A new accurate and full dimensional potential energy surface of H_5^+ based on a triatoms-in-molecules analytic functional form

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In this work a reliable full nine-dimensional potential energy surface for studying the dynamics of H_5^+ is constructed, which is completely symmetric under any permutation of the nuclei. For this purpose, we develop a triatoms-in-molecules method as an extension of the more common diatoms-in-molecules one, which allows a very accurate description of the asymptotic regions by including correctly the charge-induced dipole and quadrupole interactions. Moreover, this treatment provides a semiquantitative description of all the topological features of the global potential compared with coupled cluster results. In particular, the hop of the proton between two H_2 fragments produces a double well in the potential. This resonant structure involving the five atoms produces a stabilization, lowering the barrier, and the triatoms-in-molecules yields to a barrier significantly higher than the *ab initio* results. Therefore, to improve the triatomics-in-molecules potential surface, two five-body terms are added, which are fitted to more than 110 000 coupled-cluster *ab initio* points. The global potential energy surface thus obtained in this work has an overall root mean square error of 0.079 kcal/mol for energies below 27 kcal/mol above the global well. The features of the potential are described and compared with previous available surfaces. © 2010 American Institute of Physics. [doi:10.1063/1.3454658]

I. INTRODUCTION

The relative abundance of deuterated species is approximately 10^4 times higher than the D/H ratio of the galaxy.¹ The formation of deuterated species in gas phase at the low temperatures of interstellar medium is determined by differences in the zero-point energy (ZPE), which favors deuterated species.^{2,3} H_3^+ plays a central role in interstellar ion chemistry, specially as the universal protonator through reactions with deuterated H_2D^+ , for example.^{4–7} Deuterated H_3^+ is formed via the $\text{HD} + \text{H}_3^+ \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$ proton-deuteron exchange reaction, and isotopic variants, which has been widely studied experimentally.^{3,8–11} The characterization of these reactions experimentally is overwhelmingly difficult and some guidance from theoretical simulations is required.

From the theoretical point of view, this system is still too complicated to perform full quantum dynamical calculations, and only recently a seven-degree-of-freedom scattering calculation of the $\text{H}_2 + \text{H}_2\text{D}^+$ reaction has been reported.¹² The symmetry constraints imposed by nuclear spin angular momenta were first treated by Quack¹³ and later on by Oka,¹⁴ which were experimentally confirmed by measurements in plasmas at 300–500 K.^{15,16} These considerations were taken into account to calculate reaction rate coefficients using statistical methods.^{11,17} These approaches have assumed that the reaction is mediated by long lived resonances, and using the isotropic ion-induced dipole long range part of the potential.

A reasonable agreement between experimental and theoretical results was obtained at low temperatures (<10 K),¹¹ by making different assumptions about the hydrogen exchange, in the weak or strong ergodic limits. The validity of the assumptions needs to be confirmed by dynamical calculations, since the formation of long lived complexes is not expected to be dominant, specially at higher energies, due to the shallow H_5^+ complex well (of 8.58 kcal/mol).¹⁸ In addition, some discrepancies at very low energies between quasiclassical trajectory calculations and experiment have been attributed to possible quantum effects.¹⁹

To go beyond statistical approaches a potential energy surface (PES), including all degrees of freedom and of high accuracy (for the low interstellar temperatures of interest), is essential. Many *ab initio* calculations have been devoted to characterize this system at fixed geometries,^{18,20–27} while in contrast until now only few global surfaces have been constructed.^{19,28–31} The most accurate one³¹ presents some problems, specially at the asymptotic region, as noted by the authors, and such behavior should be improved because of its special relevance in dynamical studies at low temperatures. More recently a density functional theory (DFT) based PES has been reported for H_5^+ .³² This surface shows very good global behavior with small differences (of 0.5 kcal/mol) with respect to CCSD(T) calculations and is indicated for “on fly” dynamics calculations.

The purpose of this work is to generate a global PES of higher accuracy. To this aim, in the analogous H_3^+ system a

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diatoms-in-molecules (DIM)^{33–36} description was considered to describe the asymptotes, and three-body terms were added to fit *ab initio* points to produce a spectroscopically accurate global PES.^{37–39} The advantage of using DIM is that the asymptotes are described correctly and provides a good zero-order description of the PES. When applied this procedure to H_5^+ the problem is that the DIM method is not capable to describe the H_3^+ triatomic fragments. For this reason, in the present work an extension of the DIM method is proposed by considering a triatomics-in-molecules (TRIM) method. Such approach is able to describe accurately the H_2+H_3^+ asymptotes, and further provides a good global description of the overall interaction PES of H_5^+ . Taking TRIM as a zero-order PES, then five-body corrections are added to generate an accurate full-dimensional PES of the H_5^+ system.

The organization of the paper is as follows. Section II is devoted to describe the *ab initio* calculations, the DIM and TRIM treatments, and the fitting procedure followed to include the five-body correction terms, considering the full permutation symmetry of the system.⁴⁰ Section III presents the results and compares them with previously proposed PES for this system. Finally, in Sec. IV some conclusions are presented.

II. THEORETICAL METHODOLOGY

A. *Ab initio* calculations and coordinates

Following the analysis done previously on the accuracy of different methods and basis sets,³⁰ the *ab initio* calculations are performed using the coupled cluster treatment with single and double excitations, and perturbative treatment of triple excitations, CCSD(T), as implemented in MOLPRO package,⁴¹ and the cc-pVQZ Dunning's quadruple-zeta correlation consistent basis set.⁴² The energy of the five nuclei completely separated is $-1.999\,782\,274$ a.u. (calculated as four times the energy of the hydrogen atom with this basis), which hereafter is taken as the zero of energy.

Dealing with a chemical reaction, it is normally argued

FIG. 1. Coordinates used to describe H_5^+ . r_{12} , and r_{34} are the internuclear vectors between atoms 1 and 2 and 3 and 4, respectively, with the vector r_{12} in the xz plane. R goes from diatom 12 center of mass to diatom 34 center of mass, both placed along the z axis. Finally, r_5 goes from diatom 12 center of mass to atom 5. The azimuthal angles, ϕ and χ , are defined anticlockwise, being zero when vectors r_{34} and r_5 , respectively, are in the xz plane.

FIG. 2. Energies (in kcal/mol referred to all the atoms separated) for each stationary point calculated with CCSD(T), TRIM, and DIM methods. The geometries of the stationary points, as defined in Ref. 30, are shown with the corresponding numbering.

that it is necessary to use multireference methods to account for the full electronic correlation in which the main electronic configurations change from reactants to products. Note that in many cases multiconfigurational methods (like CCSD) using a single reference configuration are often adequate to describe some reactions. In this case, for example, the reaction implies the breaking of a bond and the formation of a similar one, and due to the high symmetry of the system it is only needed to explore one of the ten possible rearrangement channels. For all this a single-reference method like CCSD(T) is expected to work properly. To check this we use the argument, first developed in Ref. 43, of calculating the norm of the t_1 vector as *a priori* prediction of the reliability of results obtained from a single-reference-based electron correlation procedure. The t_1 amplitudes in coupled cluster theory are closely related to the coefficients of singly excited configurations in configuration interaction theory, and when it takes values smaller than 0.02 it is considered that the use of one reference configuration is enough to describe the system. Thus, the t_1 amplitudes have been calculated in all the points. Typically, for energies up to 27 kcal/mol above the bottom of the well, the t_1 factor is always of the order of 0.005, and for very high energies it may rise values up to 0.01–0.015. Thus, the use of CCSD(T) method is considered to be adequate to study this system.

In addition, in order to determine the basis set superposition error (BSSE), the counterpoise method of Boys and

Bernardi⁴⁴ has been used to estimate the corresponding corrections in about 30 000 points. The analysis has been divided in different energy intervals. Thus, for the 18 549 *ab initio* points below the $H_2+H_3^+$ limit (-324.5 kcal/mol) the average BSSE error is $1.51 \times 10^{-5} \approx 3$ cm⁻¹. Since this error is much lower than the error of the present full-dimensional fit, the BSSE error has been neglected.

The coordinates defined in Fig. 1 are used to define the grid of points at which *ab initio* calculations are performed and to describe the cuts of the PES. In addition, ten specific geometries, corresponding to the lower lying stationary points of the PES,³⁰ shown in Fig. 2, will be used to compare the accuracy of the different methods applied.

