must be zero as well. The expression of this function is

$$I\,(n_{\kappa\nu};\bar{n}) = D_{\kappa\nu}S(\bar{n})\,(n_{\kappa\nu}^2 - 2n_{\kappa\nu}) \tag{17}$$

$D_{\kappa\nu}$ is the dissociation energy of the $\kappa\nu$ diatom; $\bar{n} = (n_{\kappa\lambda} + n_{\mu\nu})/2$ and $S(\bar{n})$ is a damping function,

$$S(\bar{n}) = \begin{cases} 1 + \cos\left(\pi\dfrac{\bar{n}+p}{2p}\right) & \text{if } \bar{n} < p \\ 0 & \text{if } \bar{n} \geq p \end{cases}$$

where p is a parameter that must be tuned to make the terms I and FD match smoothly.

3. Many-Process Approach

The LAGROBO potential energy function is given as a many-process expansion. This means that the LAGROBO function is a linear combination of potential energy functions for different rearrangement channels of the four atoms of the system. In the three-atom case there are only three possible rearrangement channels between asymptotic configurations.[13] In the four-atom case, the number of rearrangement channels is 12. In each rearrangement channel the atoms A, B, C, and D can be labeled as κ, λ, μ, and ν, such as in the previous section, using all possible nonequivalent permutations, so that for all channels we always deal with the rearrangement $\kappa + \lambda\mu\nu \rightleftharpoons \kappa\lambda + \mu\nu \rightleftharpoons \kappa\lambda\mu + \nu$. A suitable choice of the rearrangement channels might be as indicated in Table 1.

TABLE 1: Permutations for All the Rearrangement Channels[a]

Channel	A	B	C	D	κ	λ	μ	ν
1	κ	λ	μ	ν	A	B	C	D
2	κ	λ	ν	μ	A	B	D	C
3	κ	μ	λ	ν	A	C	B	D
4	κ	μ	ν	λ	A	D	B	C
5	κ	ν	λ	μ	A	C	D	B
6	κ	ν	μ	λ	A	D	C	B
7	λ	κ	μ	ν	B	A	C	D
8	λ	κ	ν	μ	B	A	D	C
9	λ	μ	κ	ν	C	A	B	D
10	λ	ν	κ	μ	C	A	D	B
11	μ	κ	λ	ν	B	C	A	D
12	μ	λ	κ	ν	C	B	A	D

[a] First column: rearrangement channel. Second to fifth columns: labels (κ, λ, μ, and ν) assigned to the A, B, C, and D atoms. Sixth to ninth columns: atoms (A, B, C, and D) whose labels are κ, λ, μ, and ν.

The LAGROBO function of the potential energy surface is

$$V = \frac{\sum_{i=1}^{12} W(\phi_i,\epsilon_i,\rho_i,\alpha_i,\sigma_i)V_i^{\mathrm{ROBO}}(\rho_i,\alpha_i,\sigma_i,\tau_i,\delta_i,\gamma_i)}{\sum_{i=1}^{12} W(\phi_i,\epsilon_i,\rho_i,\alpha_i,\sigma_i)} \tag{18}$$

where $V_i^{\mathrm{ROBO}}(\rho_i,\alpha_i,\sigma_i,\tau_i,\delta_i,\gamma_i)$ is the ROBO potential energy function of channel i. Of course, the set of ROBO coordinates on which the ROBO function depends is defined in a different way for each channel, since the internuclear distances and angles from which the ROBO coordinates are obtained are different.

The ROBO contributions are multiplied by a normalized weighting function depending on ϕ, ϵ, ρ, α, and σ. The purpose of the weighting function is to privilege the ROBO contributions to the global potential which are closer to collinear configurations and cut off those corresponding to very bent configurations (hence the name LAGROBO: largest angle generalization of rotating bond order). The reason to do so is that the closer to collinearity the atoms are in the rearrangement channel the more suitable the ROBO function is to describe the potential energy of the rearrangement channel.

