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# A new functional form to obtain analytical potentials of triatomic molecules

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A new way of fitting *ab initio* values of the potential energy of triatomic molecules is discussed. The new functional form proposed for the potential energy function satisfies several criteria for use in scattering calculations and it is so stable that, when increasing the number of parameters in the fit, it maintains a good behavior at short, intermediate, and long range of the whole potential. Applications of the fitting technique to obtain the potential energy functions for the ground states of  $\text{H}_3$ ,  $\text{H}_2\text{He}^+$ , and  $\text{LiHF}$  are presented. For the  $\text{H}_3$  system, we fit all 267 of Liu and Siegbahn's *ab initio* points. With one nonlinear parameter and 23 linear parameters, the root-mean-square error was 1.21 kcal/mol and the maximum absolute deviation 7.94 kcal/mol; these values are lower than previous global fittings with a similar number of parameters except for the Truhlar and Horowitz fit of the Liu and Siegbahn data, LSTH potential, but when the number of linear parameters was increased to 71, the root-mean-square error was reduced to 0.07 kcal/mol and the maximum absolute deviation to 0.25 kcal/mol (approximately one half the corresponding values of the LSTH ones). The new global fitting procedure is then applied to obtain potential energy functions for the  $\text{H}_2\text{He}^+$  and the  $\text{LiHF}$  systems within the chemical accuracy of 1 kcal/mol.

## I. INTRODUCTION

In this paper, we describe a method for constructing analytical potential energy surfaces (PES) for triatomic molecules. The molecular dynamical calculations require a detailed knowledge of the interaction potential and its first partial derivatives with respect to interparticle distance as an input.<sup>1-3</sup> In fact, this is a serious difficulty because the collisional outcome is highly sensitive to the features of the PES. Therefore the chosen interpolating function has to meet several stringent criteria.<sup>4</sup>

Nowadays, we have more and more accurate *ab initio* PES calculations. This fact implies the need of functional forms of global nature to fit these *ab initio* data with a global root-mean-square (rms) error lower than the chemical accuracy (1 kcal/mol). Several global functional forms have been suggested for reactive scattering of triatomic systems. However, almost none of the functions proposed meets all the criteria for all the systems.<sup>4</sup>

London,<sup>5</sup> and Eyring, Polanyi, and Sato<sup>6</sup> proposed the LEPS equation that has been applied to a large number of systems mainly as an interpolatory function to connect reactants and products for which spectroscopic data are available. The LEPS function is not flexible enough when it comes to fit *ab initio* PES; sometimes it leads to spurious hollows<sup>7</sup> and it fails to reproduce even the qualitative features for the  $\text{Li} + \text{HF}$ <sup>8</sup> and  $\text{Be} + \text{HF}$ <sup>9</sup> systems due to the sudden nature of their PES. The LEPS function also leads to a discontinuity in the PES for  $\text{AB}_2$  systems.<sup>10</sup>

The diatomics-in-molecules (DIM) approach was used first by Kuntz<sup>11</sup> to fit the *ab initio* PES for the collinear  $\text{H}_2\text{He}^+$  system.<sup>12</sup> Like the LEPS, the DIM function has the advantage that it provides reasonable potential energy values at geometries for which there are no *ab initio* data available. A generalized DIM theory<sup>13</sup> has been able to fit<sup>14</sup> the  $\text{H}_3$  PES,<sup>15</sup> however, the DIM function is inadequate<sup>16</sup> to fit

a highly accurate configuration interaction (CI) calculation for the  $\text{H}_2\text{He}^+$  PES.<sup>17</sup>

The rotated-Morse-curve-spline (RMCS) approach proposed by Wall and Porter<sup>18</sup> has the advantage that the number of *ab initio* points required for a fit could be minimal.<sup>19</sup> However, for certain mass combinations such as  $L + \text{HH}$  ( $L = \text{light}$ ,  $H = \text{heavy}$ ), the RMCS approach may not be suitable for quantal reactive scattering.<sup>20</sup> Moreover, the RMCS method fails to fit the sudden surface for the reaction  $\text{Li} + \text{HF}$ .<sup>4</sup>

Sorbie and Murrell<sup>21</sup> (SM) proposed another function that has been used successfully for constructing potentials in the last few years.<sup>22-24</sup> A problem presented in fitting PES using the Sorbie and Murrell function is the existence of spurious wells in the regions where there are not enough *ab initio* data. A solution practiced by these authors is to add or subtract a Gaussian function. For instance, they subtracted a Gaussian function centered at the saddle point to reduce the barrier height for the  $\text{Li} + \text{HF}$  reaction,<sup>22</sup> introducing a certain amount of *ad hoc* character. Moreover, an investigation of the minimum energy path (MEP) shows that the  $\text{LiHF}$  PES presents spurious features.<sup>25</sup>

More recently García and Laganà proposed a new generalized bond-order (BO) functional form for triatomic molecules<sup>26</sup> based on the original bond-energy-bond-order (BEBO) idea,<sup>27</sup> obtaining the  $\text{H}_3$  and  $\text{BeHF}$  PES,<sup>26</sup> the  $\text{LiHCl}$  PES,<sup>28</sup> and the  $\text{MgHF}$  PES<sup>29</sup> with rms deviations comparable to that obtained using the Sorbie and Murrell function. However, the BO function presents a wrong behavior at the short-range part of the potential with undesirable structures of the fitted PES.<sup>29</sup>

The paper is organized as follows: In Sec. II, we give an outline of the new global fitting procedure that is first tested for the  $\text{H}_3$  system (Sec. III) in order to compare its accuracy with that of other global interpolating functional forms. In

Sec. IV and V, *ab initio* values of the  $\text{H}_2\text{He}^+$  PES and the LiHF PES are fitted, respectively, using our new global fitting procedure and the surfaces obtained in this way are discussed. We select these PES because of their fitting difficulties with several procedures cited previously and their different symmetry properties. Finally, in the last section, we present some conclusions.

## II. THE GLOBAL FITTING PROCEDURE

For the PES of the triatomic system  $ABC$ , we choose the three internuclear distances  $R_{AB}$ ,  $R_{AC}$ , and  $R_{BC}$  as variables. These are independent coordinates, but they must satisfy the triangulation relation

$$R_s + R_t \leq R_u, \quad s, t, u = AB, AC, BC. \quad (1)$$

The complete potential energy function for a triatomic system may be written as a many-body expansion<sup>30</sup>

$$V_{ABC}(\mathbf{R}) = \sum_A V_A^{(1)} + \sum_{AB} V_{AB}^{(2)}(R_{AB}) + V_{ABC}^{(3)}(R_{AB}, R_{AC}, R_{BC}), \quad (2)$$

where the summations are over all the terms of a given type and where  $V_A^{(1)}$  is the energy of atom  $A$  in its appropriate electronic state;  $V_{AB}^{(2)}$  is the two-body energy that corresponds to the diatomic potential energy curve which vanishes asymptotically when  $R_{AB} \rightarrow \infty$  and goes to infinity when  $R_{AB} \rightarrow 0$ ;  $V_{ABC}^{(3)}$  is the three-body energy; we impose the conditions that becomes zero at all the dissociation limits and when at least one of the internuclear distances is zero. This last condition is not present in previous potential energy functions as  $\text{SM}^{21}$  or  $\text{BO}^{26}$  based on the many-body expansion [Eq. (2)], but it is necessary to allow that the potential energy at short internuclear distances be only a contribution of the repulsive part of diatomic potentials.