B. DIM treatment

The DIM potential for several H_n^+ ions has been developed previously, and energies at various configurations were reported.⁴⁵ However, no explicit expressions of the matrix

$$\phi_i = s_j(1)s_k(2)s_l(3)s_m(4) \quad \text{with} \quad \begin{cases} i, j, k, l, m = 1, 2, \dots, 5 & \text{cyclic} \\ j = i + 1, k = i + 2, l = i + 3, m = i + 4. \end{cases} \quad (2)$$

The total basis set for H_5^+ , obtained by the direct product of spin and orbital functions, is composed by ten functions of the form

$$\Psi_{il} = \mathcal{A} \phi_i S_l, \quad (3)$$

corresponding to linear combinations of Slater determinants or configurations, where $\mathcal{A} = 1/\sqrt{n!} \sum_p (-1)^p \hat{P}$ is the antisymmetrization operator, with $\hat{P}$ denoting the different permutation operators, and fulfilling $\mathcal{A}\mathcal{A} = \sqrt{n!} \mathcal{A}$.

The (spinless) electronic Hamiltonian is partitioned in atomic and diatomic fragments, corresponding to different rearrangements of the electron on the nuclei according to the DIM method.³³⁻³⁶ In the present case, in agreement with the orbital functions used, the *i*th partition takes the form

$$\begin{aligned} \hat{H}_e \equiv \hat{H}_e^i &= \hat{H}_{ij}^+(1) + \hat{H}_{ik}^+(2) + \hat{H}_{il}^+(3) + \hat{H}_{im}^+(4) \\ &+ \hat{H}_{jk}^+(1,2) + \hat{H}_{jl}^+(1,3) + \hat{H}_{jm}^+(1,4) + \hat{H}_{kl}^+(2,3) \\ &+ \hat{H}_{km}^+(2,4) + \hat{H}_{lm}^+(3,4) + \mathcal{O}, \end{aligned} \quad (4)$$

where the $\hat{H}_{ik}^+$ are monoelectronic Hamiltonians of the H_2^+ fragments (*i, j* denoting the nuclei involved), $\hat{H}_{jk}$ are bielectronic Hamiltonians describing H_2 fragment *jk*, and $\mathcal{O}$ denotes the atomic fragments which yields to a constant and will be neglected hereafter.

The Hamiltonian matrix elements $\langle \Psi_{i'l'} | H_e | \Psi_{il} \rangle$ are simplified if H_e is partitioned according to the Ψ_{il} function in the right-hand side as

elements have been given. Here, the DIM matrices are explicitly described for H_5^+ , aiming to introduce the main concepts and equations needed to develop the TRIM description of H_5^+ .

For a system of four electrons there are two combinations with total spin zero, $S=0$, whose eigenfunctions are $S_1 = \frac{1}{2}[\alpha_1\beta_2\alpha_3\beta_4 - \alpha_1\beta_2\beta_3\alpha_4 - \beta_1\alpha_2\alpha_3\beta_4 + \beta_1\alpha_2\beta_3\alpha_4]$ and $S_2 = 1/2\sqrt{3}[2\alpha_1\alpha_2\beta_3\beta_4 + 2\beta_1\beta_2\alpha_3\alpha_4 - \alpha_1\beta_2\alpha_3\beta_4 - \alpha_1\beta_2\beta_3\alpha_4 - \beta_1\alpha_2\alpha_3\beta_4 - \beta_1\alpha_2\beta_3\alpha_4]$, which can be written in a general form as

$$S_I = \sum_{\sigma} C_{\sigma}^I \sigma_1 \sigma_2 \sigma_3 \sigma_4. \quad (1)$$

For the orbital part of H_5^+ a minimum basis set is considered composed by one 1s function for each hydrogen atom. Five functions ϕ_i are then obtained, corresponding to an electron hole on nuclei *i*, and one electron in each 1s function of the rest of nuclei, written in a compact way as

$$\begin{aligned} \langle \Psi_{i'l'} | H_e | \Psi_{il} \rangle &= \sum_{\sigma'} \sum_{\sigma} C_{\sigma'}^{I'} C_{\sigma}^I \\ &\times \sum_p (-1)^p \langle \hat{P} \phi_{i'} S_{l'} | \hat{H}_e^i | \phi_i S_l \rangle. \end{aligned} \quad (5)$$

The action of the permutation operator $\hat{P}$ on the $\phi_{i'} S_{l'}$ functions is given by

$$\begin{aligned} \hat{P} \phi_{i'} S_{l'} &\equiv \hat{P} \sigma'_1 \sigma'_2 \sigma'_3 \sigma'_4 s_{j'}(1) s_{k'}(2) s_{l'}(3) s_{m'}(4) \\ &= \sigma_1^{p'_1} \sigma_2^{p'_2} \sigma_3^{p'_3} \sigma_4^{p'_4} s_{j'_p}(1) s_{k'_p}(2) s_{l'_p}(3) s_{m'_p}(4). \end{aligned} \quad (6)$$

Introducing Eq. (4) in Eq. (5), individual matrix elements for H_2^+ and H_2 fragments can be distinguished, which take the form

$$\begin{aligned} \langle \hat{P} \phi_{i'} S_{l'} | \sum_{e=1}^4 \hat{H}_{i,i+e}^+(e) | \phi_i S_l \rangle &= \delta_{\sigma_1 \sigma_1'} \delta_{\sigma_2 \sigma_2'} \delta_{\sigma_3 \sigma_3'} \delta_{\sigma_4 \sigma_4'} \\ &\times \sum_{e=1}^4 \left(\prod_{e'' \neq e} \delta_{i'+e'', i+e} \right) \langle s_{i'+e}(e) | \hat{H}_{i,i+e}^+(e) | s_{i+e}(e) \rangle \end{aligned} \quad (7)$$

and

$$\begin{aligned} \langle \hat{P} \phi_{i'} S_{l'} | \sum_{e=1}^4 \sum_{e'=e+1}^4 \hat{H}_{i+e, i+e'}(e, e') | \phi_i S_l \rangle \\ = \delta_{\sigma_1 \sigma_1'} \delta_{\sigma_2 \sigma_2'} \delta_{\sigma_3 \sigma_3'} \delta_{\sigma_4 \sigma_4'} \times \sum_{e, e'} \left(\prod_{e'' \neq e, e'} \delta_{i'+e'', i+e} \right) \\ \times \langle s_{i'+e}(e) s_{i'+e'}(e') | \hat{H}_{i+e, i+e'}(e, e') | s_{i+e}(e) s_{i+e'}(e') \rangle, \end{aligned}$$

respectively. These matrix elements are evaluated in the Appendix, and after some algebra the Hamiltonian matrix can be factorized as

$$\mathbf{H} = \begin{pmatrix} \mathcal{H}^{11} & \mathcal{H}^{12} \\ \mathcal{H}^{12} & \mathcal{H}^{22} \end{pmatrix}, \quad (8)$$

where, $\mathcal{H}^{11}$ is a 5×5 matrix corresponding to the first spin component, whose matrix elements are given by

$$\mathcal{H}^{11} = \begin{pmatrix} \mathcal{H}_{11}^{11} & -\Delta^+(R_{12})/2 & \Delta^+(R_{13}) & \Delta^+(R_{14}) & -\Delta^+(R_{15})/2 \\ -- & \mathcal{H}_{22}^{11} & -\Delta^+(R_{23})/2 & \Delta^+(R_{24}) & \Delta^+(R_{25}) \\ -- & -- & \mathcal{H}_{33}^{11} & -\Delta^+(R_{34})/2 & \Delta^+(R_{35}) \\ -- & -- & -- & \mathcal{H}_{44}^{11} & -\Delta^+(R_{45})/2 \\ -- & -- & -- & -- & \mathcal{H}_{55}^{11} \end{pmatrix}. \quad (9)$$