The degree of collinearity of the four atoms is obtained from the angles ϕ and ϵ. The weighting function should be 1 (i.e., maximum) if both ϕ and ϵ are close to π, and it should be 0 if either angle is small (say less than $\pi/6$), ranging from 0 to 1 for intermediate situations. The weighting function before normalization, $W(\phi,\epsilon,\rho,\alpha,\sigma)$, is factorized as the product of two switching functions depending on ϕ and ϵ, respectively,

$$W(\phi,\epsilon,\rho,\alpha,\sigma) = W_\phi(\phi,\rho,\alpha,\sigma)W_\epsilon(\epsilon,\rho,\alpha,\sigma) \tag{19}$$

The $W_\phi(\phi,\rho,\alpha,\sigma)$ and $W_\epsilon(\epsilon,\rho,\alpha,\sigma)$ functions could in principle be given as sine-like functions depending on either ϕ or ϵ as follows:

$$w(x) = \begin{cases} 0 & \text{if } x \le x_l \\ \frac{1}{2}\left[1 + \sin\left(-\frac{\pi(x-x_o)}{2(x_l-x_o)}\right)\right] \exp[-f(x - x_m)^2] & \text{if } x_l < x < x_m \\ \frac{1}{2}\left[1 + \sin\left(-\frac{\pi(x-x_o)}{2(x_l-x_o)}\right)\right] & \text{if } x_m < x < 2x_o + x_l \\ 1 & \text{if } 2x_o + x_l \le x \end{cases}$$

However, for configurations $\kappa\lambda\mu + \nu$ (i.e., $\alpha \to 0$, $\sigma < \pi/2$ and $\rho > 0$) the weighting function (19) must depend only on ϕ. Since the ν atom is far apart from $\kappa\lambda\mu$ the potential must be independent of its position with respect $\kappa\lambda\mu$ (that is, independent of ϵ), and therefore, $W_\epsilon(\epsilon,\rho,\alpha,\sigma)$ must be 1 for any value of ϵ whereas $W_\phi(\phi,\rho,\alpha,\sigma)$ keeps a sine-like dependence on ϕ. Likewise, for configurations $\kappa + \lambda\mu\nu$ (i.e., $\alpha \to \pi/2$, $\sigma < \pi/2$, and $\rho > 0$), $W_\phi(\phi,\rho,\alpha,\sigma)$ must be 1 for any value of ϕ while $W_\epsilon(\epsilon,\rho,\alpha,\sigma)$ is sine-like. Thus, the functions $W_\phi(\phi,\rho,\alpha,\sigma)$ and $W_\epsilon(\epsilon,\rho,\alpha,\sigma)$ are like the function $w(x)$ above, but forced to be 1 at the proper values of α, σ, and ρ by means of switching functions on each coordinate:

$$W_\phi(\phi,\rho,\alpha,\sigma) = w(\phi) + [1 - w(\phi)]A_\phi(\alpha)B(\sigma)C(\rho)$$

$$W_\epsilon(\epsilon,\rho,\alpha,\sigma) = w(\epsilon) + [1 - w(\epsilon)]A_\epsilon(\alpha)B(\sigma)C(\rho)$$

The switching functions on α, σ, and ρ are simple Gaussian or hyperbolic tangent functions:

$$A_\phi(\alpha) = 1 + \tanh[\xi(\alpha - \pi/2)]$$

$$A_\epsilon(\alpha) = 1 - \tanh(\xi\alpha)$$

$$B(\sigma) = \begin{cases} 1 & \text{if } \sigma \le \sigma_l \\ \exp[-a_\sigma(\sigma - \sigma_l)^2] & \text{if } \sigma > \sigma_l \end{cases}$$

$$C(\rho) = \begin{cases} 1 & \text{if } \rho \ge \rho_l \\ \exp[-a_\rho(\rho - \rho_l)^2] & \text{if } \rho < \rho_l \end{cases}$$

For any four-atom system, the following values for the parameters of the weighting function are appropriate: $f = 11.0$, $x_m = 1.6$, $x_l = 0.5$, $x_o = 1.35$, $\rho_l = 0.01$, $\sigma_l = 1.370796$, $\xi = 300$, $a_\sigma = 690$, and $a_\rho = 2.76 \times 10^5$. A plot of the weighting function against the ϕ and ϵ angles at $\alpha = \pi/4$, $\sigma < \pi/2$ and $\rho > 0$ is shown in Figure 4.

