7118 J. Phys. Chem. A **2003,** *107,* 7118−7124

Interpolating Moving Least-Squares Methods for Fitting Potential Energy Surfaces: Illustrative Approaches and Applications[†]

Gia G. Maisuradze and Donald L. Thompson*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Received: January 31, 2003; In Final Form: April 10, 2003

We present a method based on interpolating moving least-squares (IMLS) that is designed for efficient and accurate local fitting of discrete energy values to provide global representations of potential energy surfaces (PESs) for many-atom systems. We have demonstrated the method with one-, two-, and three-dimensional fits of the $HN_2 \rightarrow N_2 + H$ PES. To allow for extensive fitting and testing, the analytical PES developed by Koizumi et al. [Koizumi, H.; Schatz, G. C.; Walch, S. P. *J. Chem. Phys.* **1991**, *95*, 4130] was used to generate energy values. Unlike the modified Shepard method this approach does not require derivatives, thus it can be used to fit energies computed using highest-level quantum chemistry methods for which forces are not directly obtainable. This fitting scheme accurately describes the PES, is not computationally time-consuming, can be improved by using higher degrees and larger numbers of basis functions, and is straightforward to apply. Extension to many-dimensional PESs seems promising.

1. Introduction

The speed with which quantum chemistry calculations can now be done allows for the direct use of ab initio forces in molecular dynamics simulations. This has obvious advantages over using global analytical representations, which involves the tedious, arduous task of selecting appropriate functions and then adjusting many parameters. Despite the ease with which direct dynamics simulations can be done, the approach is not generally applicable. A major lingering problem, which will be solved in time, is that the levels of theory that must be used to make the calculations feasible are often inadequate for reactions. The error in ab initio results is dealt with in fitting schemes by simply scaling them to empirical data. Even when high-level quantum results are accurate, it is not always possible to directly compute the ab initio forces needed for the trajectory integrations. Despite the prospects for straightforward ab initio dynamics simulations, there is still a need to develop better methods for fitting analytic potential energy surfaces (PESs).

Fitting ab initio PESs is still more an art than a science. It requires considerable skill and insight to select the best analytical functions and a lot of persistence to adjust the parameters. Global functions offer simplicity at the expense of flexibility. That prompted us in the 1970s to propose use of a scheme based on local fitting with cubic splines.[1] They provide a very flexible and numerically efficient approach to fitting a surface with smooth first and continuous second derivatives. They have mainly been used to fit 3-D surfaces,[2−7] because they require a fairly high density of points for a good fit. The challenge is to achieve highly accurate, smooth fits of ab initio data with small numbers of data points and adjustable parameters. Significant progress has been made over the past decade in developing systematic, general methods for achieving such fits.[8−10] Perhaps the more useful approaches are the interpolating moving least-squares (IMLS) methods, which have been extensively applied to small systems. Ischtwan and Collins[8] introduced a much more practical local fitting approach in 1994. It is based on a modified Shepard interpolation,[11] the simplest case of IMLS. The Shepard method[12,13] is a zero-degree IMLS method (ZD-IMLS). A serious problem with ZD-IMLS, referred to as the “flat-spot” phenomenon, is that the derivative of the interpolant is zero at every data point. This prevents the straightforward use of the Shepard method; however, the “flat-spot” problem can be avoided by using Taylor expansions instead of just data points.[11]

An attractive feature of the IMLS approach is that it can be coupled with dynamics simulations to bias the fitting. Ischtwan and Collins[8] have applied a modified Shepard interpolation method, which requires the derivatives at the data points, for constructing PESs by combining it with classical trajectory simulations in an iterative scheme for successively improving the surface. This iterative procedure places new data points in regions of the surfaces that are important dynamically, and, most importantly, the procedure is inherently simple and can be completely automated. The gradients and Hessians required in this method are not available in higher-level ab initio calculations. This approach has been refined and applied to various reactions by several groups.[14−37]

Apart from the Taylor series, the higher-degree IMLS methods[13] can be used to solve the “flat-spot” problem. McLain[38] studied two-dimensional fits for some simple functions using zero-, first-, second-, third-, and forth-degree IMLS methods. His fits were based on a tradeoff of accuracy against computing time. Ishida and Schatz[39] presented a scheme in which a second-degree IMLS (which we will refer to as SD-IMLS) method is combined with Shepard interpolation. The reason for using the higher-degree IMLS method is to avoid the need for derivatives. The scheme has two steps: first is the evaluation of first and second derivatives at the data points by the SD-IMLS method. In the second step, Shepard interpolation is used to evaluate energies and derivatives at other geometries using the information obtained from the first step.

The interpolation method presented here is the higher-degree IMLS approach directly applied to the fitting of PESs. This approach can be regarded as a natural generalization of the

---

* To whom correspondence should be addressed. Dlt@okstate.edu.

[†] Part of the special issue "Donald J. Kouri Festschrift".

10.1021/jp030144a CCC: $25.00

Shepard interpolation that leads to the elimination of the "flat-spot" problem. It can be regarded as an extension of McLain's work[38] to chemically relevant problems. It can be regarded as a simplification of Ishida and Schatz's work[39] in that no calculation of the energy gradient and second derivatives, as required by the modified Shepard interpolation, is performed. A full evaluation of higher-order IMLS methods for fitting PESs requires the resolution of many issues. What is the interplay of degree/accuracy/computational efficiency? How do the form and parameter values of the weight function (explicit in all IMLS methods) affect that interplay? How does ab initio point selection affect that interplay? What are the scaling properties of the method as the dimensions of the PES rise? What are the advantages and disadvantages of this method compared to competitive methods? This paper will *not* attempt to answer all these questions. Rather it will develop a simple first-degree IMLS fit to a chemically realistic PES in order to see if the quality of the fit and the simplicity of the method merit a more detailed evaluation of the general high degree IMLS approach. This paper thus constitutes an initial or preliminary report on the approach.