Analogously, $\mathcal{H}^{22}$ matrix, corresponding to the second spin function, is expressed as

$$\mathcal{H}^{22} = \begin{pmatrix} \mathcal{H}_{11}^{22} & \Delta^+(R_{12})/2 & -\Delta^+(R_{13}) & -\Delta^+(R_{14}) & \Delta^+(R_{15})/2 \\ -- & \mathcal{H}_{22}^{22} & \Delta^+(R_{23})/2 & -\Delta^+(R_{24}) & -\Delta^+(R_{25}) \\ -- & -- & \mathcal{H}_{33}^{22} & \Delta^+(R_{34})/2 & -\Delta^+(R_{35}) \\ -- & -- & -- & \mathcal{H}_{44}^{22} & -\Delta^+(R_{45})/2 \\ -- & -- & -- & -- & \mathcal{H}_{55}^{22} \end{pmatrix}. \quad (10)$$

The nondiagonal matrices between different spin functions, in $\mathcal{H}^{12}$, take the form

$$\mathcal{H}^{12} = \mathcal{H}^{21} = \begin{pmatrix} H_{11}^{12} & \Delta^+(R_{12})\sqrt{3}/2 & 0 & 0 & \Delta^+(R_{15})\sqrt{3}/2 \\ -- & H_{22}^{12} & \Delta^+(R_{23})\sqrt{3}/2 & 0 & 0 \\ -- & -- & H_{33}^{12} & \Delta^+(R_{34})\sqrt{3}/2 & 0 \\ -- & -- & -- & H_{44}^{12} & -\Delta^+(R_{45})\sqrt{3}/2 \\ -- & -- & -- & -- & H_{55}^{12} \end{pmatrix}. \quad (11)$$

In these matrices the following definitions have been used:

$$\begin{aligned} \mathcal{H}_{ii}^{11} = & \Sigma^+(R_{ij}) + \Sigma^+(R_{ik}) + \Sigma^+(R_{il}) + \Sigma^+(R_{im}) + V_{1\Sigma}(R_{jk}) \\ & + V_{1\Sigma}(R_{lm}) + \Sigma_3(R_{jl}) + \Sigma_3(R_{jm}) + \Sigma_3(R_{kl}) \\ & + \Sigma_3(R_{km}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ii}^{22} = & \Sigma^+(R_{ij}) + \Sigma^+(R_{ik}) + \Sigma^+(R_{il}) + \Sigma^+(R_{im}) + V_{3\Sigma}(R_{jk}) \\ & + V_{3\Sigma}(R_{lm}) + \Sigma_1(R_{jl}) + \Sigma_1(R_{jm}) + \Sigma_1(R_{kl}) \\ & + \Sigma_1(R_{km}), \end{aligned}$$

$$\mathcal{H}_{ii}^{12} = [\Delta(R_{jl}) - \Delta(R_{jm}) - \Delta(R_{kl}) + \Delta(R_{km})]\sqrt{3},$$

where the different Σ^+ , Δ^+ , $V_{1\Sigma}$, $V_{3\Sigma}$, Σ_3 , Σ_1 , Δ have been defined in the Appendix, and the potential curves used were developed in Refs. 37–39 for the DIM potential of H_3^+ in the ground $^1A'$ singlet and $^3A'$ triplet states, respectively.

The fragmentation pathway of interest corresponds to $\text{H}_2(^1\Sigma_g^+) + \text{H}_3(^1A')$. The DIM H_3^+ energies present an error with respect to the “exact” *ab initio* ones⁴⁶ of the order of $\approx 1000 \text{ cm}^{-1}$. Such difference was corrected in the analytical fits made for $\text{H}_3^+(^1A', ^3A')$ by adding three-body correction terms to the DIM eigenvalues.^{37–39} Following this procedure

highly accurate PESs were constructed with an overall root mean square (rms) error of $\approx 10 \text{ cm}^{-1}$. Such small deviation was possible because the DIM eigenvalues describe correctly both the $\text{H}^+ + \text{H}_2$ and $\text{H} + \text{H}_2^+$ fragmentation channels of H_3^+ .

Applying the DIM method to H_5^+ we found that the $\text{H}_3^+ + \text{H}_2$ fragmentation channels were not accurately described. For this reason a further refinement is considered below, in which triatomic H_3^+ fragments are considered in addition to the diatomic ones considered in the standard DIM method.

C. Triatomics-in-molecules method: TRIM

To describe asymptotically the H_3^+ fragments, it is necessary to partition the electronic Hamiltonian in a different way to the one employed in the usual DIM method, allowing the inclusion of triatomic subunits. In this case the following partitions are considered:

$$\hat{H}_e^i = \sum_{n>i, o>n} \hat{H}_{ino}^+(n-i, o-i) - 2 \sum_{p>i} \hat{H}_{ip}^+(p-i), \quad (12)$$

where the $\hat{H}_{ip}^+(p-i)$ are the monoelectronic Hamiltonians of H_2^+ fragments, as used in the DIM method, while $\hat{H}_{ino}^+(n-i, o-i)$ are bielectronic Hamiltonians (for electrons $n-i, o-i$) describing H_3^+ systems for the *ino* nuclei.

The same electronic basis set, however, will be considered. Thus, when Eq. (12) is used in Eq. (5), the Hamiltonian matrix elements become

$$\begin{aligned} \langle \Psi_{i'l'} | \hat{H}_e | \Psi_{il} \rangle &= \sum_{\sigma'} \sum_{\sigma} C_{\sigma'}^{l'} C_{\sigma}^l \\ &\times \sum_p (-1)^p \left\{ \sum_{n>i, o>n} \langle \hat{\mathcal{P}} \phi_i' S_{l'} | \hat{H}_{ino}^+(n-i, o-i) | \phi_i S_l \rangle \right. \\ &\left. - 2 \sum_{p>i} \langle \hat{\mathcal{P}} \phi_i' S_{l'} | \hat{H}_{ip}^+(p-i) | \phi_i S_l \rangle \right\}. \end{aligned} \quad (13)$$

The H₂⁺ diatomic matrix elements are those of Eq. (7) defined above. The H₃⁺ triatomic matrix elements take the form

$$\begin{aligned} &\langle \hat{\mathcal{P}} \phi_i' S_{l'} | H_{ino}^+(n-i, o-i) | \phi_i S_l \rangle \\ &= \delta_{\sigma_1 \sigma_1'} \cdots \delta_{\sigma_4 \sigma_4'} \left(\prod_{l'' \neq n-i, o-i} \delta_{l_p' + l'', n} \right) \\ &\times \langle s_{i'+n-i}(n-i) s_{i'+o-i}(o-i) | \hat{H}_{ino}^+(n-i, o-i) | \\ &| s_n(n-i) s_o(o-i) \rangle, \end{aligned} \quad (14)$$

where the bielectronic integrals are obtained from the eigenvalues of H₃⁺, as explained in the Appendix.

The resulting Hamiltonian matrix is of 10 × 10 dimensions and is also factorized in two submatrices according to Eq. (8), each one corresponding to a particular spin component. The explicit expressions of such terms are given by