4. Application to the $OH + H_2$ System

The formulation of section 3 is appropriate for any four-atom reaction. Here the method is applied to the $OH + H_2 \to H_2O + H$ reaction. This reaction has become a benchmark in the four-atom molecular collision theory (see ref 22 and references therein). It is also relevant in combustion, atmospheric chemistry and astrochemistry. Despite the importance of this reaction there have been few attempts to assemble a PES so far. The first analytical PES for $OH + H_2$ was made by Schatz and Elgersma in 1980.[23] This PES is a many-body expansion with a very simple formulation and it has been used widely by many researchers. However, it has several flaws. The PES has an spurious well in the $OH+H_2$ entrance region, which was corrected later.[24] Also, it does not describe well the potential and vibrational energy levels for H_2O. Finally, Schatz and Elgersma's PES does not describe the full symmetry of the $OH+H_2$ system. The hydrogen atoms are not indistinguishable, as they must be, and only one hydrogen atom of H_2 is allowed to react to give H_2O+H.

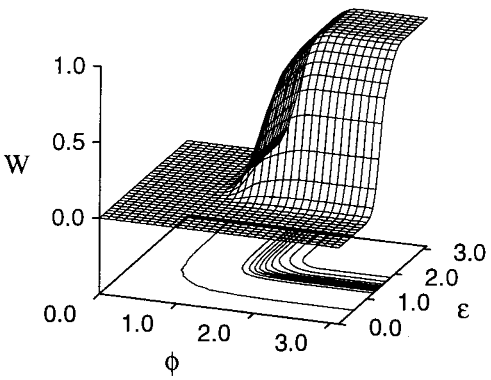

Figure 4. Weighting function $W(\phi,\epsilon,\rho,\alpha,\sigma)$ plotted against the ϕ and ϵ angles at $\alpha = \pi/4$, $\sigma < \pi/2$, and $\rho > 0$.

Isaacson[25] developed a PES function for four-atom systems consisting of two valence bond three-body terms plus some quadratic and cubic terms involving the bending and torsional angles. Some parameters of the model vary along the reaction path, so that the model provides a useful global PES at least along the minimun energy path. Isaacson fitted several versions of the PES for $OH + H_2$ using ab initio data by Dunning et al. On these PES, he calculated rate coefficients by canonical variational transition state theory and conventional transition state theory.

Recently, another PES was built by Kliesch et al.[26] from new ab initio calculations. This potential does fit the frequencies and geometries of the transition state well, but is not appropiate for out-of-plane geometries away from the transition state. Furthermore, it does not describe the full symmetry of the $OH + H_2$ system.

Jordan and Collins[4] have also assembled a PES for $OH + H_2$, but it does not have chemical accuracy since it has been made out of unrestricted Hartree-Fock level ab initio calculations.

We have used the LAGROBO model described above to build a new PES for $OH + H_2$ that fits the same ab initio data used by Kliesch. Information on the ab initio calculations can be found in ref 26.

Like in any four-atom system, there are twelve rearrangement channels in the $OH + H_2$ system. However, since the hydrogen atoms can be considered as indistinguishable, the number of different rearrangement channels can be reduced to two:

$$O + HHH \rightleftharpoons OH + HH \rightleftharpoons OHH + H \qquad (20)$$

$$H + OHH \rightleftharpoons HO + HH \rightleftharpoons HOH + H \qquad (21)$$

Therefore, to assemble a LAGROBO PES it is necessary to obtain only two different sets of parameters for the ROBO functions rather than twelve. In addition, it must be noticed that the only process that actually takes place is $OH + H_2 \rightleftharpoons H_2O + H$, described by the ROBO function of channel (21), whereas channel (20) can be considered closed for most practical purposes. As a consequence, only the parameters characterizing the strong interaction region of the ROBO function for channel (21) must be worked out carefully. For channel (20) it is enough to set up parameters that give any reasonably high potential in the strong interaction region, since it does not make any difference in the results when the PES is used for calculations of reactivity. Although the sets of parameters for $OH + H_2$ can be reduced from twelve to only two, the summation (18) must still span twelve rearrangement channels so that the