We chose for our test PES, the analytic function developed by Koizumi et al.[5] for the simple $HN_2 \rightarrow H + N_2$ dissociation reaction. We selected an analytical PES to avoid the more costly procedure of calculating ab initio points. This allowed us to do extensive testing of variations of the scheme while making direct comparisons of fits to the "exact" potential. Since the Koizumi et al.[5] PES is a close fit to an extensive set of ab initio points, this test case is fully realistic. The triatomic $HN_2 \rightarrow H + N_2$ is a bond fission reaction, making for a rather smooth PES of low dimensionality that is appropriate for an initial test of a fitting method. The focus of this study was on determining the best local fitting functions and procedure; thus we have applied the scheme to one-, two-, and three-dimensional sections of the surface.

The method is described in Section 2, the fitting scheme to obtain the global potential in Section 3, the application of the method to HN_2 in Section 4, and a summary and the conclusions in Section 5.

2. Method

Before describing the IMLS method, it is useful to review the least-squares and weighted least-squares methods. We follow Lancaster and Salkauskas[13] and discuss the basic aspects of these methods for the one-dimensional case.

Consider data that consists of $N + 1$ abscissas $\{x_i;\ i = 0, 1, ..., N\}$ with ordinates $\{f_i;\ i = 0, 1, ..., N\}$. The polynomials $p(x) = \sum_{i=0}^{m} a_i x^i$, where $p(x) \in \mathscr{P}_m$ and $m \leq N$ ($\mathscr{P}_m$ denotes the set of all polynomials p with degree not exceeding m, together with the zero polynomial), are used to fit the data, with the deviation of $p(x_i)$ from f_i at x_i being $p(x_i) - f_i$. The sum of the squared deviations for any $p \in \mathscr{P}_m$ is

$$E_x(p) = \sum_{i=0}^{N} [p(x_i) - f_i]^2 \tag{1}$$

The best least-squares fit is obtained by finding a polynomial $p \in \mathscr{P}_m$ for which E is minimized.

In the weighted least-squares method the value of g, the function used to fit the curve, at a point x is determined by giving greater weights to the data f_i at points x_i that are closest to x. Thus, instead of eq 1 we minimize

$$E_x(p) = \sum_{i=0}^{N} w_i(x)[p(x_i) - f_i]^2 \tag{2}$$

where $w_i(x)$ are positive weight functions with asymptotic behavior $w_i(x) \rightarrow \infty$ as $x \rightarrow x_i$. The most popular choices for the weight functions are

$$w_i(x) = \frac{1}{(x - x_i)^{2n}} \tag{3a}$$

$$w_i(x) = \frac{\exp[-(x - x_i)^2]}{(x - x_i)^{2n}} \tag{3b}$$

where n is a small positive integer.

The normal equations are found by considering the $m + 1$ necessary conditions $\partial E_x/\partial a_i = 0$, $i = 0, 1, ..., m$:

$$\begin{gathered}
[\sum w_i(x)x_i^{0}]a_0 + ... + [\sum w_i(x)x_i^{m}]a_m = \sum w_i(x)f_I \\
[\sum w_i(x)x_i]a_0 + ... + [\sum w_i(x)x_i^{m+1}]a_m = \sum w_i(x)x_i f_i \\
\vdots \\
[\sum w_i(x)x_i^{m}]a_0 + ... + [\sum w_i(x)x_i^{2m}]a_m = \sum w_i(x)x_i^{m} f_i
\end{gathered} \tag{4}$$

The polynomial giving the lowest value to E_x can be defined by solving eq 4 and using these solutions as the coefficients for the polynomial. We should note that the normal equations for the least-squares method can be obtained from eq 4 by the choice of weights $w_i(x) = 1$, $i = 0, 1, ..., N$.

It is customary, useful, and convenient to write eq 4 in the matrix-vector form:

$$\mathbf{B}^{\mathrm{T}}\cdot\mathbf{W}\cdot\mathbf{B}\cdot\mathbf{a} = \mathbf{B}^{\mathrm{T}}\cdot\mathbf{W}\cdot\mathbf{f} \tag{5}$$

where $\mathbf{B}$ is a $N \times (m + 1)$ matrix, and $\mathbf{B}^{\mathrm{T}}$ is its transpose, $\mathbf{W}$ is an $N \times N$ diagonal matrix, and $\mathbf{a}$ and $\mathbf{f}$ are column vectors. They have the following forms:

$$\mathbf{B} = \begin{bmatrix} 1 & x_0 & ... & x_0^{m} \\ 1 & x_1 & ... & x_1^{m} \\ & & \vdots & \\ 1 & x_N & ... & x_N^{m} \end{bmatrix} \quad \mathbf{a} = \begin{bmatrix} a_0 \\ a_1 \\ \vdots \\ a_m \end{bmatrix} \quad \mathbf{f} = \begin{bmatrix} f_0 \\ f_1 \\ \vdots \\ f_N \end{bmatrix}$$

$$\mathbf{W} = \mathrm{diag}[w_0(x), w_1(x), ..., w_N(x)] \tag{6}$$

In the highly unusual case of $m = N$, eq 5 can be simplified to $\mathbf{B}\cdot\mathbf{a} = \mathbf{f}$, since $\mathbf{B}$ is then a square matrix with a well-defined inverse. Note that $\mathbf{W}$ does not appear in this simplification because the number of unknown parameters is exactly equal to the number of constraints and the least-squares procedure can exactly satisfy the constraints no matter what weight they are assigned. The matrix $\mathbf{B}$, which is known as a Vandermonde matrix, is ill conditioned,[13] and a direct algebraic approach is not recommended for a general-purpose computer code (even for the simplest case of normal equations); rather than use matrix inversion one should use a more reliable numerical method, e.g., the singular value decomposition (SVD) method.[13]

