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Accurate global fit of the H₄ potential energy surface

Alfredo Aguado, Cristina Suárez, and Miguel Paniagua

Departamento de Química Física, Facultad de Ciencias C-XIV, Universidad Autónoma de Madrid, 28049 Madrid, Spain

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A global potential energy surface (PES) for the adiabatic ground state of the H₄ system which fit published *ab initio* data [Boothroyd, *et al.* J. Chem. Phys. **95**, 4331 (1991)] at a quantitative level has been obtained (root-mean-square error about 2 mhartree or 1–2 kcal/mol), and without any quantity of *ad hoc* character, preserving the accuracy of the *ab initio* points. The global fitting procedure used here is an extension of the corresponding procedure for triatomic systems including the functional form previously proposed by the authors. The global H₄ PES obtained here is totally symmetric with respect to permutations of the hydrogen atoms and satisfies the criteria needed to be used in scattering calculations.

I. INTRODUCTION

The quantum chemistry, molecular physics, and astrophysical importance of the interaction potential energy surface (PES) of the H₄ system is due to the fact that H₄ is the simplest test case of the molecule–molecule interactions (H₂–H₂). Then, it must be considered as a model system for studies of intermolecular energy transfer, chemical reactions between molecules, interactions in physical conditions not accessible to experiment (as the low densities characteristics of giant molecular clouds, where star formation occurs), and studies of full dimensional four-body dynamics.

H₄ is also the only four-atom system for which an extended set of accurate *ab initio* energies (6101 conformations) are tabulated.¹ This potential energy points are strategically positioned to cover all the energetically important regions of the system. However, the best existing analytic PESs for H₄ (Ref. 1–4) are shown to be accurate only for pairs of H₂ molecules with intermolecular separations greater than about 3 bohr.¹ The lowest root-mean-square (rms) error obtained when all the 6101 conformations are considered corresponds to the Schwenke⁴ H₄ PES [41.69 mhartree or 26.2 kcal/mol (Ref. 1)].

The rms values of the H₄ analytic PESs (from 26.2 kcal/mol to higher values) is far apart from the typical values (1–2 kcal/mol, ideally less than 1 kcal/mol) of analytical PESs useful for reliable scattering calculations. Therefore, a more accurate and general analytic PES for H₄ is required. The goal of this paper is to report an accurate analytical fit to the potential energy points¹ that have been determined using the multiple reference single and double excitation configuration interaction (MRDCI) program.⁵

In this paper, we present a four-body generalization of the global fitting procedure for triatomic systems proposed by the authors⁶ that has been applied successfully for several triatomic systems^{6–8} and its application to obtain an accurate PES for the H₄ system. The paper is organized as follows: in Sec. II, we give an outline of the global fitting procedure for four-body systems and particularly for A₄ systems (A being any atom). In Sec. III, we give details of the application of the fitting procedure to obtain the H₄ PES, and a convergence study reporting the rms error and the maximum deviation when we increase the number of parameters in the fit. Fi-

nally, in the last section, we present contour maps of the H₄ PES for different arrangements of the nuclei.

II. THE GLOBAL FITTING PROCEDURE

To obtain the PES of the four-body system ABCD, we choose the six internuclear distances R_{AB} , R_{AC} , R_{BC} , R_{AD} , R_{BD} , and R_{CD} as variables. The complete potential energy function may be written as a many-body expansion⁹

$$V_{ABCD} = \sum_A V_A^{(1)} + \sum_{AB} V_{AB}^{(2)}(R_{AB}) + \sum_{ABC} V_{ABC}^{(3)}(R_{AB}, R_{AC}, R_{BC}) + V_{ABCD}^{(4)}(R_{AB}, R_{AC}, R_{BC}, R_{AD}, R_{BD}, R_{CD}), \quad (1)$$

where the summations run over all the terms of a given type and where $V_A^{(1)}$ is the energy of atom A in its appropriate electronic state; usually, we adopt $\sum_A V_A^{(1)} = 0$ for all the atoms in their ground state. $V_{AB}^{(2)}$ is the two-body energy that is expressed using a polynomial form⁶

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

the polynomial Rydberg type variables¹⁰ ρ are given by

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

The linear parameters c_i , $i = 0, 1, \dots, N$ and the nonlinear parameters α_{AB} and $\beta_{AB}^{(2)}$ are determined by fitting the *ab initio* values of the diatomic fragments.