$$\begin{aligned} \mathcal{H}_{ii}^{11} &= H_{11}^0(R_{ij}, R_{jk}, R_{ki}) + H_{11}^0(R_{il}, R_{lm}, R_{mi}) \\ &+ \Sigma_{11}^1(R_{ij}, R_{jl}, R_{li}) + \Sigma_{11}^1(R_{ij}, R_{jm}, R_{mi}) \\ &+ \Sigma_{11}^1(R_{ik}, R_{kl}, R_{li}) + \Sigma_{11}^1(R_{ik}, R_{km}, R_{mi}) - 2[\Sigma^+(R_{ij}) \\ &+ \Sigma^+(R_{ik}) + \Sigma^+(R_{il}) + \Sigma^+(R_{im})], \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ji}^{11} &= -H_{21}^0(R_{ij}, R_{jk}, R_{ki})/2 - H_{21}^0(R_{ij}, R_{jm}, R_{mi})/2 \\ &- \Sigma_{21}^0(R_{ij}, R_{jl}, R_{li}) + \Delta^+(R_{ij}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ki}^{11} &= -H_{31}^1(R_{ij}, R_{jk}, R_{ki}) - \Delta_{21}^1(R_{ik}, R_{km}, R_{mi}) \\ &- \Delta_{21}^1(R_{ik}, R_{kl}, R_{li}) - 2\Delta^+(R_{ik}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{li}^{11} &= -H_{21}^1(R_{il}, R_{lm}, R_{mi}) - \Delta_{31}^1(R_{ij}, R_{jl}, R_{li}) \\ &- \Delta_{31}^1(R_{ik}, R_{kl}, R_{li}) - 2\Delta^+(R_{il}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{mi}^{11} &= -H_{31}^0(R_{ij}, R_{jm}, R_{mi})/2 - H_{31}^0(R_{il}, R_{lm}, R_{mi})/2 \\ &- \Sigma_{31}^0(R_{ik}, R_{km}, R_{mi}) + \Delta^+(R_{im}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ii}^{22} &= H_{11}^1(R_{ij}, R_{jk}, R_{ki}) + H_{11}^1(R_{il}, R_{lm}, R_{mi}) \\ &+ \Sigma_{11}^0(R_{ij}, R_{jl}, R_{li}) + \Sigma_{11}^0(R_{ij}, R_{jm}, R_{mi}) \\ &+ \Sigma_{11}^0(R_{ik}, R_{kl}, R_{li}) + \Sigma_{11}^0(R_{ik}, R_{km}, R_{mi}) - 2[\Sigma^+(R_{ij}) \\ &+ \Sigma^+(R_{ik}) + \Sigma^+(R_{il}) + \Sigma^+(R_{im})], \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ji}^{22} &= -H_{21}^1(R_{ij}, R_{jk}, R_{ki})/2 - H_{21}^1(R_{ij}, R_{jm}, R_{mi})/2 \\ &- \Sigma_{21}^1(R_{ij}, R_{jl}, R_{li}) - \Delta^+(R_{ij}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ki}^{22} &= -H_{31}^0(R_{ij}, R_{jk}, R_{ki}) - \Delta_{21}^0(R_{ik}, R_{km}, R_{mi}) \\ &- \Delta_{21}^0(R_{ik}, R_{kl}, R_{li}) + 2\Delta^+(R_{ik}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{li}^{22} &= -H_{21}^0(R_{il}, R_{lm}, R_{mi}) - \Delta_{31}^0(R_{ij}, R_{jl}, R_{li}) \\ &- \Delta_{31}^0(R_{ik}, R_{kl}, R_{li}) + 2\Delta^+(R_{il}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{mi}^{22} &= -H_{31}^1(R_{ij}, R_{jm}, R_{mi})/2 - H_{31}^1(R_{il}, R_{lm}, R_{mi})/2 \\ &- \Sigma_{31}^1(R_{ik}, R_{km}, R_{mi}) - \Delta^+(R_{im}), \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ii}^{12} &= \sqrt{3} [+ \Delta_{11}(R_{ij}, R_{jl}, R_{li}) - \Delta_{11}(R_{ij}, R_{jm}, R_{mi}) \\ &- \Delta_{11}(R_{ik}, R_{kl}, R_{li}) + \Delta_{11}(R_{ik}, R_{km}, R_{mi})], \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ji}^{12} &= \sqrt{3} [H_{21}^0(R_{ij}, R_{jk}, R_{ki}) - H_{21}^1(R_{ij}, R_{jm}, R_{mi}) \\ &+ \Delta_{21}(R_{ij}, R_{jl}, R_{li})] - \sqrt{3} \Delta^+(R_{ij}), \end{aligned}$$

$$\mathcal{H}_{ki}^{12} = \sqrt{3} [\Sigma_{21}(R_{ik}, R_{kl}, R_{li}) - \Sigma_{21}(R_{ik}, R_{km}, R_{mi})],$$

$$\mathcal{H}_{li}^{12} = \sqrt{3} [\Sigma_{31}(R_{ik}, R_{kl}, R_{li}) - \Sigma_{31}(R_{ij}, R_{jl}, R_{li})],$$

$$\begin{aligned} \mathcal{H}_{mi}^{12} &= \sqrt{3} [H_{31}^0(R_{il}, R_{lm}, R_{mi}) - H_{31}^1(R_{ij}, R_{jm}, R_{mi}) \\ &+ \Delta_{31}(R_{ik}, R_{km}, R_{mi})] - \sqrt{3} \Delta^+(R_{im}), \end{aligned}$$

where it has been considered the cyclic structure of the matrix elements in the basis set used.

The $H_{31}^S(R_{il}, R_{lm}, R_{mi})$, $\Delta_{31}^S(R_{ik}, R_{km}, R_{mi})$, ... matrix elements for H₃⁺ fragments have been evaluated according to Eq. (A7), as described in the Appendix. If the DIM coefficients and eigenvalues are used, the PES obtained is exactly the same as the one obtained with the pure DIM method applied directly to H₃⁺, as described above.

These triatomic terms include contribution of excited states of the triatomic fragments, which are missing in the DIM description. The inconvenient is that it requires the knowledge of several electronic states of the triatomic fragments. These are only available for few systems, and constitute a limitation for the application of the TRIM method. One possibility would be to use the 3 × 3 diabatic Hamiltonian matrices for ¹A' and ³A' electronic states of H₃⁺ to obtain directly the matrix elements in the TRIM treatment. This would imply an enormous effort. To overcome this difficulty, the strategy we follow here to improve the DIM description is to replace the DIM eigenvalues E_j^S , in Eq. (A7) by $E_j^S + W^S$, where W^S are the three-body correction terms developed for the ground ¹A' and ³A' electronic states of H₃⁺, in Refs. 37 and 38, respectively, to correct the DIM eigenvalues and reproduce the *ab initio* results.

It should be noted that the three-body terms used correspond to the ground singlet and triplet states of H₃⁺. For the excited states obtained by the 3 × 3 DIM matrix, we assume the same correction W^S . However, within this approximation the coefficient matrices used in Eq. (A6) are consistent with the DIM matrix, whose diagonal matrix elements are all equally shifted. Here we adopt the strategy of adding another term accounting for the five-body interaction terms to improve the description of the TRIM-PES.

TABLE I. Total energies (in kcal/mol) of optimized H_3^+ structures obtained at DIM, TRIM, and CCSD(T)/VQZ levels of theory. Zero of energy corresponds to all the atoms separated.

Conformer	CCSD(T)	DIM	TRIM	Ellison (1963)
Lineal	-291.1476	-274.2859	-270.7189	-277
Pentagonal	-178.9530	-219.4825	-207.4549	-222
Pyramid	-105.5286	-202.0241	-189.7843	-208
Bipyramid	-146.4690	-170.2538	-151.8392	-178

D. Global PES fitting

The global PES of H_3^+ is finally expressed in terms of the TRIM model potential as

$$V = V^{\text{TRIM}} + V_1^{5B} + V_2^{5B}, \quad (15)$$

so that two five-body terms are added in the analytical form in order to correct the inaccuracies appearing at short distances in the TRIM model, while it already describes correctly the fragmentation channels asymptotically. The five-body terms V^{5B} are treated following the method developed for the description of H_5 .⁴⁰ The $H_2+H_3^+$ asymptote is well reproduced by the TRIM method, and the $H+H_4^+$ asymptote is about 100 kcal/mol higher in energy,⁴⁷ so it will not be considered here. For this reason, in Eq. (15) the four-body terms^{48,49} are not included.

Each five-body term is expressed as linear combinations of symmetry adapted functions⁵⁰ as

$$V^{5B} = \sum_{ijk\dots t}^M d_{ijk\dots t} \mathcal{W}_{ABCDE}^5 \rho_{AB}^i \rho_{AC}^j \rho_{AD}^k \dots \rho_{DE}^t, \quad (16)$$

where $\mathcal{W}_{ABCDE}^5$ is a symmetrizing operator which in this case reduces to an unnormalized Young operator⁵¹ for the totally symmetric irreducible representation of the S_5 permutation group. $\rho_{\alpha\beta}$ in Eq. (16) are Rydberg-type functions⁵² defined in terms of the internuclear distance $R_{\alpha\beta}$ as

$$\rho_{\alpha\beta} = R_{\alpha\beta} e^{-\gamma_{\alpha\beta} R_{\alpha\beta}} \quad \text{with} \quad \gamma_{\alpha\beta} > 0. \quad (17)$$

In Eq. (16) the sum is done taking into account some constraints such as $i+j+k+\dots+t \leq M$, as well as additional ones to ensure that the five-body term does not contain lower order contributions.⁴⁰ Finally, the $d_{ijk\dots t}$ linear coefficients of the expansion are determined, as described previously,⁵² by minimizing the difference between the global potential, in Eq. (15), and the calculated *ab initio* CCSD(T)/cc-pVQZ points.