When $m = 0$, the normal equations, eq 4, reduce to a single equation:

$$a_0(x) = \sum_{i=0}^{N} w_i(x) f_i \Big/ \sum_{i=0}^{N} w_i(x) \tag{7}$$

This equation is credited to Shepard.[12] When $w_i(x) = (x - x_i)^{-n}$ with $n > 0$, it is easy to see that for $0 < n < 1$ the interpolating curve has cusps at the data points, for $n = 1$ the fitted curve has corners at the data points, and for $n > 1$ it exhibits the "flat-spot" phenomenon, that is, the derivative of the interpolant is zero at the data points (see section 4). There are several causes of this. First of all, there is a singularity in one of the elements of weight function **W** and the coefficients of eq 5 are not defined at data points, which causes the lack of smoothness near the data points not only in the Shepard method but also in higher-degree IMLS methods (see section 4). There are two different ways to resolve this problem. First, to avoid arithmetic overflow, McLain[38] suggested using $(x - x_i)^{2n} + \epsilon$ instead of $(x - x_i)^{2n}$ in the denominator of the weight function in eq (3b); that is,

$$w_i(x) = \frac{\exp[-(x - x_i)^2]}{(x - x_i)^{2n} + \epsilon} \tag{8}$$

where ϵ is a small positive number. Also, the singularities of **W** can be avoided by dividing both sides of eq 5 by $\sum_{i=0}^{N} w_i(x)$, then eq 5 becomes

$$\mathbf{B}^{\mathrm{T}}\cdot\mathbf{V}\cdot\mathbf{B}\cdot\mathbf{a} = \mathbf{B}^{\mathrm{T}}\cdot\mathbf{V}\cdot\mathbf{f} \tag{9}$$

where $\mathbf{V} = \mathrm{diag}[v_1(x),v_2(x),...,v_N(x)]$ and $v_j(x) = w_j(x)/\sum_{i=0}^{N} w_i(x)$, $j = 1,2,...,N$. The $v_j(x)$ are normalized weight functions and have the following properties:

(1) $v_i(x_j) = \delta_{ij}$ (Kronecker delta) for $i, j = 1, 2, ..., N$;

(2) $0 \le v_i(x) \le 1$ for all x and $v_i(x) = 0$ if and only if $x = x_j$ and $j \neq i$;

(3) $\sum_{i=0}^{N} v_i(x) = 1$ for all x; and

(4) $v_i(x) \rightarrow N^{-1}$ as $d(x,0) \rightarrow \infty$.

We followed McLain's suggestion in this work. The introduction of ϵ removes the singularity in the Shepard method, but the "flat-spot" problem persists for small enough values of ϵ.

There is a way to solve the "flat-spot" problem without sacrificing the quality of the fitting.[13] Consider the $m = 1$ case, for which eq 4 gives a pair of normal equations:

$$\begin{aligned} [\textstyle\sum w_i(x)]a_0 + [\sum w_i(x)x_i]a_1 &= \textstyle\sum w_i(x)f_i \\ [\textstyle\sum w_i(x)x_i]a_0 + [\sum w_i(x)x_i^2]a_1 &= \textstyle\sum w_i(x)x_if_i \end{aligned} \tag{10}$$

The interpolation function has the form

$$g(x) = a_1(x)x + a_0(x) \tag{11}$$

where $a_1(x)$ and $a_0(x)$ can be obtained from eq 10. If the weight function is not singular, then this function is free of "flat-spot" problems. The same is true for all higher-degree forms of IMLS.

To construct an IMLS method for surfaces, which is similar to the procedure considered above for the one-dimensional case, we introduce the basis functions (monomials) for three classes of three-variable polynomials (the monomials for two-variable polynomials are easily obtainable by deleting one variable):

$$\begin{aligned} &\mathscr{P}_0 \quad 1 \\ &\mathscr{P}_1 \quad 1\ x\ y\ z \\ &\mathscr{P}_2 \quad 1\ x\ y\ z\ x^2\ y^2\ z^2\ xy\ xz\ yz \end{aligned} \tag{12}$$

For convenience the notation (x,y,z) for a point on the 3-D surface is abbreviated to l, hence the data points are denoted by $l_i = (x_i,y_i,z_i)$, $i = 1, 2, ..., N$. Let $b_1(l), b_2(l), ..., b_n(l)$ $(n \le N)$ denote linearly independent functions defined on the whole 3-D surface. For example, according to eq 12, the least-squares approximation with bivariate quadratic polynomials requires 10 of these functions (for a 2-D surface it is six).

The interpolant has the form:

$$u(l) = \sum_{j=1}^{n} a_j(l)b_j(l) \tag{13}$$

where the $a_1, a_2, ..., a_n$ coefficients can be determined from the normal equations in the same manner as in the one-dimensional case, only with replacing x by l.

The Euclidean distance between points $l = (x,y,z)$ and $l_i = (x_i,y_i,z_i)$ is

$$d(l,l_i) = \sqrt{(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2} \tag{14}$$

Since the weighting depends on the distance between points, the weights $w_1(l), w_2(l), ..., w_N(l)$ will depend on the function $w(d)$, where $w \rightarrow \infty$ as $d \rightarrow 0$ and vice versa. It is clear that the weight functions are similar to those for the one-dimensional case eq 8; with d replacing $x - x_i$, it has the form

$$w(d) = e^{-\alpha d^2}/(d^{2n} + \epsilon) \tag{15}$$

where α is a positive number.