TABLE 2: Spectroscopic Parameters of the Diatomic Molecules of the OH + H_2 System

	OH	H_2
r_{eq} (Å)	0.96966	0.74144
D_e (kJ/mol)	445.374	458.021
ω_e (cm^{-1})	3737.76	4401.21
$\omega_e x_e$ (cm^{-1})	84.881	121.33
β ($Å^{-1}$)	2.296	1.94429

TABLE 3: Transition State Properties

	ab initio[26]	LAGROBO
r_{HO} (Å)	0.9716	0.9698
$r_{OH'}$ (Å)	1.3558	1.3552
$r_{H'H'}$ (Å)	0.8202	0.8224
ϕ (degree)	97.10	95.10
ψ (degree)	161.47	160.76
θ (degree)	0.00	0.00
barrier (kJ/mol)	24.218	24.218
ω_1 (cm^{-1})	487	474
ω_2 (cm^{-1})	576	818
ω_3 (cm^{-1})	1072	1104
ω_4 (cm^{-1})	2609	2585
ω_5 (cm^{-1})	3729	3507
ω_i (cm^{-1})	1197	1102

symmetry properties of the highly symmetric OH + H_2 system can be fully preserved in the PES. Note that although channel (20) is closed, its asymptotic zone of OH+H_2 is accessible.

The properties of the diatomic fragments used in the assemblage of the PES are taken from experimental information[27] and are listed in Table 2. The LAGROBO PES exactly reproduces these properties and converges to Morse potentials for the diatomic fragments OH and H_2 in the asymptotic configurations. In general, Morse potentials for the diatoms are a good enough approximation for the purpose of reactive dynamics. For the OH + H_2 reaction this assumption holds even better, since few vibrational levels are open at the total energies considered in calculations of reaction probabilities and rate constants. Nevertheless, if a better representation of the diatomic potentials were required it could be obtained using a higher degree polynomial of ρ in (6).

The geometry of H_2O in the LAGROBO PES is $r_{OH} = 0.9577$ Å and $H\hat{O}H = 104.30°$, in close agreement with the experimental geometry ($r_{OH} = 0.9572$ Å and $H\hat{O}H = 104.52°$), and its energy is 62.505 kJ/mol below that of the HO+H_2 entrance channel. The vibrational frequencies of H_2O in the PES are $w_1 = 1595$ cm^{-1}, $w_2 = 3654$ cm^{-1}, and $w_3 = 3764$ cm^{-1}, whereas the experimental frequencies are 1595, 3657, and 3756 cm^{-1} for the bend, symmetric, and asymmetric stretch vibrations, respectively.[28] The energies of the low-lying vibrational levels of H_2O do not show Fermi resonances, unlike the Schatz–Elgersma surface.[23]

The minimum energy path of the LAGROBO PES shows a barrier of 24.218 kJ/mol between reactants and products. The geometry of the transition state is planar and noncollinear. The properties of the transition state of the LAGROBO PES (geometry, energy, and frequencies) are given in Table 3, along with the properties obtained in the ab initio calculation. The minimum energy surface for the ϕ, ψ, and θ angles of the transition state is depicted in Figure 2. The minimum energy path from OH + H_2 to H_2O + H, containing the transition state, is tracked by an arrow in the underlying contour map.

The local minimum corresponding to the D_{3h} symmetric configuration of H_3O has a bond length of $r_{OH} = 0.9602$ Å and an energy of 35.600 kJ/mol below that of the OH + H_2 configuration. It is separated from the H_2O + H asymptotic channel by a small barrier, 0.280 kJ/mol high. However, these features may not correspond to the true values, since we did not have ab initio data on the D_{3h} configuration to which fit the PES.