The three-body terms $V_{ABC}^{(3)}$ of the potential in Eq. (1) are also expressed as polynomials of order M in the same Rydberg type variables ρ_{AB} , ρ_{AC} , and ρ_{BC} [see Eq. (3) with $p=3$]

$$V_{ABC}^{(3)}(R_{AB}, R_{AC}, R_{BC}) = \sum_{i,j,k} d_{ijk} \rho_{AB}^i \rho_{AC}^j \rho_{BC}^k, \quad (4)$$

where some constraints are forced on the indices so that the three-body terms have good behavior.⁶ If the system under

consideration has two or three atoms of the same type (A_3 or AB_2 systems), there is an evident permutational symmetry in Eq. (4) that implies additional constraints in the linear d_{ijk} and nonlinear $\beta_{AB}^{(3)}, \beta_{AC}^{(3)}, \beta_{BC}^{(3)}$ parameters⁶ that are determined by fitting the difference between the *ab initio* values of each triatomic system and their corresponding diatomic potential.⁶

The functional form for the four-body term of the potential in Eq. (1) may be written again in a form similar to that of the three-body terms, i.e., as a polynomial of order L in the same Rydberg type variables $\rho_{AB}, \rho_{AC}, \rho_{BC}, \rho_{AD}, \rho_{BD}$, and ρ_{CD} [see Eq. (3) with $p=4$]

$$V_{ABCD}^{(4)}(R_{AB}, R_{AC}, R_{BC}, R_{AD}, R_{BD}, R_{CD}) = \sum_{i,j,k,l,m,n}^L e_{ijklmn} \rho_{AB}^i \rho_{AC}^j \rho_{BC}^k \rho_{AD}^l \rho_{BD}^m \rho_{CD}^n, \quad (5)$$

where we impose the following constraints on the indices of the four-body term to ensure a good behavior at short, intermediate, and long ranges of the whole potential. With these constraints, the four-body term becomes zero at all the dissociation limits and all the internuclear distances tend to zero, these constraints are:

$$\begin{aligned} i+j+k+l+m+n &\neq q; & q=0, i, j, k, l, m, n; \\ \alpha+\beta+\gamma &\neq 0; & \alpha\beta\gamma = ijl, ikm, jkn, lmn; \\ \alpha+\beta+\gamma+\delta &\neq 0; & \alpha\beta\gamma\delta = jklm, ikln, ijmn; \\ i+j+k+l+m+n &\leq L. \end{aligned} \quad (6)$$

If we adopt the Born–Oppenheimer approximation and solve the electronic Schrödinger equation to obtain a PES, the symmetry group (G) containing those symmetry operations which do not change the nuclear Hamiltonian may be given by the direct product of smaller groups, each one describing the invariance of the nuclear Hamiltonian to particular types of operations

$$G = T \otimes R_3 \otimes C_i \otimes S_n, \quad (7)$$

where T is the translation group (i.e., the Hamiltonian is unchanged by a change in the origin of the space fixed Cartesian coordinates), R_3 is the three-dimensional rotation group (i.e., the Hamiltonian is unchanged by a rotation of the coordinate axes), C_i is the inversion group (i.e., the Hamiltonian is unchanged by a change of sign of all Cartesian coordinates), and S_n is the symmetric group or the permutation group of n objects (i.e., the Hamiltonian is unchanged by an interchange of indistinguishable nuclei). If we take into account that we choose the six internuclear distances in our potential function V_{ABCD} [see Eq. (1)], it is clear that our potential function is invariant with respect to operations belonging to translation, three-dimensional rotation, and inversion groups, because these operations keep the internuclear distances unchanged. However, the four-body term $V_{ABCD}^{(4)}$ given by Eq. (5) is not invariant to an interchange of indistinguishable nuclei.

If the system under consideration has four, three, or two atoms of the same type (systems A_4 , A_3B , A_2B_2 , and A_2BC), the four-body term of the potential $V_{ABCD}^{(4)}$ must be

totally symmetric with respect to permutations of identical atoms. In the sequel, we restrict ourselves to the case A_4 , i.e., $A=B=C=D$. Hence, to obtain the condition that the four-body term must be totally symmetric with respect to permutations of all atoms, we apply the unnormalized Young operator,¹¹ corresponding to the totally symmetric irreducible representation (named [4]) of the S_4 permutation group given by

$$\omega^{[4]} = \sum_P^{4!} P, \quad (8)$$

where the summation over P runs over all the $4!$ permutations of the atoms (A, B, C , and D) in the group S_4 . Operator (8) is a symmetrizing operator. Then, Eq. (5) is replaced by

$$V_{ABCD}^{(4)}(R_{AB}, R_{AC}, R_{BC}, R_{AD}, R_{BD}, R_{CD}) = \sum_{i,j,k,l,m,n}^{L, \text{all different SAFs}} e_{ijklmn} (\omega^{[4]} \rho_{AB}^i \rho_{AC}^j \rho_{BC}^k \rho_{AD}^l \rho_{BD}^m \rho_{CD}^n), \quad (9)$$