The diatomic terms  $V_{AB}^{(2)}$  of the potential [Eq. (2)] are expressed using a polynomial form

$$V_{AB}^{(2)}(R_{AB}) = \frac{c_0 e^{-\alpha_{AB} R_{AB}}}{R_{AB}} + \sum_{i=1}^N c_i \rho_{AB}^i, \quad (3)$$

where the first term in Eq. (3), with the restriction  $c_0 > 0$ , ensures that the diatomic potential goes to infinity when  $R_{AB} \rightarrow 0$ ; this term was first used by Hellmann for the  $\text{K}_2$  molecule.<sup>31</sup> The polynomial variables  $\rho$  are given by

$$\rho_{AB} = R_{AB} e^{-\beta_{AB}^{(l)} R_{AB}}, \quad l = 2 \text{ or } 3. \quad (4)$$

The linear parameters  $c_i$ ,  $i = 0, 1, \dots, N$  [Eq. (3)] and the nonlinear parameters  $\alpha_{AB}$  [Eq. (3)] and  $\beta_{AB}^{(2)}$  [Eq. (4)] are determined by fitting the *ab initio* values of the diatomic fragments computed with the same basis set as the corresponding atoms in the triatomic system and using the same *ab initio* procedure. Sometimes an improved potential can be obtained by combining experimentally determined two-body terms with an *ab initio* three-body term.<sup>23</sup> The reason for this is that an inaccurate treatment of electronic correlation or errors due to incomplete basis sets are carried through to the triatomic calculations. However, the handling of empirical diatomic potentials introduce certain

*ad hoc* character and may produce spurious structures in the PES.<sup>24</sup>

Moreover, the diatomic potentials must be fitted with a rms error of at least one-half than the rms error that one wants to obtain in the fitting of the three-body term. The reason for this is that in the fit of the three-body term, we use as data points the difference between the *ab initio* values and the diatomic potentials; accordingly, a great error on these potentials can produce a distortion in the three-body term.

The three-body term  $V_{ABC}^{(3)}$  of the potential [Eq. (2)] is also expressed as a polynomial of order  $M$  in the same variables  $\rho_{AB}$ ,  $\rho_{AC}$ , and  $\rho_{BC}$  [Eq. (4) with  $l = 3$ ]:

$$V_{ABC}^{(3)}(R_{AB}, R_{AC}, R_{BC}) = \sum_{i,j,k}^M d_{ijk} \rho_{AB}^i \rho_{AC}^j \rho_{BC}^k, \quad (5)$$

where the next constraints must be fulfilled to ensure the conditions that becomes zero at all the dissociation limits and when at least one of the internuclear distances is zero, these constraints are

$$i + j + k \neq i \neq j \neq k, \quad (6a)$$

$$i + j + k \leq M. \quad (6b)$$

The linear parameters  $d_{ijk}$  [Eq. (5)] and the nonlinear parameters  $\beta_{AB}^{(3)}$ ,  $\beta_{AC}^{(3)}$ , and  $\beta_{BC}^{(3)}$  [Eq. (4)] are determined by fitting the *ab initio* values of the triatomic system minus the diatomic potentials at the corresponding internuclear distances.

If the system under consideration has two or three atoms of the same type (systems  $A_3$  or  $AB_2$ ), there is an evident symmetry in Eq. (5) that implies additional constraints in the linear  $d_{ijk}$  and nonlinear  $\beta_{AB}^{(3)}$ ,  $\beta_{AC}^{(3)}$ ,  $\beta_{BC}^{(3)}$  parameters with a minor number of parameters in the global fit.

To apply our fitting procedure, we select the three systems  $\text{H}_3$ ,  $\text{H}_2\text{He}^+$ , and LiHF because they are interesting test cases and because they belong to the three different symmetries ( $A_3$ ,  $AB_2$ , and  $ABC$ ).

## III. THE $\text{H}_3$ SYSTEM

The  $\text{H}_3$  system is usually considered as the prototype of reactive systems, its electronic energy has been calculated accurately<sup>15,32</sup> and the *ab initio* points have been fitted using a functional form given by Truhlar and Horowitz (LSTH)<sup>33</sup> that has a rather complex analytical structure that cannot be extended to other systems in a straightforward manner.<sup>26</sup> The LSTH functional form is preserved, as much as possible, in a more recent double many-body expansion (DMBE) surface of Varandas *et al.*,<sup>34</sup> although having a larger rms error than the LSTH one may be more accurate at higher energies. For comparative purposes, the performances of the  $\text{BO}^{26}$  and LSTH<sup>33</sup> are discussed. Another fitting<sup>35</sup> of the Siegbahn and Liu points<sup>15</sup> will not be examined here. In fact, their rms deviation is not smaller than the one obtained for the BO potential.

In our approach, the *ab initio* values of  $\text{H}_2$  calculated with the same basis set as the  $\text{H}_3$  system<sup>15</sup> are fitted to a functional form given in Eq. (3) up to sixth order ( $N = 6$ ) with a rms deviation of 0.0027 kcal/mol and a maximum error of 0.0056 kcal/mol. In Table I, we report the value of

TABLE I. Parameters of the  $H_3$  PES.

Two-body terms $V_{HH}^{(2)*}$	
$i$	$c_i$
0	0.105 458 829( + 01)
1	- 0.246 365 037( - 01)
2	- 0.759 893 317( + 01)
3	0.419 034 407( + 02)
4	- 0.132 708 934( + 03)
5	0.228 198 527( + 03)
6	- 0.166 018 453( + 03)
$\alpha_{HH}$	0.230 433 887( + 01)
$\beta_{HH}^{(2)}$	0.109 344 220( + 01)
Three-body term $V_{HHH}^{(3)}$ for $M = 7^a$	
$ijk$	$d_{ijk}^b$
1 1 0	0.993 901 213( + 01)
1 1 1	- 0.176 136 667( + 02)
2 1 0	- 0.401 767 696( + 02)
2 1 1	0.292 520 486( + 03)
2 2 0	0.103 301 598( + 04)
3 1 0	- 0.382 882 412( + 03)
2 2 1	0.406 756 601( + 03)
3 1 1	- 0.336 751 437( + 04)
3 2 0	- 0.201 570 127( + 04)
4 1 0	0.226 782 981( + 04)
2 2 2	- 0.316 917 152( + 05)
3 2 1	0.135 800 928( + 05)
3 3 0	0.132 921 615( + 05)
4 1 1	- 0.802 180 366( + 04)
4 2 0	- 0.696 835 758( + 04)
5 1 0	- 0.999 310 416( + 03)
3 2 2	0.558 344 966( + 04)
3 3 1	0.925 854 411( + 05)
4 2 1	- 0.820 217 694( + 05)
4 3 0	- 0.956 839 251( + 04)
5 1 1	0.649 080 710( + 05)
5 2 0	0.138 432 602( + 05)
6 1 0	- 0.667 736 057( + 04)
$\beta_{HH}^{(3)}$	0.119 436 989( + 01)
Three-body term $V_{HHH}^{(3)}$ for $M = 11$	
$ijk$	$d_{ijk}^{a,b}$
1 1 0	0.146 770 877( + 02)
1 1 1	- 0.483 260 642( + 03)
2 1 0	- 0.162 448 772( + 03)
2 1 1	0.634 377 178( + 04)
2 2 0	0.732 211 907( + 04)
3 1 0	- 0.100 646 029( + 04)
2 2 1	- 0.107 658 664( + 06)
3 1 1	- 0.976 804 037( + 04)
3 2 0	- 0.556 101 593( + 05)
4 1 0	0.280 447 190( + 05)
2 2 2	0.110 838 286( + 07)
3 2 1	0.592 971 658( + 06)
3 3 0	0.658 281 908( + 06)
4 1 1	- 0.225 451 437( + 06)
4 2 0	0.124 609 545( + 06)
5 1 0	- 0.273 118 730( + 06)
3 2 2	- 0.564 854 415( + 07)
3 3 1	- 0.361 874 751( + 07)
4 2 1	- 0.401 815 356( + 06)
4 3 0	- 0.261 354 176( + 07)
5 1 1	0.375 164 869( + 06)
5 2 0	- 0.148 254 430( + 06)
6 1 0	0.198 982 137( + 07)
3 3 2	0.187 393 087( + 08)
4 2 2	0.201 321 891( + 08)
4 3 1	0.111 554 806( + 08)
4 4 0	0.166 243 684( + 08)

TABLE I. (Continued.)