As in the one-dimensional case, we consider an interpolant with four basis functions for the 3-D surface (three monomials for 2-D) to avoid the "flat-spot" phenomenon. Thus, we have four normal equations and the interpolant has the form

$$u(x,y,z) = a_1(x,y,z) + a_2(x,y,z)x + a_3(x,y,z)y + a_4(x,y,z)z \tag{16}$$

where $a_1(x,y,z)$, $a_2(x,y,z)$, $a_3(x,y,z)$, and $a_4(x,y,z)$ can be defined from the normal equations. The functions given in eqs 11 and 16 are the fitting functions used in the method presented in this paper. We will refer to this as the first-degree IMLS (FD-IMLS) method.

We will have occasion to calculate gradients with the FD-IMLS method. For convenience, the gradients will be calculated by central finite differencing.

Our calculations were performed on the IBM RS/6000 7043 model 260 workstations (512 MB memory, one 200 MHz processor) and took only a few seconds to fit the 2-D and 3-D "global" surfaces.

3. Potential Energy Values

Although our focus is on methods that can be used to fit *ab initio* energies to obtain "analytical" representations, we have chosen to avoid the expense of carrying out quantum chemistry calculations. Instead, we have used an analytical function to compute points that we then fit or use to evaluate the fits. This permits more extensive testing of the method than we could have done had we used *ab initio* points.

The data points used in the fitting and evaluations of the results were obtained from the global function for the reaction $HN_2 \rightarrow N_2 + H$ developed by Koizumi, Schatz, and Walch.[5] This global potential is based on the rotated Morse oscillator approach[40,41] and is written in terms the coordinates R, r, and θ; where R is the distance between the H and the center of mass of N_2, r is the N−N distance, and θ is the angle between the Jacobi vectors **R** and **r**, such that $\theta = 0°$ corresponds to linear HNN. We computed points that span the ranges $2.0a_0 \le R \le$

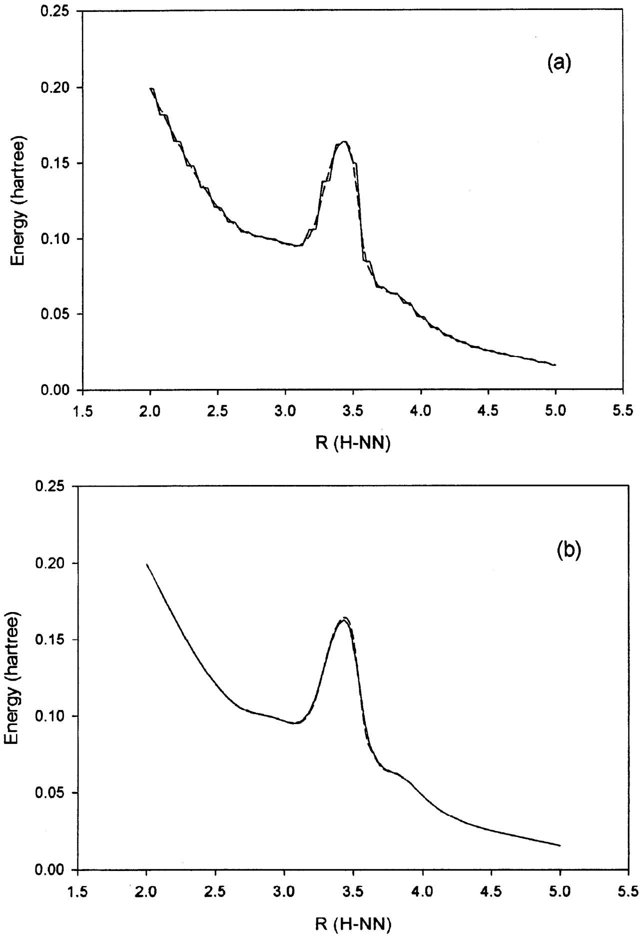

Figure 1. Potential energy for $HN_2 \rightarrow H + N_2$ along R for $\theta = 0°$ and $r = 2.0a_0$. The dash lines present curves calculated by Koizumi et al.[5] code and the solid lines correspond to (a) Shepard interpolation and (b) FD-IMLS.

$5.0a_0$, $2.0a_0 \leq r \leq 2.6a_0$, and $\theta = 45°$, for the two-dimensional fits. We used internuclear distances r_1(H−N), r_2(N−N), and r_3(H−N) for the calculation of 3-D surface. Taking advantage of symmetry, we fit the surface over the range for which the Koizumi et al.[5] analytical function is valid: $0.7a_0 \leq r_1 \leq 6.3a_0$, $2.0a_0 \leq r_2 \leq 2.6a_0$, $0.7a_0 \leq r_3 \leq 6.3a_0$.[42] We used equally spaced data points along each axes, with increments of 0.2, 0.15, or 0.1.

4. Results

The main goal in this initial study was to test the FD-IMLS method. We eventually want a fitting method that is highly accurate and applicable to many-dimensional systems. We begin, however, with a careful analysis of the FD-IMLS for one-, two-, and three-dimensional potentials. We do this within the context of previous work,[8,14−36,39] much of which is based on the Shepard method. Thus, we demonstrate the advantages of the present method by making direct comparisons with Shepard interpolation.