where the effect of the symmetrizing operator ($\omega^{[4]}$) on the product functions ($\rho_{AB}^i \rho_{AC}^j \rho_{BC}^k \rho_{AD}^l \rho_{BD}^m \rho_{CD}^n$) results in the production of a symmetry adapted function (SAF) as a linear combination of product functions. Then, we must add the condition that the summation runs over all the different SAFs to the constraints given by Eq. (6). Moreover, we do not include constant factors in the SAFs [appearing in the application of the symmetrizing operator on the product functions (see Appendix A in PAPS¹² for more details)].

To obtain the corresponding four-body term [Eq. (9)] for other tetra-atomic systems A_3B , A_2B_2 , and A_2BC , we must change only the symmetrizing operator $\omega^{[4]}$ in Eq. (9) by $\omega_A^{[3]}, \omega_A^{[2]} \omega_B^{[2]}$, and $\omega_A^{[2]}$, respectively.

III. THE H₄ SYSTEM

A “global” fit of the H₄ PES to only seven four-body energies was attempted, several years ago, by Varandas and Murrell,¹³ but they tried an optimum fit of the D_{2h} and $D_{\infty h}$ surfaces only, with nonanalytic behavior for T_d or C_{3v} symmetries. From the year 1991, work is in progress¹ on devising a more general analytic PES for H₄ (fitted to the 6101 conformations of the cited paper).

In the application of our fitting procedure, outlined in the previous section, we must first consider the H₂ potential. Maintaining that the distances between two hydrogen atoms in the H₄ data points¹ cover regions from 0.6 to 10.2 a_0 , we select as data points the accurate values of Kolos and Wolniewicz¹⁴ (87 energies corresponding to distances from 0.4 to 10.0 a_0). Therefore, our H₂ asymptotes, corresponding to these data, were fitted to the functional form given in Eq. (2) up to $N=11$ with a rms deviation of 0.013 mhartree (0.01 kcal/mol) and a maximum error of 0.028 mhartree (0.02 kcal/mol). We must stress that we stop the fitting procedure when we obtain a rms deviation that is about two to three times the estimated error in the data. We report the value of the parameters of this fit (see Table I of the PAPS¹² docu-

TABLE I. Comparisons of *ab initio* energies for some PES conformation.^a

N_{abs}^b	Boothroyd <i>et al.</i> (Ref. 1) results			Present results					
	$C_R^2^c$	E^{FCI}	E^{final}	C_R^2	E_1^{FCI}	C_R^2	E_2^{FCI}	C_R^2	E_3^{FCI}
822	0.9615	0.319 371	0.314 814	0.9761	0.302 258	0.9748	0.325 551	0.9713	0.410 316
3 129	0.9720	0.481 507	0.479 293	0.9716	0.459 338	0.9724	0.478 868	0.9777	0.595 356
91 125	0.9690	-0.016 150	-0.019 275	0.9723	-0.041 344	0.9753	-0.017 242	0.9726	-0.016 905
91 126	0.9726	-0.051 536	-0.054 590	0.9763	-0.076 019	0.9787	-0.052 941	0.9753	-0.052 739

^aEnergies in hartrees. The zero energy corresponds to H+H+H+H.^b N_{abs} is an "absolute" conformation identification number (see Ref. 1).^c C_R^2 is the sum of the squares of the coefficients of all the reference configurations.

ment) being the calculated D_e , r_e , and ω_e equal to 0.174 hartree (4.74 eV), 1.4012 a_0 , and 4401.2 cm^{-1} , respectively. These values are very close to the experimental ones.¹⁵ However, it is also possible to use another accurate H₂ potential curve such as Schwenke's.⁴

To obtain the three-body terms in Eq. (1) corresponding to the H₃ asymptotes, it is desirable to employ the most accurate PES possible fulfilling several symmetry conditions⁶ and other stringent criteria.¹⁶ Therefore, we could use as three-body terms several accurate H₃ PESs,^{6,17-19} but for coherency in the many-body expansion (1), we will use our functional form⁶ [see Eq. (4)]. However, it is also possible to use the most accurate Boothroyd-Keogh-Martin-Peterson (BKMP) H₃ PES.¹⁹

Moreover, in our previous H₃ PES,⁶ we include only 267 energies, while in a recent paper, Boothroyd *et al.*¹⁹ report *ab initio* calculations for new conformations with higher energies, giving a total of 772 energies in the H₃ dataset. Then, we refit our H₃ PES including all 772 energies obtaining for $M=10$ a rms deviation of 1.65 mhartree (1.04 kcal/mol) and a maximum error of 11.97 mhartree (7.51 kcal/mol), the worse behavior corresponding to the D_{3h} geometries (at the conical intersection in H₃), where the adiabatic approximation is not applicable.²⁰ As for H₂, we stop the fitting proce-

dure when we obtain a rms deviation that is about twice the estimated error in the data.²¹ The best-fit parameters d_{ijk} and $\beta_{\text{HH}}^{(3)}$ for $M=10$ (56 linear parameters) are reported in PAPS¹² (see Table II in that document).