III. RESULTS AND DISCUSSION

A. DIM results

For the DIM model the H_2 and H_2^+ curves used are those previously reported for H_3^+ .^{37,38} In Table I, the DIM results obtained here are compared with those obtained previously at some fixed configurations in Ref. 45. The agreement between the two sets of DIM results is very good, and the small differences being attributed to the use of different diatomic potential curves. However, in the previous study only unstable configurations were reported, corresponding to energies above the $H_3^+ + H_2$ asymptote.

Here a more detailed analysis is performed, using the nuclear configurations of the stationary points determined previously with CCSD(T) calculations, and shown in Fig. 2. It is found that while the CCSD(T) minimum appears in the $1C_{2v}$ configuration, the minimum with the DIM model is that of $10C_{3v}$ configuration. In fact, the DIM model overestimates the stability of configurations with a maximum number of atom-atom configurations, with four atoms in a square or a tetrahedron. On the contrary, the CCSD(T) results show that the structures with a proton in between two H_2 molecules (the $1C_{2v}$, $2D_{2d}$, $3C_{2v}$, and $4D_{2h}$) are the most stable ones. Clearly, the DIM treatment fails in describing such structures, since the contribution of triatomic fragments must play a fundamental role for such configurations in which a proton is stabilized by a resonant H_3^+ .

Regarding the description of the $H_3^+ + H_2$ interaction at short and intermediate distances, the energy obtained with the DIM method is compared in Fig. 3 with that obtained with CCSD(T) calculations for several approaching configurations corresponding to the orientations of the stationary points of Fig. 2. First, the DIM asymptotic energy is too low by about 10 kcal/mol, as a consequence of the inaccuracy of the DIM model to perfectly describe H_3^+ alone.³⁷ Second, the potential wells are too shallow and placed at longer distances with respect to the CCSD(T) ones, as seen in Fig. 3. Third, the relative energies of the different stationary points, in Fig. 2, vary significantly, providing a wrong description of the H_3^+ interaction well. All these demonstrate that the DIM model provides a poor description of the H_3^+ system and further improvements are needed.

This failure is due to the inability of the traditional DIM method to describe three- or five-body interactions as a consequence of using incomplete basis set and the (usual) neglect of overlaps between basis set functions. One possible way to improve the DIM description is to use the so-called dressed-DIM approach.^{53,54} In this method, a many-body term is added to each diatomic term, what modifies the whole DIM matrix. When applied to triatomic systems, this implies three-body terms in the diagonal and off-diagonal DIM matrix, and has been successfully applied to obtain multisheeted PESs of the singlet states of H_3^+ . When this method is applied to H_3^+ , the generalization of the method would imply the inclusion of five-body terms in diagonal and off-diagonal terms. Such terms are very difficult to obtain accurately, specially when taking into account that the procedure of changing the terms of a matrix is highly nonlinear.

For this reason, in this work we use the alternative of generalizing the DIM approach to directly account for three-body terms.

B. TRIM results

1. H_3^+ PESs used within TRIM

The TRIM model constructs the zero-order PES by combining all possible triatomic arrangements within the pentatomic H_5^+ system. It is then very important to properly describe the triatomic PESs for the H_3^+ . In addition, the inclusion of long range term interaction is very important, specially when treating charged systems, and many methods

FIG. 3. Energy as a function of R for different geometries, as defined in Fig. 2, with the following coordinates: $1C_{2v}$: $r_{12}=0.812\,66$, $r_{34}=0.7662$, $r_5=0.7895$, $\alpha=\beta=\phi=\pi/2$, $\gamma=\chi=0$, $3C_{2v}$: $r_{12}=0.814\,05$, $r_{34}=0.764\,44$, $r_5=0.647\,07$, $\alpha=\beta=\pi/2$, $\phi=\gamma=\chi=0$, $5C_{2v}$: $r_{12}=0.872\,36$, $r_{34}=0.749\,74$, $r_5=0.753\,26$, $\alpha=\beta=\phi=\pi/2$, $\gamma=\pi$, $\chi=0$, $6C_{2v}$: $r_{12}=0.858\,449$, $r_{34}=0.745\,71$, $r_5=0.778\,16$, $\alpha=\pi/2$, $\beta=\phi=\gamma=\chi=0$, $7C_{2v}$: $r_{12}=0.872\,22$, $r_{34}=0.748\,74$, $r_5=0.752\,46$, $\alpha=\beta=\pi/2$, $\phi=\chi=0$, $\gamma=\pi$, and $8C_{2v}$: $r_{12}=0.873\,45$, $r_{34}=0.743\,19$, $r_5=0.756\,50$, $\alpha=\pi/2$, $\beta=\phi=\chi=0$, $\gamma=\pi$ (distances are in a.u., energy in kcal/mol referred to the five hydrogen fragments as zero of energy).

have been developed for this aim.^{39,53,55} The TRIM approach allows not only to describe properly the vibrations of H_3^+ and H_2 fragments, but also the long range ion-induced dipole and induced quadrupole interactions among them. For describing this last interaction it is then very important to represent as accurately as possible the $\text{H}^+ + \text{H}_2$ and $\text{H} + \text{H}_2^+$ interactions. At this regard, here we use the procedure described in Ref. 39 applied to the ground singlet state of H_3^+ . Briefly, this method consists in partition the total interaction potential as a DIM contribution plus a three-body term as previously reported,^{37,38} and in order to improve the long range $\text{H}^+ + \text{H}_2(X^1\Sigma_g^+)$ the ion-induced dipole and induced quadrupole interactions have been included³⁹ in the diagonal matrix elements of DIM matrix as

$$V_{\text{H}^+-\text{H}_2}(R', r', \theta') = Q_2(r') P_2(\cos \theta') (R')^{-3} - [\alpha_0(r')/2 + \frac{1}{3}(\alpha_{\parallel}(r') - \alpha_{\perp}(r')) P_2(\cos \theta')] (R')^{-4}, \quad (18)$$

where R' is the distance from the H_2 center of mass to H^+ , r' is the H_2 internuclear distance, and θ' is the angle between $\mathbf{r}'$ and $\mathbf{R}'$. The quadrupole moment $Q_2(r')$ of H_2 and the average, parallel, and perpendicular polarizabilities of the H_2 , $\alpha_0(r')$, $\alpha_{\parallel}(r')$, and $\alpha_{\perp}(r')$, respectively, as a function of the H_2 internuclear distance r' are described in Ref. 39.

The $\text{H} + \text{H}_2^+(^2\Sigma_g^+)$ long range interaction energy is well represented by the spherical charge-induced dipole and induced quadrupole dispersion energies as³⁹

$$V_{\text{H}-\text{H}_2^+}(R'') = -\frac{9}{4}(R'')^{-4} - \frac{15}{2}(R'')^{-6}, \quad (19)$$

which essentially corresponds to the $\text{H}-\text{H}^+$ long range interaction,⁵⁶ and where R'' is the distance between the H_2^+ center of mass and the H atom.

These two terms diverge at origin (R' or R'' tending to zero) and should be dumped at a suitable distance to avoid singularities in the global PES. As it is mentioned in Ref. 39, to do this we have replaced the distance R' or R'' by a modified distance of the form (for example for R')

$$\tilde{R}' = R' + R'_0 \exp(-(R' - R'_0)).$$

The advantage is that this procedure is done in the diagonal DIM matrix elements, each one corresponding to a particular diabatic $\text{H} + \text{H}_2$ channel. Thus, when the DIM matrix is diagonalized to provide the ground eigenvalue, it produces completely symmetric results for the exchange of the atoms, allowing a high accuracy when the three-body terms are added.³⁹

Here, this procedure has been used to fit the ground singlet and triplet states of H_3^+ using CCSD(T) points obtained here with the same basis set, as mentioned in Sec. II A, for H_5^+ . In this way, we minimize any possible small disagreement with the results of H_5^+ . A total number of 7878 and 8000 *ab initio* points were calculated for the singlet and triplet states, respectively, obtaining overall rms errors in these fits of 0.012 and 0.16 kcal/mol, respectively.