Three-body term $V_{HHH}^{(3)}$ for $M = 11$	
5 2 1	- 0.149 776 794( + 08)
5 3 0	0.199 439 657( + 07)
6 1 1	0.136 263 633( + 08)
6 2 0	0.265 912 502( + 07)
7 1 0	- 0.106 033 621( + 08)
3 3 3	- 0.465 868 040( + 07)
4 3 2	- 0.500 720 867( + 08)
4 4 1	0.630 672 996( + 08)
5 2 2	- 0.461 834 855( + 08)
5 3 1	- 0.728 959 891( + 08)
5 4 0	- 0.335 028 511( + 08)
6 2 1	0.100 727 195( + 09)
6 3 0	0.566 816 579( + 07)
7 1 1	- 0.959 253 619( + 08)
7 2 0	- 0.134 248 831( + 08)
8 1 0	0.350 805 564( + 08)
4 3 3	0.213 131 653( + 08)
4 4 2	0.337 158 307( + 09)
5 3 2	- 0.130 478 878( + 09)
5 4 1	- 0.987 250 013( + 08)
5 5 0	0.123 130 205( + 09)
6 2 2	0.213 609 586( + 09)
6 3 1	0.184 028 066( + 09)
6 4 0	- 0.187 542 019( + 08)
7 2 1	- 0.269 834 441( + 09)
7 3 0	0.100 039 222( + 08)
8 1 1	0.248 507 918( + 09)
8 2 0	0.217 067 235( + 08)
9 1 0	- 0.622 858 531( + 08)
4 4 3	0.719 140 621( + 09)
5 3 3	- 0.122 589 423( + 10)
5 4 2	- 0.217 980 053( + 09)
5 5 1	0.506 243 084( + 09)
6 3 2	0.636 731 398( + 09)
6 4 1	- 0.304 483 357( + 09)
6 5 0	- 0.755 609 115( + 08)
7 2 2	- 0.519 660 651( + 09)
7 3 1	- 0.706 290 113( + 08)
7 4 0	0.738 833 575( + 08)
8 2 1	0.265 745 458( + 09)
8 3 0	- 0.412 827 062( + 08)
9 1 1	- 0.230 070 976( + 09)
9 2 0	- 0.853 939 833( + 07)
10 1 0	0.451 635 127( + 08)
$\beta_{HH}^{(3)}$	0.116 609 001( + 01)

\* All the coefficients are given in atomic units.

<sup>b</sup> The coefficients differing in permutations of the  $ijk$  labels are equal and therefore have been omitted in this table.

the parameters of this fit being the calculated  $D_e$ ,  $r_e$ , and  $\omega_e$  equal to 4.73 eV, 1.4014 a.u., and 4402.9  $\text{cm}^{-1}$ , respectively. These values are very close to the experimental ones.<sup>36</sup> We must stress that other authors<sup>26,33</sup> prefer to fit the most accurate values of Kolos and Volniewicz.<sup>37</sup> In fact, we verify that in the  $H_3$  system, there are no important differences in the global PES.

The difference between the *ab initio* values<sup>15</sup> (267 points) and the sum of the diatomic potentials is fitted to Eq. (5). The best-fit parameters  $d_{ijk}$  and  $\beta_{HH}^{(3)}$  for  $M = 7$  (23 linear parameters, rms = 1.21 kcal/mol) and  $M = 11$  (71 linear parameters, rms = 0.07 kcal/mol) are reported in Table I, where linear coefficients are labeled by their  $ijk$  values