An important step in fitting a PES is to examine the data. So, we have made tentative fittings to do a systematic analysis on the residuals (algebraic deviations δ) by plotting them against the energies (see Fig. 1, corresponding to all the 6101 data points). In this figure, we can see that the residuals are scattered uniformly on either side of the zero value, but with a slight imbalance of a few points towards the positive residuals, suggesting that the corresponding energies are higher than those obtained by the interpolating function. We also plot the resulting tentative PES to study all the regions.

From these analyses, we suspect that there were some errors in the original data set. In fact, we have made MRDCI⁵ calculations of all the 51 H₄ conformations with absolute deviations greater than 8 mhartree (5 kcal/mol) using the same basis set corresponding to the original data points.²² All the calculations were carried out using the maximum symmetry group whenever it was possible and all 76 molecular orbitals were used in the configuration interaction (CI) step. The CI space of each irreducible representation was constructed using 101 reference configurations. The se-

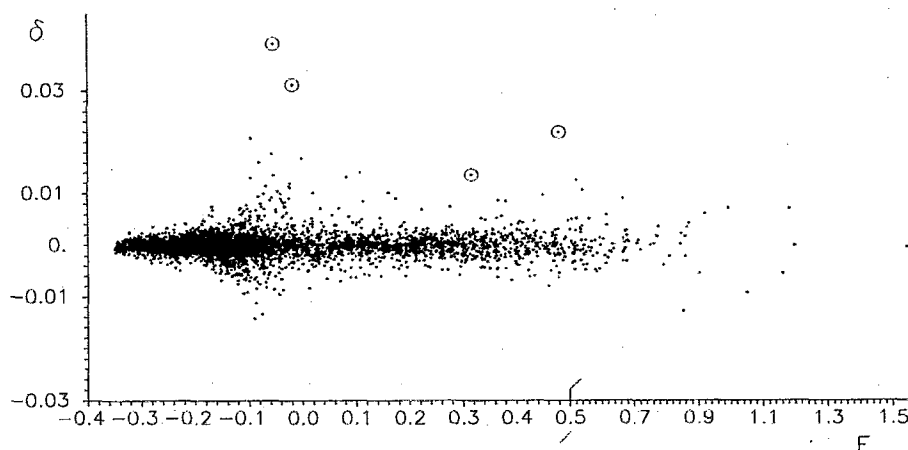


FIG. 1. Residuals (algebraic deviations δ) vs the energies referred to the four separated hydrogens (zero energy). All data points are in hartrees; the scale of this figure has been changed from an energy of 0.5 hartree to higher energies. Circled points correspond to improper energies (excited states).

TABLE II. Accuracy vs the order of the fit for the H₄ system.

<i>L</i>	<i>n</i> _{par} ^a	H ₂ and H ₃ from this paper		H ₂ and H ₃ from Refs. 4 and 19	
		rms ^b	Δ <i>V</i> _{max} ^b	rms ^b	Δ <i>V</i> _{max} ^b
6	40	12.88	59.39	12.77	79.22
7	77	10.29	80.33	10.15	72.31
8	138	6.98	50.52	7.29	64.30
9	233	5.11	33.93	5.66	53.91
10	374	3.61	30.22	4.40	35.67
11	577	2.54	22.98	3.42	28.21
12	865	1.92	20.86	2.69	26.13

^a*n*_{par} is the number of linear parameters of the fit, corresponding to different SAFs. For all the *L* values, there is only one nonlinear parameter.

^bAll rms errors and maximum deviations (Δ*V*_{max}) are in mhartree.

lection threshold used was 1.0 μhartree. This resulted in the generation of about 180 000 configuration functions by irreducible representation (for molecular symmetry groups different from *C*₁) or 362 000 configuration functions (for the *C*₁ group, with only one irreducible representation), out of which about 8000 by irreducible representation (cases different from *C*₁) or 12 000 (*C*₁ cases) were selected for the final CI calculation. Extrapolation of the energy to zero threshold gave the MRDCI energy. Finally, we use the multireference analog⁵ of the Davidson correction²³ to obtain the full CI extrapolated energy (*E*^{FCI}) that we use to compare with the Boothroyd *et al.*¹ calculations.