The excited states have been approximated using the second DIM eigenvalue plus the three-body term developed

FIG. 4. Energy as a function of R for the geometries considered in Fig. 3 in the asymptotic region. The curves “ASYMP” correspond to the asymptotic $\text{H}_2 + \text{H}_3^+$ long range interaction of Eq. (18), in which the positive charge is placed at the H_3^+ center of mass.

for the fit of the ground H_3^+ eigenvalues. This approximation is described in section II C and the Appendix, and its effects on the TRIM method are discussed below.

2. Asymptotic $\text{H}_2 + \text{H}_3^+$ interaction

The asymptotic $V_{\text{H}^+ - \text{H}_2}$, in Eq. (18), can also be used for describing the long range asymptotic $\text{H}_2 + \text{H}_3^+$ interaction.³⁰ This is good provided that the distance among them is sufficiently long, as compared with the size of H_3^+ molecule. However, as the two fragments approach each other, the effect of the delocalization of the positive charge in the whole H_3^+ should be taken into account, making possible to also describe intermediate-long distances.

This is accomplished when using the TRIM model for H_5^+ combined with the use of H_3^+ with the correct long range interactions at the asymptotes. By construction, the H_5^+ is a linear combination of all possible H_3^+ fragments. Thus, for $\text{H}_2 + \text{H}_3^+$ at long distances there are contributions from the interaction of the H_2 fragment and each one of the three atoms of the H_3^+ . At long distances, these correspond to $\text{H}_2 - \text{H}^+$ long range interactions, which are properly described in the triatomic case. When combining the contribution of each of these H_3^+ subsystems, the interaction potential takes into account the delocalization of the positive charge in H_3^+ and describes the anisotropy corresponding to approaches at different geometries. Thus, the resulting potential describes better the $\text{H}_2 + \text{H}_3^+$ interaction at intermediate distances.

As an example, in Fig. 4 the interaction potential for long distances, $10 \leq R \leq 50$ a.u., for several geometries corresponds to H_2 center of mass in the plane of the H_3^+ subsystem, whose coordinates are given in Fig. 3. The comparison is made in total energy. For the analytical asymptotic model of Eq. (18) (ASYMP in Fig. 4) the energy of the TRIM method at $R=50$ a.u. has been added, and the positive charge is considered to be at the H_3^+ center of mass. The energy difference between the CCSD(T) and the rest of the methods at $R=50$ a.u. is 1.1 cm^{-1} . That corresponds to the value of the accuracy of the fit of the $\text{H}_3^+(X^1A)$ PES described above. This is the same for distorted H_3^+ geometries (not equilateral anymore) as for the $1C_{2v}$, $3C_{2v}$, and out of plane considered in the figures. All the energy curves are

parallel until $R \approx 30$ a.u. At this distance, the analytical form of Eq. (18) deviates from all the other curves, which continue being parallel and very close to each other.

A similar situation occurs when H_2 approaches perpendicularly to the plane of H_3^+ , as shown in Fig. 5. All this analysis demonstrates that the TRIM model describes with an accuracy of $\approx 1 \text{ cm}^{-1}$ the long range interaction up to distances of $R \approx 10\text{--}20$ a.u. The TRIM model gets a significant improvement with respect to the pure asymptotic expression of Eq. (18). This is accomplished by taking into account the delocalization of the positive charge within the whole H_3^+ , that is, the interaction between the H_3^+ dipole and the induced dipole of H_2 .

FIG. 5. Energy as a function of R (short distances in left panels, long distances in right panels) for three geometries in which H_2 approach H_3^+ out of plane for the three β, ϕ cases indicated in the figure and $r_{12}=0.81266 \text{ \AA}$, $r_{34}=0.76620 \text{ \AA}$, $r_{5}=0.7895 \text{ \AA}$, and $\alpha=\gamma=\chi=\pi/2$.

FIG. 6. Contours of the PES of H_3^+ obtained with TRIM (left panel), CCSD(T) (middle panel), and TRIM+FIT (right panel), as a function of $R-r_5$ and r_5 distances, for several configurations as indicated in the figure, whose nuclear configurations are given by $r_{12}=r_{34}=0.74$ Å, $\alpha=\pi/2$ and the rest of the angles are $1C_{2v}(\beta=\phi=\pi/2, \gamma=\chi=0)$, $3C_{2v}(\beta=\pi/2, \phi=\gamma=\chi=0)$, $5C_{2v}(\beta=\phi=\pi/2, \gamma=\pi, \chi=0)$, $6C_{2v}(\beta=\phi=\gamma=\chi=0)$, and $7C_{2v}(\beta=\pi/2, \phi=0, \gamma=\pi, \chi=0)$. The energy contours are -330 , -320 , -310 , -290 , -270 , and -250 kcal/mol.

3. Short-intermediate distances

For shorter distances, however, the discrepancies between TRIM and CCSD(T) data are larger, and the potential wells appearing at all configurations, in Fig. 3, are always deeper than the CCSD(T) ones by about 3–5 kcal/mol. The actual position of the wells, however, is almost correct as compared with those appearing using the CCSD(T) data.

The TRIM method improves significantly the DIM model, as can be seen in Fig. 3, which is not able to properly describe neither the position nor the depths of the wells. This is summarized in Fig. 2 where the energy of the stationary points shows that the TRIM model recovers the fact that the most stable configurations correspond to a proton in between two H_2 molecules the ($1C_{2v}$, $2D_{2d}$, $3C_{2v}$, and $4D_{2h}$), and any square or tetrahedron structure is higher in energy. In fact, nearly all the overall behavior is excellent, except for the $2D_{2d}$ and $4D_{2h}$ resonant structures, which correspond to saddle points and whose barrier height is overestimated.

To get a better description of the potential, in Fig. 6 several contour plots correspond to some selected configurations with the H_2 center of mass in the plane of the H_3^+ molecule. For the $1C_{2v}$ and $3C_{2v}$, which correspond to two H_2 molecules with a proton in between, with the two molecules being perpendicular or parallel, respectively, there is a

FIG. 7. Potential energy curves obtained with TRIM, CCSD(T), and FIT describing the double well for the proton hop at two $1C_{2v}$ (top panel) and $3C_{2v}$ (bottom panel) as a function of r_5 for $R=4$ a.u., for $r_{12}=r_{34}=1.4$ a.u. (left panels), and for r_{12} and r_{34} optimized to get the lower energy (right panels). The rest of coordinates are given in Fig. 6.

double well structure, which is magnified by the TRIM (with a barrier of ≈ 5 kcal/mol), while for the CCSD(T) there is a very low barrier between them of only 0.002 kcal/mol at the geometries shown in the left panels of Fig. 7 with more detail for $r_{12}=r_{34}=1.4$ a.u. This distance corresponds to the bare H_2 equilibrium distance, which is different from that of the H–H internuclear distance in the H_3^+ which is ≈ 1.61 a.u. Thus, when the proton “moves” in between the two H_2 molecules, r_{12} and $r_{34}=r_{12}$ vary in between these two limiting values. When these two distances are optimized, the total energy decreases significantly, and CCSD(T) barrier for the proton hop increases slightly, but keeps significantly lower than the one obtained with the TRIM model.

This region of the PES is very much affected by the approximation made to treat the diabatic states of the triatomic H_3^+ fragments, in particular for the $^3A'$ state. At equilateral triangles, the $\text{H}_3^+(^3A')$ state presents a conical intersection.^{38,57–60} In such situation the approximation described in the Appendix is not appropriate, and further corrections should be considered. Thus, several parametrization of the energies of the two states involved in the conical intersection were used, getting a substantial change in the PES, specially near the $2D_{2d}$ and $4D_{2h}$ geometries. To improve the description of the TRIM model a diabatic representation of the PES should be employed for the description of the triatomic H_3^+ , as recently performed for its ground singlet state.^{53,61}

FIG. 8. Energy contour plot as a function of the β, ϕ angles, describing the rotation of the H_2 molecules, obtained with TRIM, CCSD(T), and FIT methods, showing the transition between the $1\text{C}_{2v}(\beta=\pi/2, \phi=\pi/2)$ and $3\text{C}_{2v}(\beta=\pi/2, \phi=0)$ and $r_{12}=0.812\ 66, r_{34}=0.7662\ \text{\AA}, R=4.00\ \text{a.u.}, r_5=0.7895\ \text{\AA}, \alpha=\pi/2$, and $\gamma=\chi=0$. The contours are $-331.25, -331, -330, -325, -320$, and $-315\ \text{kcal/mol}$.