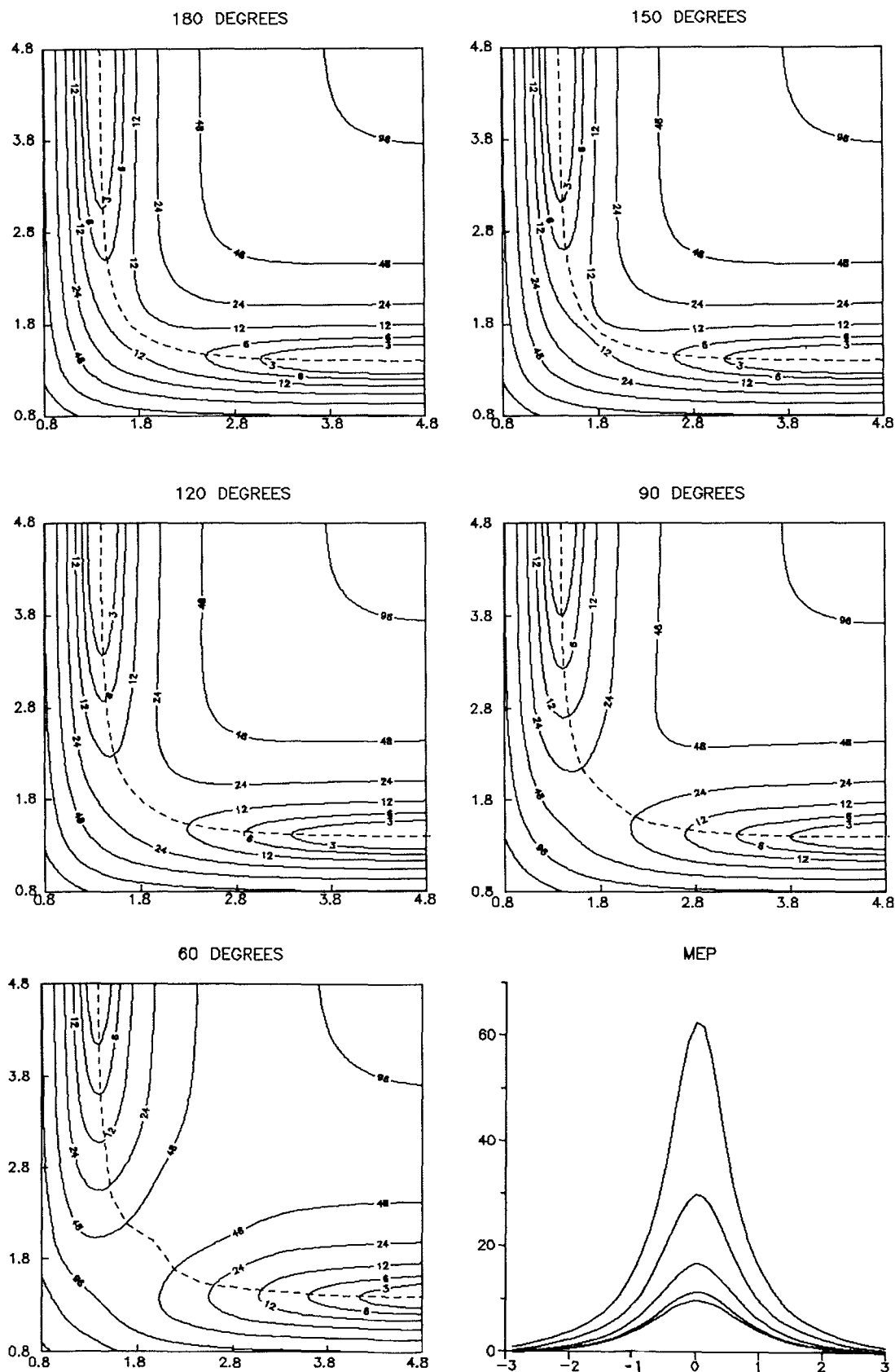


FIG. 1. Potential contours of the interaction potential for  $H_3$ . For each contour map, one internal bond angle is fixed. The fixed internal bond angle is indicated at the top of each figure. The solid curves are contours of the interaction potential corresponding to 3, 6, 12, 24, 48, 96, 192, and 384 kcal/mol. The dashed curves are the minimum energy paths. In the right-hand bottom panel, we show the potential energy barriers for the  $H_3$  system at fixed internal bond angle as functions of distance from saddle point along MEP through the plane; in order of increasing barrier height, the curves are for 180°, 150°, 120°, 90°, and 60°. All the energies are in kcal/mol and all the interatomic distances in atomic units.

corresponding to all the possible and different permutations of these labels. All the parameters are given in atomic units.

In the Fig. 1, we present contour maps of the PES for  $H_3$  corresponding to the same contours as Ref. 33 (LSTH) and using our  $M = 11$  fit, for each contour map one internal bond angle is fixed to  $180^\circ$ ,  $150^\circ$ ,  $120^\circ$ ,  $90^\circ$ , and  $60^\circ$ . All of these contour maps are identical to the corresponding LSTH ones, except for  $60^\circ$ , where we have no discontinuous derivatives as occur<sup>38</sup> for the LSTH functional representation, although this is not a serious problem for representing the PES in the regions that are most important for the chemical reaction. This problem has also been solved in the more recent DMBE PES.<sup>34</sup> In the same figure, we report a panel with the corresponding minimum-energy paths (MEPs) that are very close to those obtained by Truhlar and Horowitz.<sup>33</sup>

Comparison of the rms deviations relative to the BO,  $M = 7$  (this paper), LSTH, and  $M = 11$  (this paper) functional forms are reported in Table II for comparative purposes. In this table, the rms deviation is reported separately for different values of the bond angle, following the scheme suggested by Truhlar and Horowitz.<sup>33</sup> Symmetric and asymmetric points are reported separately in order to have a more detailed view of the accuracy of the different functional forms. When compared with the BO method, our approach appears to be more efficient; only the LSTH procedure leads to a rms deviation smaller than our  $M = 7$  fit with a similar number of parameters (eight nonlinear parameters and 15 linear parameters in the LSTH fit vs 1 nonlinear parameter and 23 linear parameters in our  $M = 7$  fit). If we increase the order of the fit up to  $M = 11$ , we can obtain a PES with a global correct behavior and with a rms error and a maximum deviation that are approximately one-half the corresponding values of the LSTH ones (see the last two columns in Table II). However, as for the LSTH fit, we include only seven points with  $D_{3h}$  symmetry and do not include any nonsymmetric points in the vicinity of  $D_{3h}$  geometries, therefore, the DMBE fit may be more accurate in this region of the PES.

In Table III, we report the rms error and the maximum deviation when we increase the order  $M$  of our fitting procedure

TABLE III. Accuracy vs the order of the fit for the  $H_3$  system.

$N$	$n_{\text{par}}^a$	rms <sup>b</sup>	$\Delta V_{\text{max}}^b$
5	10	2.260	13.012
6	16	1.788	11.839
7	23	1.211	7.944
8	32	0.602	3.421
9	43	0.421	1.600
10	56	0.179	0.839
11	71	0.073	0.246
12	89	0.043	0.212
13	109	0.022	0.178

<sup>a</sup>  $n_{\text{par}}$  is the number of linear parameters of the fit; in all cases there is only one nonlinear parameter.

<sup>b</sup> In kcal/mol.

to test the stability and the convergence properties of our procedure. From this table, we can see that the rms error decreases exponentially with the number of linear parameters of the fit (approximately as  $5e^{-0.067n}$ ,  $n$  being the number of linear parameters). We stress that all the PES obtained up to  $M = 13$  have a correct behavior at short, intermediate, and long range of the whole potential as for the  $M = 11$  fit that we can see in Fig. 1. In fact, we verify that the BO approach presents undesirable structures at the short-range part of the potential when we increase the order of the fit. The good behavior and stability are the best attributes of our functional form.

#### IV. THE $H_2\text{He}^+$ SYSTEM

McLaughlin and Thompson<sup>17</sup> have published Hartree-Fock (HF) and configuration interaction (CI) PES for the endothermic reaction  $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$ . Hopper<sup>39</sup> had earlier published a multiconfiguration self-consistent field (MCSCF) surface for this reaction in collinear geometry. Prior to that Brown and Hayes<sup>12</sup> had published a linear combination of atomic orbitals-molecular orbital SCF

TABLE II. A comparison between different functional forms.

Points	$s/a$	$N_{\text{pts}}$	BO <sup>a</sup>		Present ( $M = 7$ )		LSTH <sup>b</sup>		Present ( $M = 11$ )	
			rms <sup>c</sup>	$\Delta V_{\text{max}}^c$	rms <sup>c</sup>	$\Delta V_{\text{max}}^c$	rms <sup>c</sup>	$\Delta V_{\text{max}}^c$	rms <sup>c</sup>	$\Delta V_{\text{max}}^c$
All	$s/a$	267	2.06	15.53	1.21	7.94	0.17	0.55	0.073	0.246
180	$s$	15	2.59	6.85	0.68	1.41	0.074	0.23	0.065	0.182
180	$a$	122	0.83	1.68	0.62	1.84	0.091	0.21	0.050	0.117
180	$s/a$	137	1.16	6.85	0.63	1.84	0.089	0.23	0.052	0.182
Bent	$s$	34	3.89	15.53	2.22	7.94	0.28	0.55	0.101	0.246
Bent	$a$	96	2.09	8.91	1.33	4.25	0.21	0.52	0.086	0.225
Bent	$s/a$	130	2.70	15.53	1.61	7.94	0.23	0.55	0.090	0.246
150	$s/a$	40	1.48	5.93	0.45	1.53	0.19	0.42	0.107	0.246
120	$s/a$	50	1.94	6.59	1.05	2.08	0.22	0.53	0.073	0.225
90	$s/a$	33	3.12	8.91	2.32	4.25	0.25	0.48	0.084	0.208
60	$s$	7	7.19	15.53	3.71	7.94	0.37	0.55	0.120	0.234

<sup>a</sup> Reference 26.

<sup>b</sup> Reference 33.

<sup>c</sup> Units are in kcal/mol.