In Table I, we report a comparison of our results for four H₄ conformations with the corresponding results of Boothroyd *et al.*¹ As we can see in Table I, the results (*E*^{FCI}) obtained by Boothroyd *et al.*¹ are always higher than our ground state (marked in this table by *E*₁^{FCI}) and this is also true for their final corrected energies (*E*^{final} in the Table I). Considering that their MRDCI zero threshold and Davidson corrections are about four times than ours, we conclude that they have obtained convergence to the first excited state [our *E*₂^{FCI} (see Table I)]. Then, the inclusion of these points in the H₄ fit may cause steps or spurious maxima in the final PES. However, we must assert that in our remaining 47 conformations, we obtain the same energy values for our ground state (within an uncertainty of about 1–2 mhartree) than those

obtained by Boothroyd *et al.*¹ The residuals of these four conformations (corresponding to the first excited state) are marked as circled points in Fig. 1, corresponding to the worst positive ones.

Moreover, in Fig. 1, we can see a region, centered at energies about −0.08 hartree, where the residuals are also high, but scattered uniformly on either side of the zero value. In these conformations, our calculations confirm the energy values obtained by Boothroyd *et al.*,¹ but we notice intersections between states belonging to the same symmetry while the system passes from high symmetry (*C*_{3v}, *D*_{3h}, or *T*_d) structures to nonsymmetry ones (*C*₁). Therefore, the high residuals (about 14 mhartree or 9 kcal/mol) for these structures may be due to the fact that the Born–Oppenheimer separation is not valid and the adiabatic approximation fails, resulting in wrong energy values. There are also intersections, corresponding to states belonging to different symmetry, that may produce a slight maxima in the PES. It would be interesting a more detailed study of these intersections.

In Table II, we present our results, rms errors, and maximum deviations for the H₄ global fits as we increase the order *L* of the fit [see Eq. (9)]. In these fits, we include 6097 input data points (we reject only the four *E*^{final} energies given in Table I) that have been obtained as the difference between the *ab initio* energies (the *E*^{final} of Boothroyd *et al.*¹) and the sum of the two-body (six times) and three-body (four times) terms. We select two different sets of input data points based on the same *ab initio* energies, but with different two- and three-body terms. The first set includes two- and three-body terms computed here [see PAPS¹² (Tables I and II)]. In the second set, we include as a two-body term Schwenke's highly accurate H₂ potential⁴ and as a three-body term the BKMP H₃ potential.¹⁹ The results for both input data sets are presented in Table II. From Table II, we can see that the best results have been obtained when using the first data set (*L* = 12, rms = 1.92 mhartree, or 1.2 kcal/mol and a maximum deviation of 20.86 mhartree or 13.1 kcal/mol), but all the fits obtained with rms about 3.5 mhartree (about 2 kcal/mol) are also accurate enough.

Obviously, it is not practical to present here tables for the coefficients corresponding with all the fits given in Table II,

TABLE III. Accuracy^a of analytic H₄ PES for various subsets of *ab initio* energies.

Subset	<i>N</i> _{pts}	London ^b (B&S)	London ^b (BKMP)	Rigid rotor ^b	Schwenke surface (Ref. 4) ^b	Best present results (<i>L</i> = 12) ^c
All H ₄ energies	6101	53.70	46.87	73.81	41.69	2.05
... <i>A</i> < 1 <i>a</i> ₀	1055	97.03	70.60	138.14	87.35	1.99
... <i>A</i> ≥ 1 <i>a</i> ₀	5046	38.96	40.18	50.96	22.49	2.06
... <i>t</i> ≥ 3.5 <i>a</i> ₀	5279	53.05	50.33	79.16	44.80	2.17
... <i>t</i> < 3.5 <i>a</i> ₀	822	57.66	6.49	13.78	3.04	0.94
... <i>s</i> < 4 <i>a</i> ₀	742	74.25	98.84	94.19	74.85	2.40
... <i>s</i> ≥ 4 <i>a</i> ₀	5359	50.19	33.89	70.52	34.68	1.99
... T ₂ energies	122	41.76	48.73	63.44	23.66	2.50
... Schwenke's energies	87	11.30	10.84	20.64	3.84	1.99

^aAll rms errors are in mhartrees. See Ref. 1 for the definition of the parameters *A*, *t*, and *s*.

^bAll tabulated values have been taken from Ref. 1.