In spite of this approximation, the double-well region must be affected by five-body terms. In particular, this region of the PES is stabilized by a sort of resonant structure in which the proton can hop forward and backward between the two H_2 molecules. This effect should low down the barrier between the two wells (and as it is not well described by the TRIM method), should be accounted for through the use of five-body terms as described below.

For the 5C_{2v} and 7C_{2v} in Fig. 6 the proton hop is not feasible. Two H_2 molecules are facing each other in a perpendicular and parallel configuration, respectively, while the fifth atom is on the other side. In such configuration there is no double well structure and r_5 cannot increase since it would imply the departure of the fifth atom leading the other four behind, what is energetically not accessible. There is a well slightly swallower at $R \approx 2\ \text{a.u.}$ which is much deeper than the weak van der Waals interaction of the $(\text{H}_2)_2$ dimer. This could imply that the charge of the H_3^+ fragment strongly stabilizes such structures. As can be seen in Fig. 6, both the position and the depth of the well obtained with the TRIM model are in very good agreement with the CCSD(T) results, where simply the well depth is slightly overestimated.

In the 6C_{2v} geometry in Fig. 6, one hydrogen of H_3^+ faces the H_2 molecule, being the three in a line. In such situation the proton can hop but at a much higher energy, since in H_3^+ such linear geometry is rather high by about $40\ \text{kcal/mol}$. Again the agreement between TRIM and CCSD(T) results in this case is also good.

The most favorable geometries for the proton hop are the 1C_{2v} and the 3C_{2v} ones. The transition from one to the other of these geometries is simply a rotation of the H_2 molecule around the z-axis. Figure 8 shows the PES as a function of the two angles, β and ϕ , describing the H_2 rotation. Around the minimum of energy, at $\beta=\pi/2$, the PES is nearly constant as a function of ϕ , showing a nearly free rotation around the z-axis, between 1C_{2v} and 3C_{2v} configurations. The PES as a function of β shows a higher slope, but still allows a rather wide amplitude of motion. TRIM model shows a very similar behavior to that of the CCSD(T) results, with the only difference that the energies are slightly lower.

The proton hop takes place when one of the atoms of H_3^+ is pointing the approaching H_2 molecule at the 1C_{2v} and/or 3C_{2v} configurations preferentially. Due to the presence of the relatively deep well, of $\approx 8\ \text{kcal/mol}$, a H_5^+ complex can be

FIG. 9. Energy contour plot as a function of the R and γ (with $\alpha=\gamma+\pi/2, \chi=0$) describing the rotation of the H_3^+ molecule in the xz plane, with the H_2 molecule at three different configurations and its center of mass at the z-axis at a distance R . (Bottom panels) 1C_{2v} with H_2 along the y axis ($\beta=\phi=\pi/2$). (Middle panels) 3C_{2v} with H_2 along the x axis ($\beta=\pi/2, \phi=0$). (Top panels) 6C_{2v} with H_2 along the z axis ($\beta=\phi=0$). The energies obtained with TRIM, CCSD(T), and FIT methods are compared, showing the transition between $r_{12}=0.812\ 66, r_{34}=0.7662\ \text{\AA}$ and $r_5=0.7895\ \text{\AA}$. The contours are $-335, -330, -325, -320, -310, -290, -270$, and $-250\ \text{kcal/mol}$.

formed, as assumed in the statistical models.^{2,11,17} For sufficiently long lived complexes, the question is if H_3^+ can rotate in the xz plane. If so, any of the three H_3^+ atoms could hop from the original H_3^+ to form a new one by a simple rotation, allowing the scrambling mechanism. Figure 9 shows several contour plots corresponding to such mechanism at different orientations of H_2 along the three Cartesian axes. The rotation of H_3^+ shows a barrier of the order of $5\ \text{kcal/mol}$. Since the complex is about $8\ \text{kcal/mol}$ deep, this barrier is below the H_2+H_3^+ asymptote, even without considering ZPE. Therefore, the scrambling mechanism is highly probable. As in all the previous cases, the TRIM method describes rather well the PES along these motions, being again slightly deeper than the CCSD(T) results.

In addition, the exchange mechanism,⁶² in which one of the atoms of the H_2 is transferred to the H_3^+ subunit, is possible by considering one proton hop followed by the scrambling of the new H_3^+ thus formed and a subsequent proton hop back.

Summarizing, the overall behavior of the TRIM PES is rather satisfactory and provides a reasonable zero-order description of the H_5^+ system. In order to improve the accuracy the five-body terms are added as described below, providing

TABLE II. Accuracy vs the order of the fit. n_{par} is the number of linear parameters. rms error in kcal mol^{-1} .

M	n_{par}	rms
6	96	1.718
7	266	1.126
8	652	0.646
9	1444	0.341

TABLE III. Accuracy of the fitted H_3^+ PES for several subsets of the *ab initio* CCSD(T) energies (energies and rms in kcal mol⁻¹). Zero of energy corresponds to all the atoms separated.

Subset	Energies	N_{pts}	rms
Energies below $\text{H}_3^+\cdots\text{H}_2$	$-333.0 \leq E \leq -324.5$	18 549	0.022
Energies below $\text{H}_3^+(\text{ZPE})\cdots\text{H}_2$	$-333.0 \leq E \leq -312.0$	43 529	0.060
Energies below $\text{H}_3^+(\text{ZPE})\cdots\text{H}_2(\text{ZPE})$	$-333.0 \leq E \leq -305.8$	48 567	0.079
Energies below $\text{H}_4^+\cdots\text{H}$	$-333.0 \leq E \leq -220.9$	92 570	0.390
All H_3^+ energies	$-333.0 \leq E \leq -62.9$	112 196	0.646

a PES in very good agreement with the exact CCSD(T) results, as shown in all the figures discussed so far.

C. *Ab initio* calculations and PES fitting

An initial grid of points is defined using the coordinates of Fig. 1 as follows: $r_{12}, r_{34} \in 1.4, 1.5, 1.6$, $R \in 2.0, 2.5, \dots, 4.0$, $r_e \in 1.0, 1.5, \dots, R-1$ a.u., $\alpha, \beta \in 0, \pi/6, 2\pi/6, \pi/2$, $\phi, \gamma \in 0, \pi/6, 2\pi/6, \pi/2, 4\pi/6, 5\pi/6, \pi$, and $\chi \in 0, \pi/6, 2\pi/6, \dots, 2\pi$. Thus, the total amount of points to calculate is about 2×10^6 . To reduce such a quantity, first at the so defined configurations the energy is evaluated using the TRIM model described above, and if it is higher than an energy cutoff, the point is not evaluated. Thus, the initial set of points is significantly reduced to about 50 000. This set of points is increased by performing more detailed calculations at few chosen configurations, as those showing in Figs. 2–9. In addition, several thousands of points were chosen randomly in different coordinate and energy intervals. Thus, about 110 000 points were finally used in the fit.

For the H_3^+ ground $^1A'$ singlet^{37,39} a linear combination of different three-body terms is able to reproduce the short and intermediate part of the global potential. In the global H_3^+ PES adding two five-body terms of degree M to the TRIM

approach allows to describe accurately the short and intermediate region. In Table II we present the rms values for different fits to the 112 196 CCSD(T) *ab initio* energies. Increasing the degree of the fit M (that is the number of linear parameters), a better global fit can be reached. We have selected as the final fit that with $M=8$, corresponding to only 652 linear parameters and two nonlinear ones. Those parameters are listed in the accompanying supplementary material.⁶³

In Table III we compare the rms error of the fit with $M=8$ with respect to different subsets of the *ab initio* CCSD(T) energies. With 652 linear parameters and two nonlinear parameters, the rms error of the fit is only of 0.039 kcal/mol for energies below the $\text{H}_3^+\cdots\text{H}_2$ channel. The global PES obtained has a rms deviation of 0.079 kcal/mol for energies below the ZPE of H_3^+ and H_2 (energies below 27 kcal/mol above the global well).