(LCAO-MO-SCF) surface for the same collinear reaction. The DIM semiempirical method was used to fit the collinear SCF surface<sup>12</sup> and the resulting potential function was used to construct an approximate PES for nonlinear geometries.<sup>11,40</sup> Joseph and Sathyamurthy<sup>16</sup> report an analytic fit to the accurate *ab initio* points of the  $\text{H}_2\text{He}^+$  PES<sup>17</sup> using the SM function with a rms deviation of 1.6 kcal/mol, but they did not give details of this analytic fit.

It has been demonstrated that collinear trajectories on the ground-state DIM  $\text{H}_2\text{He}^+$  PES<sup>11</sup> do not exhibit vibrational enhancement for reaction between He and  $\text{H}_2^+$  in both the quasiclassical<sup>41</sup> and quantal<sup>42</sup> treatments, contrary to experimental findings.<sup>43</sup> When the *ab initio* SCF<sup>12</sup> collinear points were spline fitted directly, however, vibration enhancement was reported for quasiclassical trajectories.<sup>41</sup> On the other hand, Kuntz and Whitton<sup>40</sup> have found strong vibrational enhancement for quasiclassical trajectories using a three-dimensional DIM PES. Recently, 3D quantum scattering calculations of the  $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$  reaction have been reported using the DIM PES<sup>44</sup> and the SM PES.<sup>45</sup> Sometimes small changes in the PES may lead to dramatically different collision events; it is clear that a definitive three-dimensional PES could resolve some of the ambiguities involved with interpolating and theoretical scattering techniques.

We start fitting the diatomic molecules  $\text{H}_2^+$  ( $1^2\Sigma_g^+$ ) and  $\text{HHe}^+$  ( $1^1\Sigma$ ) from the accurate *ab initio* CI calculations for the  $\text{H}_2\text{He}^+$  system made by McLaughlin and Thompson.<sup>17</sup> In Table IV, we report the coefficients up to fourth order [ $N = 4$  in Eq. (6)], where the rms deviations are lower than 0.05 kcal/mol. Then, we obtain the three-body term of the PES as for the  $\text{H}_3$  system. Here we use the  $\text{H}_2\text{He}^+$  *ab initio* points corresponding to internuclear distances from 1 to 10 a.u. and bond angles of  $0^\circ$ ,  $30^\circ$ ,  $60^\circ$ ,  $90^\circ$ ,  $120^\circ$ ,  $150^\circ$ , and  $180^\circ$  (with a total of 551 points). The best-fit parameters  $d_{ijk}$ ,  $\beta_{\text{HH}^+}^{(3)}$ , and  $\beta_{\text{HHe}^+}^{(3)}$  for  $M = 6$  (37 linear

TABLE V. The three-body terms  $V_{\text{HHe}^+}^{(3)}$  for  $M = 6$ .<sup>a</sup>

$ijk$	$d_{ijk}$
1 1 0	0.127 946 000( + 02)
0 1 1	0.353 392 133( + 02)
1 1 1	0.292 471 126( + 03)
1 2 0	-0.433 904 279( + 02)
0 2 1	-0.417 751 317( + 03)
2 0 1	-0.143 070 459( + 03)
1 2 1	0.107 581 926( + 04)
2 1 1	-0.240 449 187( + 04)
2 2 0	0.671 154 302( + 03)
0 2 2	0.312 544 310( + 04)
1 3 0	-0.158 255 169( + 02)
0 3 1	0.810 802 828( + 03)
3 0 1	0.595 507 758( + 03)
2 2 1	0.518 706 891( + 04)
1 2 2	-0.949 728 988( + 04)
1 3 1	-0.690 746 610( + 04)
3 1 1	0.365 145 729( + 04)
2 3 0	-0.485 047 295( + 03)
0 3 2	-0.554 719 384( + 04)
3 0 2	-0.262 898 353( + 04)
1 4 0	-0.264 276 243( + 02)
0 4 1	0.130 742 987( + 04)
4 0 1	-0.926 575 362( + 03)
2 2 2	0.208 590 994( + 05)
2 3 1	0.217 310 348( + 05)
1 3 2	-0.297 064 764( + 04)
3 1 2	-0.198 544 356( + 05)
3 3 0	0.168 872 993( + 04)
0 3 3	0.195 293 305( + 05)
1 4 1	-0.989 564 785( + 04)
4 1 1	0.210 984 760( + 04)
2 4 0	-0.451 701 748( + 03)
0 4 2	0.180 156 350( + 04)
4 0 2	0.312 359 925( + 04)
1 5 0	0.725 395 017( + 03)
0 5 1	0.108 480 933( + 04)
5 0 1	0.275 557 091( + 03)
$\beta_{\text{HH}^+}^{(3)}$	0.153 556 550( + 01)
$\beta_{\text{HHe}^+}^{(3)}$	0.105 398 199( + 01)

<sup>a</sup> All the coefficients are given in atomic units and  $d_{ijk} = d_{ikj}$ .

TABLE IV. Two-body terms of the  $\text{H}_2\text{He}^+$  PES.

Two-body term $V_{\text{HH}^+}^{(2)}$	$c_i$
$i$	
0	0.602 282 014( + 00)
1	-0.781 317 912( + 00)
2	0.112 448 130( + 01)
3	-0.211 822 858( + 01)
$\alpha_{\text{HH}^+}$	0.731 416 390( + 00)
$\beta_{\text{HH}^+}^{(2)}$	0.997 206 724( + 00)
Two-body terms $V_{\text{HHe}^+}^{(2)}$	$c_i$
$i$	
0	0.283 322 994( + 01)
1	-0.270 314 749( - 01)
2	-0.187 839 429( + 01)
3	0.217 238 959( + 01)
$\alpha_{\text{HHe}^+}$	0.316 094 949( + 01)
$\beta_{\text{HHe}^+}^{(2)}$	0.119 204 421( + 01)

<sup>a</sup> All the coefficients are given in atomic units.

parameters and two nonlinear parameters) with a rms error of 0.71 kcal/mol (lower than the chemical accuracy) and a maximum deviation of 4.25 kcal/mol (corresponding to a point in the zone of higher energies) are reported in Table V, where the coefficients  $d_{ijk}$  are equal to  $d_{ikj}$  because of the symmetry in Eq. (5). We must stress that the fit presented here is the best fit up to date of the  $\text{H}_2\text{He}^+$  system, preserving the accuracy of the *ab initio* points.

In Fig. 2, we show contour maps of the  $\text{H}_2\text{He}^+$  PES using our fit (Tables IV and V); for each contour map, one internal bond angle is fixed to  $180^\circ$ ,  $135^\circ$ ,  $90^\circ$ ,  $45^\circ$ , and  $0^\circ$ . In fact, the contour maps corresponding to  $135^\circ$  and  $45^\circ$  are totally interpolated maps because there are no calculated *ab initio* points for these internal bond angles.<sup>17</sup> As we can see in this figure, all the maps present a correct behavior at short, intermediate, and long range of the potential. Moreover, we draw the corresponding MEP over the contour map