^cFor comparison purposes, we compute our rms errors including all the 6101 data energies; if we remove the four improper energies, our rms error for all H₄ cases (6097) is 1.92 mhartree as indicated in Table II.

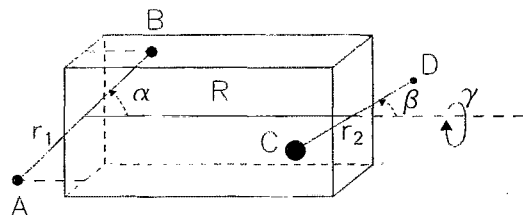


FIG. 2. A view of the six independent coordinates selected here.

but we have prepared a FORTRAN-77 program to generate the H_4 PES using any of the fits presented here (using the coefficients as block data). The program and the different block data are available from the authors upon request.²⁴ Moreover, a table with the coefficients corresponding with the best fit given here (see Table II) may be found as Table III in PAPS¹² document.

Finally, we must compare our results with the best existing analytic PESs for H_4 . Table III presents the rms errors of five analytic H_4 PESs with respect to the 6101 *ab initio* data,¹ both as a whole and for various subsets, that have been characterized in the first column of Table III by imposing conditions on the geometrical parameters A , t , and s defined in Ref. 1; the T_2 's are the most accurate energies in Ref. 1. The five PESs are the Brown and Silver² London equation surface (B&S header in Table III), the Boothroyd *et al.* London equation surface^{1,19} (BKMP header in Table III), Schaefer and Köhler³ rigid-rotor surface, Schwenke's surface,⁴ and the global H_4 PES with $L=12$ of this paper corresponding to our best results (see Table II). Except for the last column in Table III, all the tabulated values for the analytic H_4 PESs have been taken from Ref. 1.

We must stress that in the last column of Table III, we compute our rms errors including the four improper energies given in Table I (the E^{final}) only for comparison purposes. As we can see from Table III, our results are definitely more accurate for all the subsets of *ab initio* energies. Even for Schwenke's energies, his fit⁴ to only these 87 energies gives a rms error higher than ours. The conclusion previously¹ obtained is the best explanation to this behavior, i.e., except for our global H_4 PES presented here, the existing analytic PESs for H_4 are accurate only for pairs of H_2 molecules with large intermolecular separations (local PESs).

IV. H_4 CONTOUR MAPS

There are six independent degrees of freedom allowed in the placement of nuclear centers for a four-atom system. We choose three distances and three angles as independent coordinates (see Fig. 2) named r_1 , r_2 , R , α , β and γ ; r_1 being the distance between atoms A and B; r_2 being the distance between atoms C and D; R being the distance between the mass centers of the AB and CD diatomic molecules; α being the $\widehat{R, r_1}$ angle; β being the $\widehat{R, r_2}$ angle; and γ being the dihedral angle formed by the Rr_1 and Rr_2 intersecting planes. These independent coordinates are based on the consideration of the H_4 system as two interacting H_2 molecules, but they include all possible four-atom arrangements.

To get the PES defined by Eq. (1), we must obtain the six internuclear distances for a given set of independent coordinates. For the set defined above, the internuclear distances may be obtained by