The differences in the quality of the fits are illustrated in Figure 1 where we make direct comparisons of the Shepard and present methods by superimposing 1-D fits on the "exact" potential curve (as a function R at $\theta = 0°$ and $r = 2.0a_0$) computed with the Koizumi et al.[5] PES. In Figure 1a, in which the Shepard fit (solid curve) is compared with the exact curve (dashed curve), we see that the "flat-spot" problem results in an obviously bad fit. The comparison for the FD-IMLS fit (solid curve) is shown in Figure 1b and clearly illustrates a better (though not perfect) representation of the potential. The average absolute rms deviation between the fitted curve and 301 exact points, computed with the Koizumi et al.[5] PES, is 9.34×10^{-4} hartree. We have used 61 data points in the fitting with the weight function given by eq 8 with $n = 5$ and $\epsilon = 1.5 \times 10^{-13}$.

We calculated the gradients of the energy (numerically) to examine the smoothness of potential. The average absolute rms deviation for the gradients is 1.82×10^{-2} au for 301 points.

In Figure 2 the FD-IMLS fit of the 2-D HN_2 ($\theta = 45°$) potential using different numbers of data points are superimposed on the exact surface computed by using the Koizumi et al.[5] analytic function. The fits in Figure 2 were obtained by using the weight function of eq 15, with $n = 3$, $\alpha = 0.08$, and $\epsilon = 1 \times 10^{-4}$ (64 data points), $\epsilon = 1 \times 10^{-5}$ (105 data points), and $\epsilon = 5 \times 10^{-7}$ (217 data points). Figure 2a,b,c illustrates a direct comparison of the exact surface with those obtained by FD-IMLS fitting using 64, 105, and 217 data points, respectively. The fit is worst in the areas close to the edges of the surface. The fit improves with increasing number of data points as the results in Figure 2 illustrate. Also, a much better fit could be obtained by using a nonuniform grid; however, we have not explored this since our purpose here was to make direct comparisons to demonstrate the present method.

A quantitative comparison of the two surfaces is more meaningful, thus we computed the average absolute rms deviations of the potential and gradients between the exact surface[5] and surfaces constructed by FD-IMLS fitting using different numbers of data points and values of the parameters (ϵ, n) in the weight function, eq 15. The rms deviation for the two best fits, i.e., best choices of values for ϵ and n, are given in Table 1. The average absolute rms deviations of the values of the potential energy and gradient are based on 18 361 points. As expected, the rms error decreases with increasing number of data points. The fit with weight function parameter $n = 3$ is better than that with $n = 5$. The difference in the rms values for $n = 3$ and $n = 5$ is larger for the potential than for the gradients.

We have also used the FD-IMLS method to fit the 3-D PES for HN_2. We calculated points that span the ranges given in section 3. Again, we computed the average rms deviations of the potential and the gradients between the Koizumi et al.[5] surface and the FD-IMLS fits for different numbers of data points (2688, 4590, 11 914) and weight function parameters ($n = 3$ and 5). Table 2 shows the rms values based on 407 050 points. It is clear that the fit improves with increasing of number of data points. The rms values for the energy are better for $n = 3$ than for $n = 5$. However, for the gradients it is the opposite. One might expect the fitting errors for the potential and gradients to be consistent; however, as is the case here, they may not be because of the low-amplitude oscillations that are characteristic of polynomials. For another example of this behavior, see Table 1 of ref 39, where the same discrepancy between the rms deviations in the energies and gradients for some n was observed. For some n the best fit for energies does not give the best fit for the gradients.

As in the 1-D case, the method gives a good fit for the 2-D and 3-D surfaces. However, it is important to note that it was necessary to use a different weight function for each case. The critical point is that when irregularities in the fit occur they can be due to a poor choice of the form the weight function, the values of the parameters in it, or, of course, the number and distribution of points. These issues are illustrated by the results in Tables 1 and 2, where the rms deviations for energies and