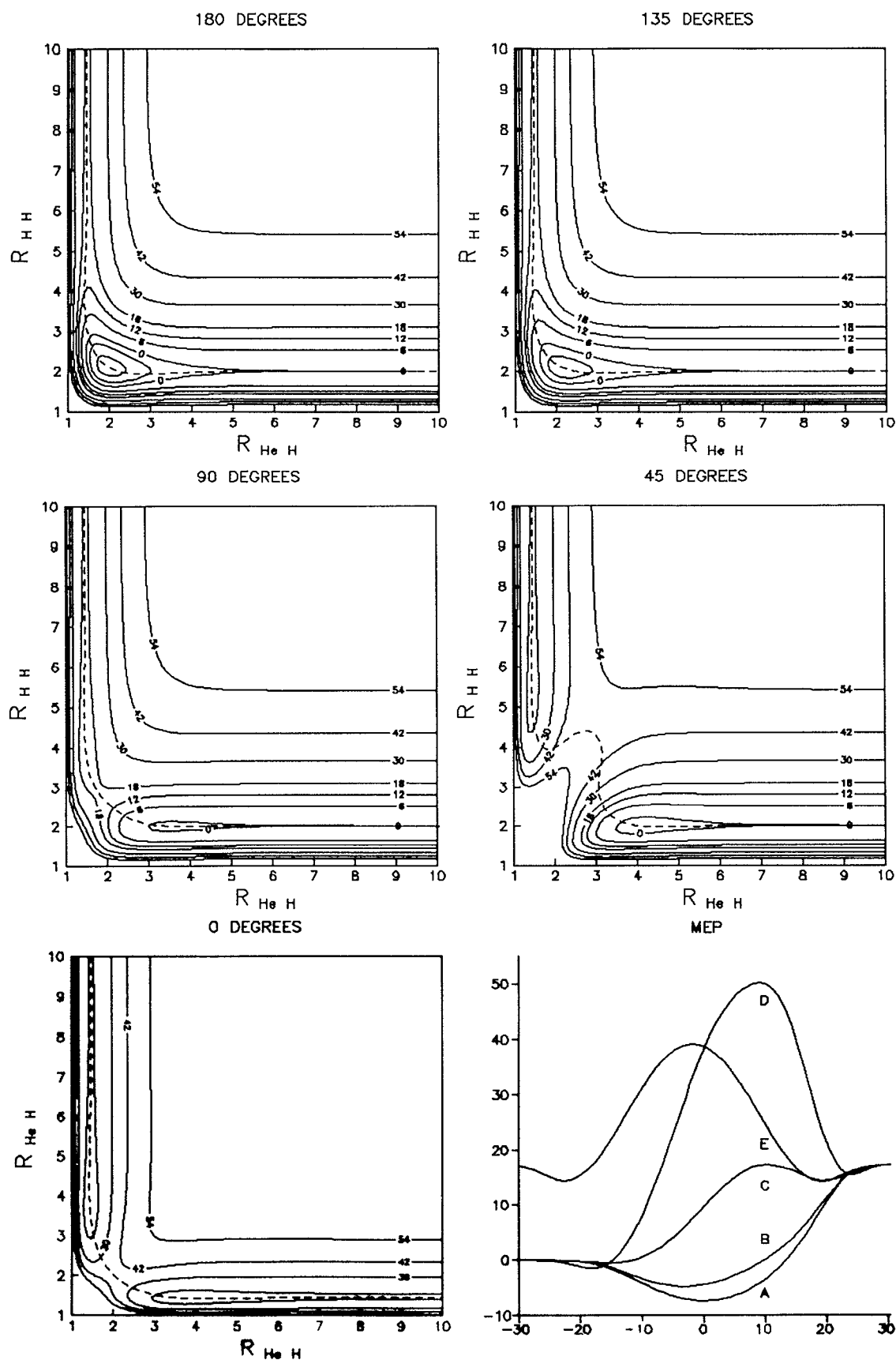


FIG. 2. Potential contours of the interaction potential for  $\text{H}_2\text{He}^+$ . For each contour map, one internal bond angle is fixed. The fixed internal bond angle is indicated at the top of each figure. The solid curves are contours of the interaction potential corresponding to  $-6$ ,  $-3$ ,  $0$ ,  $6$ ,  $12$ ,  $18$ ,  $30$ ,  $42$ , and  $54$  kcal/mol. The dashed curves are the minimum energy paths. In the right-hand bottom panel, we show the potential energy barriers for the  $\text{H}_2\text{He}^+$  system at the fixed internal bond angle as functions of the angle of rotation from the saddle point along the cutting line; the curves are for (A)  $180^\circ$ ; (B)  $135^\circ$ ; (C)  $90^\circ$ ; (D)  $45^\circ$ ; and (E)  $0^\circ$ . All the energies are in kcal/mol and all the interatomic distances in atomic units.



for each bond angle (dashed curves) and we report a panel with the corresponding potential energy barriers.

As for the  $H_3$  system, in Table VI we report the rms error and the maximum deviation when we increase the order  $M$  of our fitting procedure to test the stability and the convergence properties of our procedure. From this table, we can see that, as for the  $H_3$  system, the rms error decreases exponentially with the number of linear parameters of the fit, but less rapidly (approximately as  $5e^{-0.053n}$ ,  $n$  being the number of linear parameters). Here, we also obtain a correct behavior at short, intermediate, and long range of the whole potential as for the  $M = 6$  fit that we can see in Fig. 2.

## V. THE LiHF SYSTEM

It was two decades ago that the first study on the LiHF system (HF level)<sup>46</sup> appeared; several years later an application of valence bond techniques to the  $Li + HF \rightarrow LiF + H$  reaction<sup>47</sup> was published. Zeiri and Shapiro<sup>48</sup> attempted to construct a DIM type PES for the LiHF system, but failed in that it produced surfaces which compared very poorly with the *ab initio* ones; however, they published a PES for this system based on a new semiempirical method,<sup>48</sup> but the barrier heights were too high when compared with recent *ab initio* calculations.<sup>49,50</sup> In fact, the CI calculations of this PES by Chen and Schaefer III<sup>49</sup> predict a barrier height of 10.0 kcal/mol, about 3 kcal/mol higher than the true value<sup>51</sup> (with a more extended basis set). Then, for the LiHF system, the *ab initio* calculations are not as accurate as for  $H_3$  or  $H_2He^+$  systems; however, several methods failed to fit this PES making it a good test case for our new functional form.

Several fitting procedures have been applied to construct an analytical potential for the LiHF system. Carter and Murrell<sup>22</sup> have derived the PES for this system starting from the Chen and Schaefer III *ab initio* data<sup>49</sup> modified by subtraction of a Gaussian function with an amplitude of 2.4 kcal/mol centered at the transition state and by scaling the calculated diatomic bond lengths to obtain a good agreement with the experimental ones. After this *ad hoc* manipulation of the original *ab initio* data, they fitted the resulting points using the SM<sup>21</sup> approach, obtaining a rms error of 1.87 kcal/mol and a maximum deviation of 6.7 kcal/mol on the scaled *ab initio* points. Garcia and Laganà<sup>25</sup> have analyzed the MEP of the Carter and Murrell PES<sup>22</sup> and they found bar-

riers placed in the entrance channel; at the approaching angle at which the lowest saddle to reaction occurs, the barrier is high enough to dominate the saddle. These features are external to the region covered by the *ab initio* points leading to unexpected situations and introducing severe constraints on the efficiency of the reagents translational energy and on the characteristics of the reactive paths. To obtain a PES free of these spurious features, García and Laganà<sup>25</sup> have discussed a technique for a piecewise fit of the *ab initio* values of the LiHF system. They fitted the inner part of the potential using a polynomial in the internuclear distances that reproduces the features of the strong interaction region, but with a wrong behavior at the long-range interaction that they avoid introducing three outer regions connected with the inner function using sinusoidal switching functions. The rms error obtained for the inner part of the potential is 1.54 kcal/mol. Finally, Alvarino *et al.*<sup>52</sup> have presented a BO fit of the LiHF PES based on a 3D quasiclassical trajectory test in order to remedy the deficiencies of the Carter and Murrell PES,<sup>22</sup> although the spurious structure was not removed entirely.<sup>53</sup>

In our opinion, there are two main error sources that explain the spurious structure presented in the several fitted LiHF PES cited above. First, the *ab initio* calculations<sup>49</sup> do not give the diatomic fragments, then the diatomic data used in the preceding fits of the LiHF PES are fittings to the experimental data producing the necessary adjustments to put the calculated data points in essential agreement with these

TABLE VI. Accuracy vs the order of the fit for the  $H_2He^+$  system.