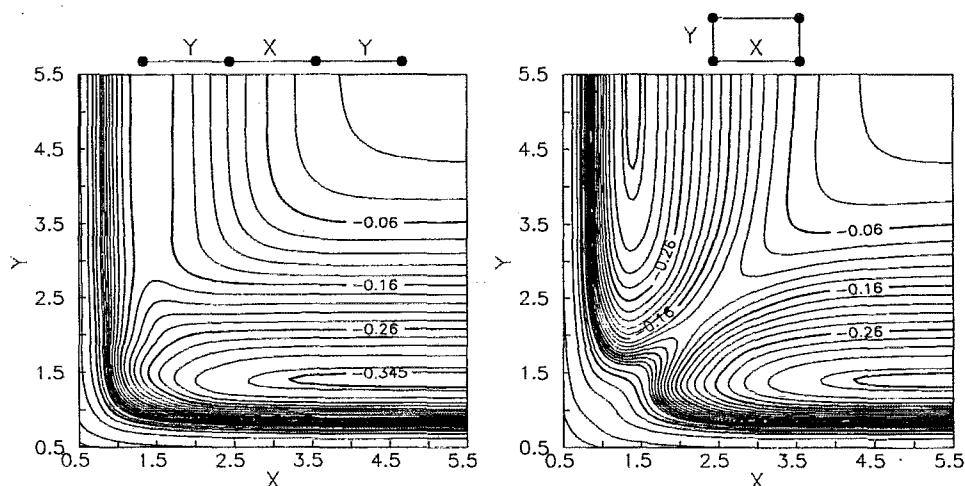


FIG. 3. Potential contours of the H_4 interaction potential, corresponding to linear (left-hand panel) and rectangular (right-hand panel) arrangements of the four hydrogen atoms. The curves are contours of the interaction potential corresponding to $-0.345, -0.34, -0.32, -0.30, -0.28, -0.26, -0.24, -0.22, -0.20, -0.18, -0.16, -0.14, -0.12, -0.10, -0.08, -0.06, -0.04, -0.02, 0.0, 0.05, 0.10, 0.20, 0.40, 1.0$, and 2.0 hartree with respect to the zero energy fixed at the separated atoms. All the interatomic distances are in atomic units.

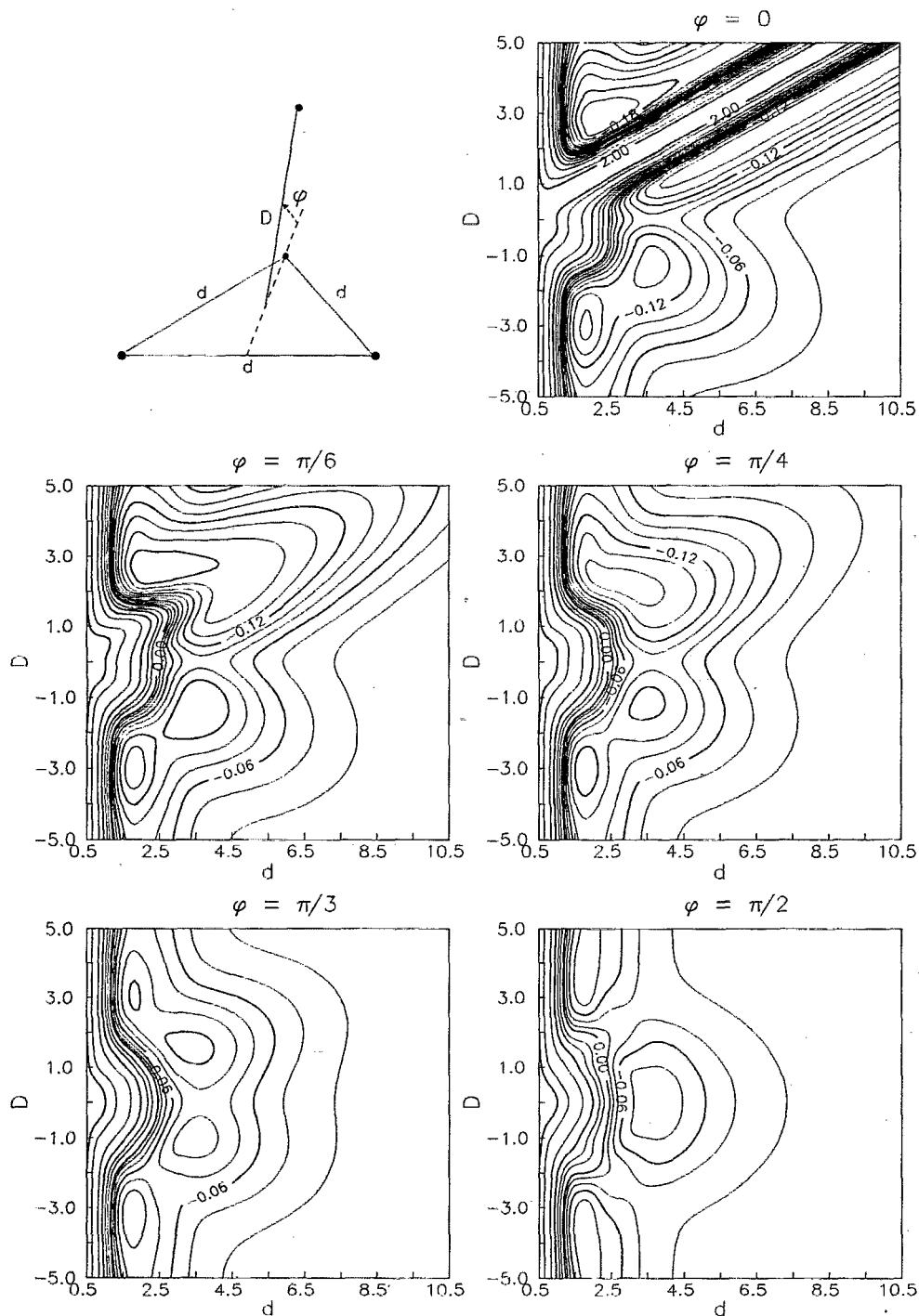


FIG. 4. Potential contours of the H₄ interaction potential, corresponding to a pyramidal arrangement shown in the left-hand top panel. For each contour map, the φ value is fixed, as indicated at the top of each panel. Contour levels and units are the same as in Fig. 3.