In the entrance channel of the OH + H_2 PES there should be a very shallow well, 2.250 kJ/mol deep, corresponding to the Van der Waals bond between OH and H_2, in which the OH and H_2 molecules are perpendicular, with the H-side of OH pointing at the center of the H_2 bond.[29] This feature has not been included in the present version of the PES as it is intended for carrying out reactive scattering calculations. However, it should be straightforward to modify the entrance channel potential in the future to include this feature.

The new PES is being used to study theoretically the OH + $H_2 \rightarrow H_2O$ + H reaction with quasiclassical trajectories, reduced dimensionality quantum methods and exact quantum methods. A detailed report on these results will be given elsewhere.[30]

Due to lack of space and in order to keep the explanation of the LAGROBO model simple some of the less important details of the formulation in section 2.2 have not been given, neither are given the numeric values of the parameters for the OH + H_2 LAGROBO PES. However, the FORTRAN code of the PES is available on request.[31]

5. Remarks on the LAGROBO model

In the previous sections the formulation of the LAGROBO model for four-atom systems is described, along with its application to the OH+H_2 system. However, since it is difficult to convey the advantages of the model just by giving its mathematical formulation, it is worth emphasizing here some of the features of the model that make it a valuable tool in the theoretical study of elementary reactions.

The mathematical formulation of the LAGROBO model is based largely on functions with clear physical meaning, like the polynomic dependence of the potential on ρ, the minimun energy paths in the three-atom case or the minimum energy surfaces in the four-atom case, for instance. As a consequence, the procedure for fitting the surface is not a blind algorithm in which only the final global potential energy function has meaning. Rather, during the fitting procedure it is known how every function of the model relates to the global potential energy function and the role that the different parameters play in the functions of the model are clear.

The LAGROBO model can guarantee that the PES does not have spurious structures and that it is continuous and smooth in the whole domain of configurations, even in zones for which there is no ab initio information about the potential energy. Also, as long as correct values for the properties of the diatoms (and triatoms, in the four-atom systems) are used in the data, the ergicity between reagents and products will be always correct for all rearrangement channels in all systems. This feature is not guaranteed in other methods and it has been cause of major flaws in other PESs.

Once enough information about the potential energy of a system has been gathered it is a straightforward task to fit the LAGROBO function. As the parameters have clear physical meaning, their determination is not computer time-consuming, since the fitting is not carried out by any iterative technique.

The aim of the LAGROBO method is to provide a smooth PES that is easy to use in reaction dynamics calculations and has a good accuracy for the energetics and properties of the reactants, products and transition state. For reactive scattering the quality of the surface is critically dependent on the accuracy in reproducing the properties of the transition state calculated by ab initio means. For zones of the strong interaction region away from the transition state the method is able to provide a shape of the PES in reasonable agreement with ab initio information, if such is available.

Some of the advantages of the LAGROBO model become evident when it is applied to four-atom systems. It is particularly important that the model allows fitting feasible and smooth PESs out of little ab initio information and that it treats the full symmetry of the system. The calculation of ab initio points of the potential energy is a very expensive task in terms of computing time, particularly when atoms with high atomic number are involved. For any given fixed resolution of the potential energy surface the number of points to be calculated increases exponentially with the number of dimensions. Thus, such number is N^3 for a three-atom system and N^6 for a four-atom system, where N is the number of points per dimension. Methods that require a large number of ab initio points of even resolution all over the surface to fit an analytical function are very difficult to apply when either the number of atoms of the system or their atomic numbers increase. For four-atom systems the availability of a method that keeps the number of ab initio points low may be not only a major advantage, but crucial to the possibility of assembling a PES.

For these reasons we think that the LAGROBO method will be of great help in developing PESs for four-atom systems beyond $OH + H_2$. For example, at the time of writing the LAGROBO model is being applied to build a PES for the $OH + HCl$ reaction.[32]

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