$N$	$n_{\text{par}}^a$	rms <sup>b</sup>	$\Delta V_{\text{max}}^b$
4	13	2.333	15.785
5	23	1.471	8.393
6	37	0.711	4.246
7	55	0.531	3.912
8	78	0.306	2.373
9	106	0.233	2.682

<sup>a</sup>  $n_{\text{par}}$  is the number of linear parameters of the fit; in all cases, there are only two nonlinear parameters.

<sup>b</sup> In kcal/mol.

TABLE VII. Two-body terms of the LiHF PES.<sup>a</sup>

The two-body term $V_{\text{LiF}}^{(2)}$	
$i$	$c_i$
0	0.102 208 371( + 02)
1	- 0.106 744 749( + 01)
2	0.229 226 446( + 01)
3	- 0.488 846 361( + 01)
$\alpha_{\text{LiF}}$	0.104 770 898( + 01)
$\beta_{\text{LiF}}^{(2)}$	0.686 938 383( + 00)
The two-body term $V_{\text{LiH}}^{(2)}$	
$i$	$c_i$
0	0.159 107 103( + 01)
1	- 0.100 813 204( + 01)
2	0.582 231 838( + 00)
3	- 0.880 914 673( + 00)
$\alpha_{\text{LiH}}$	0.416 379 915( + 00)
$\beta_{\text{LiH}}^{(2)}$	0.831 223 223( + 00)
The two-body term $V_{\text{HF}}^{(2)}$	
$i$	$c_i$
0	0.416 129 666( + 02)
1	0.644 419 094( - 01)
2	- 0.146 170 741( + 02)
3	0.449 119 139( + 02)
$\alpha_{\text{HF}}$	0.443 749 156( + 01)
$\beta_{\text{HF}}^{(2)}$	0.123 030 793( + 01)

<sup>a</sup> All the coefficients are given in atomic units.

experimental data. The second error source may be produced by the subtraction of a Gaussian function that may produce undesirable structures at the transition state region. To avoid these error sources, we calculate the *ab initio* CI diatomic potentials for the LiF, LiH, and HF molecules using the same basis set and calculation technique as Ref. 49. Then, we fit these diatomic potentials to the new *ab initio* data. In Table VII, we report the coefficients corresponding to the three diatomic molecules, where the rms errors are lower than 0.1 kcal/mol. Then, we obtain the three-body term of the PES as for the  $H_3$  and  $H_2He^+$  systems reported above. Here, we must stress that we do not subtract anything to the *ab initio* energies; then our fitted PES is 2.4 kcal/mol higher at the saddle point. The best-fit parameters  $d_{ijk}$ ,  $\beta_{LiF}^{(3)}$ ,  $\beta_{LiH}^{(3)}$ , and  $\beta_{HF}^{(3)}$  for  $M = 6$  (65 linear parameters and three nonlinear parameters) with a rms error of 0.94 kcal/mol and a maximum deviation of 4.59 kcal/mol are reported in Table VIII. Now, there is no symmetry in Eq. (5) and there are no restrictions on the coefficients  $d_{ijk}$ .

In Fig. 3, we report contour maps of the LiHF PES using our fit (Tables VII and VIII); for each contour map, one internal bond angle is fixed to  $180^\circ$ ,  $135^\circ$ ,  $90^\circ$ ,  $45^\circ$ , and  $0^\circ$ . In fact, the contour map corresponding to  $0^\circ$  is a fully extrapolated map because there are no calculated *ab initio* points for this internal bond angle.<sup>49</sup> In fact, this extrapolated map is very similar to that obtained by the authors using a different *ab initio* procedure.<sup>50</sup> As we can see in this figure, all the maps present a correct behavior at short, intermediate, and long range of the potential. Moreover, we draw the corresponding MEP over the contour map for each bond angle (dashed curves) and we report a panel with the corresponding potential energy barriers. From this last panel, we can see that no spurious structures, such as barriers that dominate the saddle, are presented.

As for the  $H_3$  and  $H_2He^+$  systems, in Table IX, we report the rms error and the maximum deviation when we increase the order  $M$  of our fitting procedure to test the stability and the convergence properties of our procedure. From this table, we can see that as for the  $H_3$  and  $H_2He^+$  systems, the rms error decreases exponentially with the number of linear parameters of the fit, but less rapidly (approximately as  $5e^{-0.026n}$ ,  $n$  being the number of linear parameters). In fact, from Tables III, VI, and IX, we can see that the decrease of the rms error is more pronounced for systems with higher symmetry. Here, we also obtain a correct behavior at short, intermediate, and long range of the whole potential as for the  $M = 6$  fit that we can see in Fig. 3.

## VI. CONCLUSIONS

The new functional form presented here has been shown to lead to PES that fit the requirements making a functional form excellent for reproducing the PES of a reactive system. It has been also shown that the new fitting procedure does not give rise to spurious features and that the obtained PES has a good behavior at short, intermediate, and long range of the whole potential and has a reasonable behavior in the regions where extrapolation is not supported by *ab initio* information. In addition, the manageable form of the func-