$$\begin{aligned}
 R_{AB} &= r_1, \quad R_{CD} = r_2, \quad R_{AC} = \left(\frac{r_1^2 + r_2^2}{4} + R^2 + r_1 R \cos \alpha - r_2 R \cos \beta - \frac{r_1 r_2 \cos \delta}{2} \right)^{1/2}, \\
 R_{BC} &= \left(\frac{r_1^2 + r_2^2}{4} + R^2 - r_1 R \cos \alpha - r_2 R \cos \beta + \frac{r_1 r_2 \cos \delta}{2} \right)^{1/2}, \\
 R_{AD} &= \left(\frac{r_1^2 + r_2^2}{4} + R^2 + r_1 R \cos \alpha + r_2 R \cos \beta + \frac{r_1 r_2 \cos \delta}{2} \right)^{1/2}, \\
 R_{BD} &= \left(\frac{r_1^2 + r_2^2}{4} + R^2 - r_1 R \cos \alpha + r_2 R \cos \beta - \frac{r_1 r_2 \cos \delta}{2} \right)^{1/2}, \quad \cos \delta = \cos \alpha \cos \beta + \sin \alpha \sin \beta \cos \gamma
 \end{aligned} \tag{10}$$

To obtain contour maps for a six-dimensional PES, we must do a drastic discrete representation of the independent coordinates. We select r_1 and r_2 to vary continuously on the interval $(0.5a_0, 10.5a_0)$, then the remaining independent coordinates must take discrete values. So R takes the values 0.5, 1.0, 2.0, 4.0, and $8.0a_0$; α , β , and γ angles take the values $0, \frac{1}{4}\pi, \frac{1}{2}\pi$, and $\frac{3}{4}\pi$ rad. Now, the 64 sets of α , β , and γ angles that may be reduced to only 14 different arrangements by symmetry considerations give to us a more restricted four-atom arrangements, but including the major part of those studied previously.^{25,26} For all the graphical analysis, we use our best fit presented in Table II ($L=12$, 865 linear parameters, and rms=1.92 mhartree).

This analysis supposes 70 contour maps that have been placed in 14 pages of figures (see Figs. 1–14 in PAPS¹² document) corresponding to the 14 different arrangements. Each page of figures is formed by a H₄ scheme of the corresponding arrangement and five contour plots corresponding to different R values. Symmetry is fulfilled in such a way that identical energies have been obtained for equivalent configurations. For instance, the contour maps of Fig. 2 in PAPS with $\alpha=0$, $\beta=\frac{1}{4}\pi$, and $\gamma=0$ have been obtained identically for all γ values and also for $(\alpha=0, \beta=\frac{3}{4}\pi)$, $(\alpha=\frac{1}{4}\pi, \beta=0)$, and $(\alpha=\frac{3}{4}\pi, \beta=0)$. From this graphical analysis, we obtain that for large R values, little or no distortion occurs with respect to the energies corresponding to two diatomic H₂ molecules. We also obtain an accurate characterization of the asymptotic H₂ regions.

For comparative purposes, we also plot a different view of the linear and rectangular arrangements of the four atoms (see Fig. 3) similar to that obtained by Silver and Brown.² Here, our PESs do not present spurious properties at short distances.

We also obtain a view of the H₃ asymptotes by plotting ten contour maps of the H₄ PES for one hydrogen atom impinging on a determined H₃ arrangement (see Figs. 15 and 16 in PAPS¹² document). These figures indicate that when the distance between the impinging atom and the H₃ arrangement is large, the contour maps correspond accurately to the H₃ asymptotes.

Finally, to obtain a view of other pyramidal (including C_{3v} and T_d) and plane (including C_{2v} and D_{3h}) structures, and to also obtain a view of the change produced from plane to pyramidal structures, we plot contour maps in Fig. 4 giving minima and saddle points corresponding to all of these structures.

V. CONCLUSIONS

An accurate global fit of the PES corresponding to the lowest adiabatic ground state for the H₄ system, to an analytic function satisfying the criteria¹⁶ needed for use in full dimensional (6D) scattering calculations, using the accurate MRDCI energy values obtained by Boothroyd *et al.*¹ has been made. A generalization of the four-body term of the potential for other four-atom systems has also been advanced.

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- ²⁴The authors may be reached by electronic mail at the following address: panifabi@vml.sdi.uam.es (or panifabi@emduamll.bitnet).
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