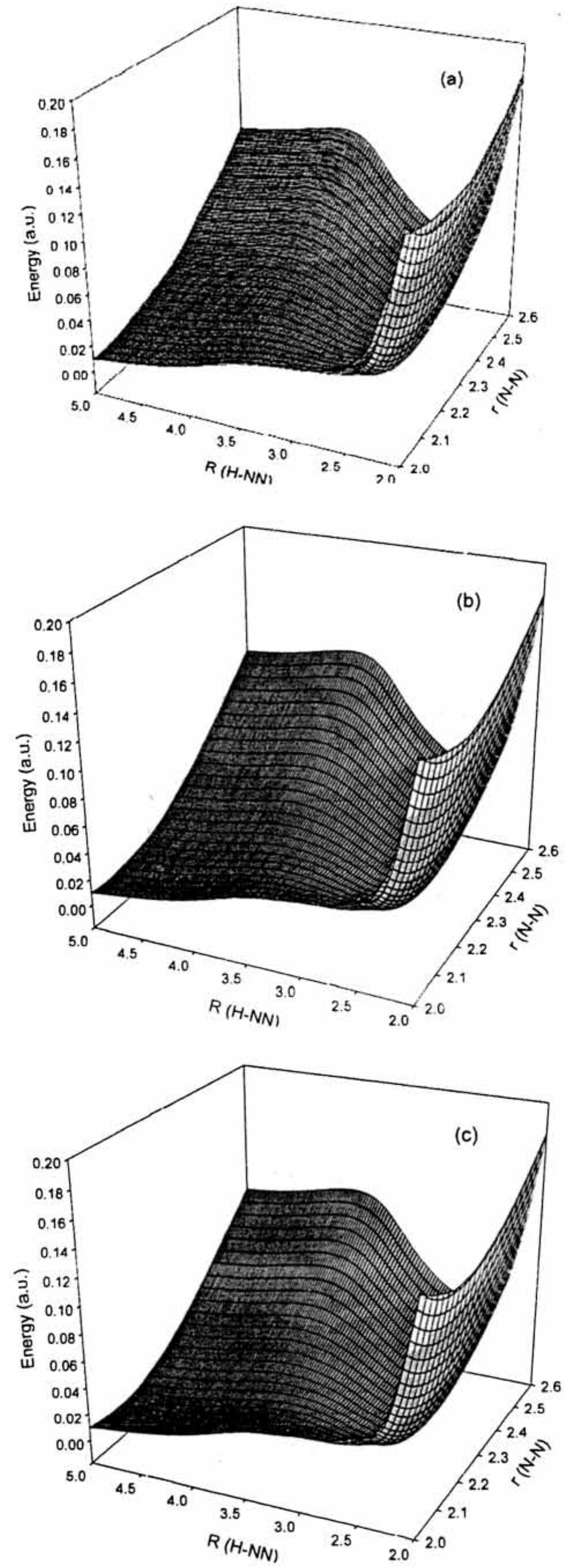

Figure 2. Fitted (by the FD-IMLS method) and actual (Koizumi et al.[5]) potential-energy surfaces for $HN_2 \rightarrow H + N_2$ as a function of the H−NN and N−N distances for $\theta = 45°$, for (a) 64, (b) 105, and (c) 217 data points. The rms deviations are given in Table 1 ($n = 3$) for the three fits shown here.

TABLE 1: Root-Mean-Square (rms) Deviations of Potential Energies (in hartree) and Gradients (in au) between the Fitted and Exact[5] 2-D Surfaces for 18361 Points

			rms^c	
N_d^{a}	ϵ^b	n^b	potential	gradients
64	1×10^{-4}	3	7.86×10^{-3}	7.14×10^{-2}
64	1×10^{-5}	5	1.09×10^{-2}	7.68×10^{-2}
105	1×10^{-5}	3	4.25×10^{-3}	5.36×10^{-2}
105	3×10^{-7}	5	6.29×10^{-3}	5.46×10^{-2}
217	5×10^{-7}	3	1.77×10^{-3}	3.97×10^{-2}
217	1×10^{-8}	5	3.44×10^{-3}	4.25×10^{-2}

[a] The total number of data points. [b] The weight function parameters, see eq 14. [c] Root-mean-square deviation based on 18 361 points.

TABLE 2: Root-Mean-Square (rms) Deviations of Potential Energies (in hartree) and Gradients (in au) between the Fitted and Exact[5] 3-D Surfaces for 407 050 Points

			rms^c	
N_d^{a}	ϵ^b	n^b	potential	gradients
2688	1×10^{-4}	3	6.52×10^{-3}	6.56×10^{-2}
2688	1×10^{-5}	5	7.83×10^{-3}	6.15×10^{-2}
4590	2×10^{-5}	3	3.74×10^{-3}	5.08×10^{-2}
4590	1×10^{-6}	5	5.08×10^{-3}	4.87×10^{-2}
11914	1×10^{-6}	3	1.57×10^{-3}	3.15×10^{-2}
11914	1×10^{-8}	5	2.32×10^{-3}	2.89×10^{-2}

[a] The total number of data points. [b] The weight function parameters, see eq 14. [c] Root-mean-square deviation based on 407 050 points.

TABLE 3: The Root-Mean-Square (rms) Deviations of Potential Energies (in hartree) and Gradients (in au) in the Vicinity of IRC between the Interpolated and Koizumi et Al.[5] 3-D Surface for 49 120 Points

			rms^c	
N_d^{a}	ϵ^b	n^b	potential	gradients
3070	3×10^{-6}	3	2.23×10^{-3}	3.87×10^{-2}
3070	5×10^{-8}	5	2.81×10^{-3}	3.98×10^{-2}

[a] The total number of data points. [b] The weight function parameters, see eq 14. [c] Root-mean-square deviation based on 49 120 points.

gradients for different numbers of data points and weight function parameters are given. The choice of the values of the weight function parameters is based on the smoothness of gradient surfaces.

We should emphasize that we have fit "global" surfaces; that is, we fit the entire range of geometries covered by the analytical PES. That is why the numbers of data points used in our fitting are large compare to the numbers of data points used by others[8,14−28,31,32,39] who have restricted their fits to the vicinity of the intrinsic reaction coordinates (IRC). Thus, for a more direct comparison we did some fits of the PES in the vicinity of the IRC. Koizumi et al.[5] have described the properties of the HN_2 minimum and $H{\cdots}N_2$ saddle point on the ab initio and analytical surfaces. Since the energy at the saddle point is 0.69 eV for the analytical surface, we have restricted the FD-IMLS fit to energies below that value. The rms deviations based on 49 120 points for energies and gradients between the exact, i.e., the Koizumi et al.,[5] and 3-D fitted surfaces in the neighborhood of the IRC are given in Table 3. To fit the potential in the vicinity of the IRC we needed only ∼25% as many data points as used in the fitting of the "global" 3-D surface. Again, the fit is better for the weight function parameter $n = 3$ than for $n = 5$.

Figure 3(a) shows a comparison of gradient surfaces calculated by the FD-IMLS method and the exact potential[5] in the vicinity of the IRC. These 2-D surfaces are functions of internuclear distances r_1 and r_3 ($r_2 = 2.1a_0$). The rms deviation