TABLE VIII. The three-body term  $V_{LiHF}^{(3)}$  for  $M = 6$ .<sup>a</sup>

$ijk$	$d_{ijk}$
1 0 1	0.905 175 485( + 00)
1 1 0	0.154 024 023( + 02)
0 1 1	- 0.601 464 609( + 01)
1 1 1	- 0.573 569 232( + 02)
2 0 1	- 0.206 119 829( + 02)
2 1 0	- 0.365 796 663( + 02)
0 1 2	0.160 596 379( + 02)
0 2 1	0.764 365 494( + 02)
1 0 2	0.540 015 558( + 02)
1 2 0	- 0.965 572 279( + 02)
2 1 1	0.117 726 106( + 02)
1 1 2	0.452 828 444( + 03)
1 2 1	- 0.881 217 497( + 02)
2 0 2	- 0.155 132 227( + 03)
2 2 0	0.492 134 780( + 03)
0 2 2	- 0.464 089 962( + 03)
3 0 1	0.831 142 599( + 02)
3 1 0	- 0.202 972 011( + 02)
0 1 3	- 0.528 991 511( + 02)
0 3 1	0.124 314 609( + 03)
1 0 3	- 0.345 095 241( + 02)
1 3 0	- 0.120 780 993( + 02)
2 1 2	- 0.112 977 834( + 04)
2 2 1	- 0.882 892 135( + 03)
1 2 2	0.272 538 798( + 04)
3 1 1	0.658 632 384( + 03)
1 1 3	- 0.148 375 386( + 04)
1 3 1	- 0.724 486 670( + 03)
3 0 2	- 0.182 778 777( + 03)
3 2 0	- 0.975 936 138( + 03)
0 2 3	- 0.309 502 769( + 03)
0 3 2	0.367 564 819( + 03)
2 0 3	0.120 156 222( + 04)
2 3 0	- 0.335 923 398( + 02)
4 0 1	- 0.104 506 118( + 03)
4 1 0	0.145 249 475( + 03)
0 1 4	0.971 877 795( + 03)
0 4 1	- 0.645 284 409( + 03)
1 0 4	- 0.106 719 071( + 04)
1 4 0	0.563 715 280( + 03)
2 2 2	- 0.787 478 895( + 03)
3 1 2	- 0.497 968 505( + 03)
3 2 1	0.163 468 945( + 04)
1 2 3	- 0.357 064 606( + 04)
1 3 2	0.144 819 528( + 03)
2 1 3	0.261 535 544( + 04)
2 3 1	- 0.521 340 630( + 03)
3 0 3	- 0.416 276 957( + 02)
3 3 0	- 0.149 142 200( + 03)
0 3 3	- 0.123 295 043( + 04)
4 1 1	- 0.667 952 064( + 03)
1 1 4	0.108 987 524( + 04)
1 4 1	0.134 920 635( + 04)
4 0 2	0.177 196 398( + 03)
4 2 0	0.732 821 259( + 03)
0 2 4	0.222 974 188( + 04)
0 4 2	0.919 273 419( + 03)
2 0 4	- 0.177 925 864( + 04)
2 4 0	- 0.146 195 780( + 03)
5 0 1	0.538 896 692( + 02)
5 1 0	- 0.142 219 419( + 03)
0 1 5	- 0.207 834 068( + 04)
0 5 1	- 0.191 002 873( + 02)
1 0 5	0.218 507 375( + 04)
1 5 0	- 0.679 437 928( + 03)
$\beta_{LiF}^{(3)}$	0.670 591 220( + 00)
$\beta_{LiH}^{(3)}$	0.953 194 320( + 00)
$\beta_{HF}^{(3)}$	0.103 503 282( + 01)

<sup>a</sup> All the coefficients are given in atomic units.

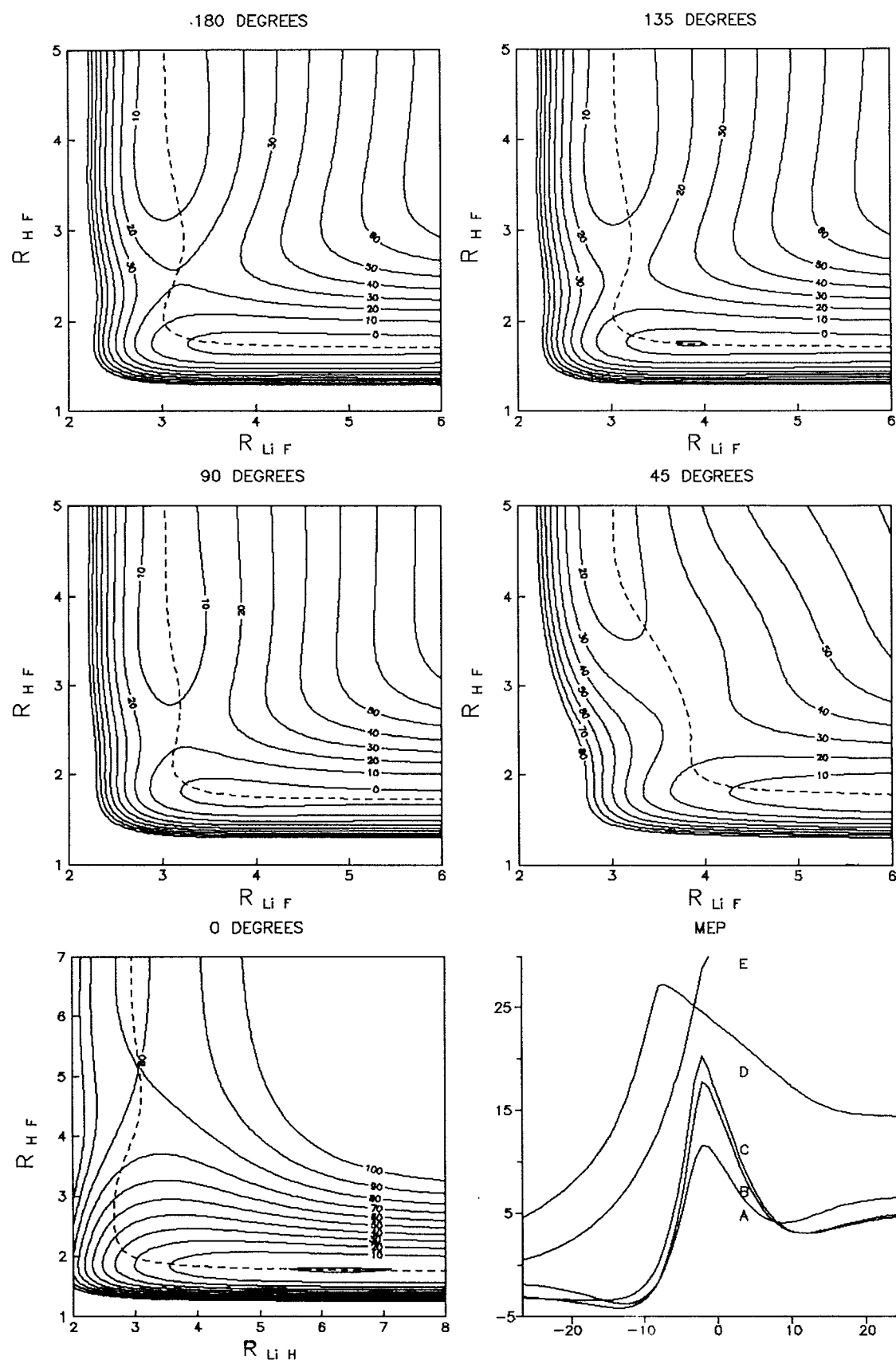


FIG. 3. Potential contours of the interaction potential for the LiHF. For each contour map, one internal bond angle is fixed. The fixed internal bond angle is indicated at the top of each figure. The solid curves are contours of the interaction potential corresponding to  $-4, 0, 10, 20, 30, 40, 50, 60, 70, 80, 90$ , and  $100$  kcal/mol. The dashed curves are the minimum energy paths. In the right-hand bottom panel, we show the potential energy barriers for the LiHF system at the fixed internal bond angle as functions of the angle of rotation from the saddle point along MEP through the cutting line; the curves are for (C)  $180^\circ$ ; (B)  $135^\circ$ ; (A)  $90^\circ$ ; (D)  $45^\circ$ ; and (E)  $0^\circ$ . All the energies are in kcal/mol and all the interatomic distances in atomic units.

TABLE IX. Accuracy vs the order of the fit for the LiHF system.

$N$	$n_{\text{par}}^a$	rms <sup>b</sup>	$\Delta V_{\text{max}}^b$
3	10	4.470	13.980
4	22	2.905	8.768
5	40	1.315	6.432
6	65	0.917	4.587
7	98	0.517	2.248

<sup>a</sup>  $n_{\text{par}}$  is the number of linear parameters of the fit; in all cases there are only three nonlinear parameters.

<sup>b</sup> In kcal/mol.

tions adopted with a simple global function with simple derivatives makes the procedure ideal for the determination of a reactive PES. Finally, all the subroutines (FORTRAN-77) to generate all the PES presented here and their first partial derivatives are available from the authors upon request.

## ACKNOWLEDGMENTS

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