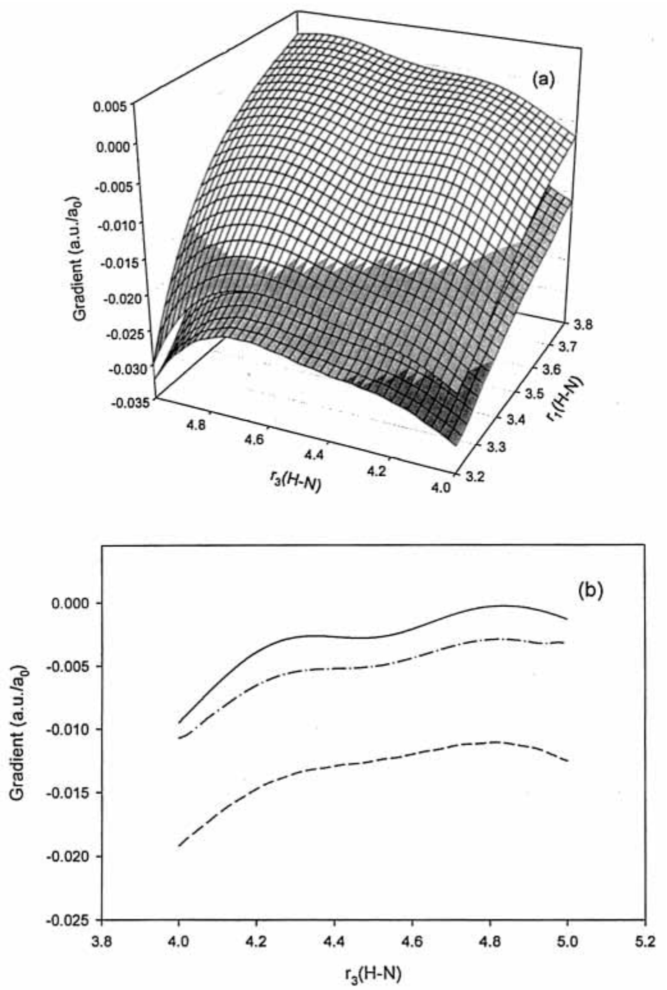

Figure 3. (a) 2-D gradient surface slices as a function of the r_1 and r_3 for $r_2 = 2.1a_0$ in the vicinity of IRC for $HN_2 \rightarrow H + N_2$. The top surface represents the gradients computed by using the Koizumi et al.[5] code, and the bottom surface is obtained by FD-IMLS fitting to 77 points. (b) The gradients as a function of r_3 for $r_1 = 3.65a_0$ and $r_2 = 2.1a_0$. The solid curve was calculated by using the Koizumi et al.[5] code, and the dash and dash−dot curves are FD-IMLS fits based on 11 and 21 points, respectively.

between the surfaces is 9.16×10^{-3} au, which compares well to the rms deviations for gradients obtained in other, related methods.[39] When the number of data points along each axis (step is 0.05) is doubled, the rms deviation for the gradients is 2.36×10^{-3} au. Again, this compares favorably with the results in ref 39. The quality of the fits are illustrated in Figure 3b, where we show the gradients as a function of r_3 for $r_1 = 3.65a_0$ and $r_2 = 2.1a_0$. The solid curve was calculated by using the Koizumi et al.[5] code, and the dash and dash−dot curves are FD-IMLS fits based on 11 and 21 points, respectively.

Although we cannot directly compare our results to those given in ref 39, it is clear that we need more points for the FD-IMLS fitting to achieve a comparable accuracy to that obtainable by SD-IMLS. But the FD-IMLS method has some advantages for applications to the many-atom systems. The number of basis functions in the SD-IMLS method for N atoms is $(N + 1)(N + 2)/2$; for example, for a triatomic system 10 basis functions are needed, whereas in the FD-IMLS method only four basis functions are required. A practical illustration of this is that in the study of the H_3 PES by SD-IMLS method, authors have been forced to employ a modified Shepard method for trajectory calculations, because SD-IMLS is somewhat time consuming.

Although, more data points are needed for the FD-IMLS fitting than in the SD-IMLS method in order to obtain the same quality fit, the simplicity of the FD-IMLS and the fact that it requires less CPU time can compensate for this drawback. In other words, the CPU time spent computing the extra data points can be regained in the fitting, and certainly in direct dynamics simulations this could be critically important.

5. Conclusions

We have presented a fitting method for PESs based on first-degree IMLS, and have tested it for one-, two-, and three-dimensional potentials. Our objective was to develop a method that eliminates the “flat-spot” phenomenon observed in Shepard interpolation and that does not require derivatives as does modified Shepard interpolation. Furthermore, our goal was to develop a simple algorithm that is not expensive in CPU time so that it could be useful in trajectory calculations. These objectives are achieved with the approach described in section 2. We have shown the advantages of this method over the Shepard approach. Unlike the modified Shepard method, the present method was tested for fitting of global 2-D and 3-D surfaces as well as the region in the vicinity of the IRC. Although the SD-IMLS method gives a better fit than does the FD-IMLS for the same number of data points, the simplicity of the FD-IMLS and the fact that it requires less CPU time can compensate for this drawback.

The results given by this first-degree IMLS application to a PES of one-, two-, and three-dimensions are encouraging. They motivate a more detailed look at the application of higher-degree IMLS methods to the fitting of PESs. Among the many issues that have to be resolved are the tradeoffs between IMLS degree, fit accuracy, computational efficiency, and weight function selection, as well as the scalability of these tradeoffs with increasing PES dimension. Future papers in this series will systematically take up these issues.

Acknowledgment. We are grateful to Drs. Albert Wagner and Michael Minkoff for many fruitful discussions on this work. We thank Prof. George C. Schatz for supplying a copy of the computer code for the HN_2 analytical potential energy surface and for helpful comments. We thank Prof. Ward H. Thompson for helpful comments in the early stage of this work. This work was supported by the Department of Energy, Office of Basic Energy Sciences, SciDAC Computational Chemistry Program (Grant No. DE-FG02-01ER15231).

References and Notes

(1) McLaughlin, D. R.; Thompson, D. L. *J. Chem. Phys*. **1973**, *59*, 4393.
(2) Sathyamurthy, N.; Raff, L. M. *J. Chem. Phys*. **1975**, *63*, 464.
(3) Sathyamurthy, N.; Rangarajan, R.; Raff, L. M. *J. Chem. Phys*. **1976**, *64*, 4606.
(4) Bowman, J. M.; Bittman, J. S.; Harding, L. B. *J. Chem. Phys.* **1985**, *83*, 660.
(5) Koizumi, H.; Schatz, G. C.; Walch, S. P. *J. Chem. Phys.* **1991**, *95*, 4130.
(6) Bentley, J. A.; Bowman, J. M.; Gazdy, B.; Lee, T. J.; Dateo, C. E. *Chem. Phys. Lett.* **1992**, *198*, 563.
(7) Bowman, J. M.; Gazdy, B.; Bentley, J. A.; Lee, T. J.; Dateo, C. E. *J. Chem. Phys*. **1993**, *198*, 308.
(8) Ischtwan, J.; Collins, M. A. *J. Chem. Phys.* **1994**, *100*, 8080.
(9) Frishman, A.; Hoffman, D. K.; Kouri, D. J. *J. Chem. Phys.* **1997**, *107*, 804.
(10) Hoffman, D. K.; Wei, G. W.; Zhang, D. S.; Kouri, D. J. *Phys. Rev. E* **1998**, *57*, 6152.
(11) Farwig, R. in *Algorithms For Approximation*; Mason, J. C., Cox, M. G., Eds.; Clarendon: Oxford, 1987; p 194.
(12) Shepard, D. *Proceedings of the 23rd ACM National Conference*; ACM: New York, 1968; p 517.
(13) Lancaster, P.; Salkauskas, K. *Curve and Surface Fitting. An Introduction*; Academic: London, 1986. (b) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in Fortran 77*; Cambridge University Press: Cambridge, 1996.
(14) Jordan, M. J. T.; Thompson, K. C.; Collins, M. A. *J. Chem. Phys*. **1995**, *102*, 5647.
(15) Jordan, M. J. T.; Thompson, K. C.; Collins, M. A. *J. Chem. Phys*. **1995**, *103*, 9669.
(16) Jordan, M. J. T.; Collins, M. A. *J. Chem. Phys*. **1996**, *104*, 4600.
(17) Thompson, K. C.; Collins, M. A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 871.
(18) Thompson, K. C.; Jordan, M. J. T.; Collins, M. A. *J. Chem. Phys*. **1998**, *108*, 564.
(19) Thompson, K. C.; Jordan, M. J. T.; Collins, M. A. *J. Chem. Phys.* **1998**, *108*, 8302.
(20) Collins, M. A.; Bettens, R. P. A. *Phys. Chem. Chem. Phys.* **1999**, *1*, 939.
(21) Bettens, R. P. A.; Collins, M. A. *J. Chem. Phys.* **1999**, *111*, 816.
(22) Duncan, A. H.; Collins, M. A. *J. Chem. Phys.* **1999**, *111*, 1346.
(23) Bettens, R. P. A.; Hansen, T. A.; Collins, M. A. *J. Chem. Phys.* **1999**, *111*, 6322.
(24) Collins, M. A.; Zhang, D. H. *J. Chem. Phys.* **1999**, *111*, 9924.
(25) Bettens, R. P. A.; Collins, M. A.; Jordan, M. J. T.; Zhang, D. H. *J. Chem. Phys.* **2000**, *112*, 10162.
(26) Zhang, D. H.; Collins, M. A.; Lee, S.-Y. *Science* **2000**, *290*, 961.
(27) Yang, M.; Zhang, D. H.; Collins, M. A.; Lee, S.-Y. *J. Chem. Phys*. **2001**, *114*, 4759.
(28) Fuller, R. O.; Bettens, R. P. A.; Collins, M. A. *J. Chem. Phys*. **2001**, *114*, 10711.
(29) Nguyen, K. A.; Rossi, I.; Truhlar, D. G. *J. Chem. Phys.* **1995**, *103*, 5522.
(30) Kim, Y.; Corchado, J. C.; Villa, J.; Xing, J.; Truhlar, D. G. *J. Chem. Phys*. **2000**, *112*, 2718.
(31) Ishida, T.; Schatz, G. C. *J. Chem. Phys.* **1997**, *107*, 3558.
(32) Ishida, T.; Schatz, G. C. *Chem. Phys. Lett*. **1998**, *298*, 285.
(33) Rhee, Y. M.; Lee, T. G.; Park, S. C.; Kim, M. S. *J. Chem. Phys*. **1997**, *106*, 1003.
(34) Moon, J. H.; Park, S. T.; Kim, M. S. *J. Chem. Phys.* **1999**, *110*, 972.
(35) Dzegilenko, F. N.; Qi, J.; Bowman, J. M. *Int. J. Quantum Chem*. **1997**, *65*, 965.
(36) Rhee, Y. M. *J. Chem. Phys.* **2000**, *113*, 6021.
(37) Eckert, F.; Werner, H. J. *Chem. Phys. Lett.* **1999**, *302*, 208.
(38) McLain, D. H. *Comput. J.* **1974**, *17*, 318.
(39) Ishida, T.; Schatz, G. C. *Chem. Phys. Lett.* **1999**, *314*, 369.
(40) Bowman, J. M.; Kuppermann, A. *Chem. Phys. Lett.* **1975**, *34*, 523.
(41) Wall, F. T.; Porter, R. N. *J. Chem. Phys.* **1962**, *36*, 3256.
(42) We have used different coordinate systems for fitting the 2- and 3-D surfaces. Since the Koizumi et al.[5] potential is written as a function of R, r, and θ, it was convenient to use those coordinates in the 2-D fitting. However, the internuclear distances have commonly been used for fitting 3-D surfaces and it seemed appropriate to use them here.