In Fig. 10 we show the comparison of the TRIM and fitted PESs with respect to the calculated CCSD(T) energies. In the top panel of Fig. 10 the residuals (algebraic deviations δ in kcal/mol) are represented as a function of the energy (in kcal/mol) up to the ZPE of H_3^+ and H_2 . In the bottom panel of Fig. 10 the energies of the fitted PES are represented with

FIG. 10. Comparison of the TRIM (left panels) and fitted (right panels) global PESs of H_3^+ with the CCSD(T) energies. In the top panel are the residuals (algebraic deviations) of the TRIM and fitted PESs vs the energy. In the bottom panel the energy of the TRIM and present global PESs is represented with respect to the CCSD(T) energies.

TABLE IV. Total energy (in a.u.) for the global $1C_{2v}$ minimum and relative energies (in kcal/mol) for the rest nine lowest lying structures obtained by the CCSD(T)/cc-pVQZ calculations, the present analytical PES, and their comparison with the ones from previous available surfaces. In all cases, the relative energies are referred to its own $1C_{2v}$ energy. The energy difference (in kcal/mol) between the *ab initio* calculations and the fitted surface is also listed.

Conformer	This work			CCSD(T)-R12 ^a	PES ^b	PES ^c	DFT PES ^d
	CCSD(T)	PES	Difference				
$1C_{2v}$	-2.530 509	-2.530 526	-0.010	-2.531 794	-2.518 215	-2.528 015	-2.532 656
$2D_{2d}$	0.183	0.387	0.192	0.176	0.080	0.149	0.090
$3C_{2v}$	0.273	0.265	-0.018	0.276	0.256	0.294	0.302
$4D_{2h}$	0.520	0.656	0.125	0.521	0.419	0.458	0.483
$5C_{2v}$	4.413	4.440	0.016	...	5.635	4.477	5.075
$7C_{2v}$	4.781	4.813	0.021	...	5.687	4.795	5.455
$9C_s$	6.208	6.225	0.006	...	7.264	6.021	7.198
$6C_{2v}$	6.573	6.612	0.029	...	6.076	6.886	7.021
$8C_{2v}$	7.615	7.641	0.015	...	7.139	7.144	8.384
$10C_{3v}$	8.104	8.095	-0.020	...	8.011	7.755	9.105

^aReference 18.

^bReference 19.

^cReference 31.

^dReference 32.

respect to the CCSD(T) ones for all the fitted points. The fit improves the TRIM results two orders of magnitude in the region of interest.

In addition, the behavior of this fit has been shown in Figs. 2–9 and compared with the CCSD(T) and TRIM results. In all the cases the fit shows an extraordinary good agreement with the CCSD(T), improving the TRIM description of the PES.

D. Comparison with previous results

In Table IV we present the energies of the ten lower lying stationary points on the H_3^+ surface, as predicted by this work, and compare them with previous available results. The current parametrized PES agrees very well with the CCSD(T) and CC-R12¹⁸ benchmark calculations with an average deviation of 0.045 kcal/mol, whereas for the most recent surface by Xie *et al.*³¹ a value of 0.15 kcal/mol has been

reported from their *ab initio* data. One can also see that the MP2 surface¹⁹ presents larger deviations and different ordering for the $9C_s$, $6C_{2v}$, and $8C_{2v}$ structures. By comparing now with a new DFT based surface³² we found that this surface predicts deeper well depth for the $1C_{2v}$ configuration by 0.002 and 0.0009 a.u. lower than the CCSD(T) and CC-R12 data, respectively. This surface has larger average deviation of 0.522 kcal/mol compared to the CCSD(T) data and predicts a reverse order for the $9C_s$ and $6C_{2v}$ conformers.

A further comparison of the present fit with the most recent and accurate PESs reported is made in Fig. 11 for different approaching geometries between H_3^+ and H_2 , both kept in their equilibrium configuration. The PES of Ref. 31 describes correctly the wells in general, but at distances of the order of 8 a.u. it presents some oscillatory artifacts with spurious maxima of the order of 0.4 kcal/mol. In addition, in H_3^+ geometries deviating from equilibrium these artifacts are

FIG. 11. Comparison of the potential energy curves of H_3^+ obtained with CCSD(T) method (points), the present fit, that of Ref. 31, and the DFT based one of Ref. 32. The different cuts correspond to H_3^+ at its equilateral equilibrium distance ($r_{12}=0.8738$ Å) and the H_2 at $r_e=0.7419$ Å and different orientations: $1C_{2v}$ ($\beta=\phi=\pi/2, \gamma=\chi=0$), $3C_{2v}$ ($\beta=\pi/2, \phi=\gamma=\chi=0$), $5C_{2v}$ ($\beta=\phi=\pi/2, \gamma=\pi, \chi=0$), $6C_{2v}$ ($\beta=\phi=\gamma=\chi=0$), $7C_{2v}$ ($\beta=\pi/2, \phi=0, \gamma=\pi, \chi=0$), and $8C_{2v}$ ($\beta=\phi=0, \gamma=\pi, \chi=0$), out: ($\gamma=\chi=\pi/2$ and β, ϕ indicated in the figure), with $\alpha=\pi/2$.

magnified. For example, for 1C_{2v} and 3C_{2v} geometries of Fig. 3 and those of Fig. 5, in which the H_3^+ is isosceles, the PES of Ref. 31 shows larger artifacts which do not appear either in the CCSD(T) results nor the present fit.

The DFT based PES of Ref. 32 does not present the artifacts arising from a fit to a limited number of *ab initio* points. The reason is that the fit is replaced by on fly direct first principle electronic structure calculations. Thus, the only problem when using DFT method is the inaccuracy of the functional used, which for H_5^+ has been extensively studied in Ref. 32. Its accuracy is very good, and the only difference with the CCSD(T) results is that the well depth is slightly overestimated by the DFT method by less than 0.5 kcal/mol.

Among all of them, the present fit is the most accurate one, as compared with the CCSD(T) calculations. As discussed above the rms error is 0.079 kcal/mol in energies below 27 kcal/mol above the global well, and it behaves correctly at all the configurations analyzed, being exceptionally good at those shown in Fig. 11.

IV. CONCLUSIONS

In the present work a global PES for the description of the $\text{H}_3^+ + \text{H}_2$ reaction has been developed, which describes very accurately the intermediate distances region (with errors lower than 0.1 kcal/mol). In addition, the asymptotic behavior of the present global potential energy surface (GPES) is extraordinarily good and describes perfectly (with an error of few cm^{-1}) the charge-induced dipole and quadrupole interactions. This is achieved by using a TRIM method developed in this work as a zero-order description. The TRIM method constructs the PES as a linear combination of all possible triatomic fragments of the system (as a generalization of the more common DIM treatment that fails to describe H_5^+ producing a very poor description of the system). Using triatomic potential analytical functions which describe properly the charge-induced dipole and quadrupole interactions in H_3^+ ,³⁹ it is therefore possible to describe the equivalent $\text{H}_3^+ + \text{H}_2$ interactions taking into account the delocalization of the charge among the three nuclei of H_3^+ . Thus, the asymptotic expressions are extended to shorter distances (up to 10–15 a.u.) than the usual expression in which the charge is located at the H_3^+ center of mass, which are only valid up to 30 a.u. or longer distances as described in this work.

The TRIM model describes qualitatively well also the short distance region, nearly semiquantitatively, with a slight overestimation of the well depths. The main failure corresponds to the double well appearing for the proton hop mechanism, in which the TRIM method overestimates the energy barrier between the two wells, corresponding to $\text{H}_3^+ + \text{H}_2$ and $\text{H}_2 + \text{H}_3^+$, respectively. Such resonant structure produces a stabilization and is due to the five atoms of the system, thus explaining the larger disagreement between the TRIM and the CCSD(T) results in that region. Nevertheless, the addition of five-body terms, to generate the final fit, corrects this problem and provides a very accurate PES.

The TRIM and fit of the GPES developed in this work are analyzed extensively along this work. The geometries at which the proton hop mechanism takes place are described in

detail. It is seen that the H_2 molecule can rotate almost freely around the z-axis. Also, the scrambling mechanism has been analyzed, finding a barrier for the rotation of the H_3^+ within the H_5^+ complex of about 5 kcal/mol, which is lower than the dissociation potential energy by about 3–4 kcal/mol. Thus, the full scrambling mechanism is possible provided that the H_5^+ complex lives during sufficiently long time.

This surface can be used not only for classical and quantum dynamical studies, for which it is designed for, but also to improve the statistical methods used up to now^{11,17} by incorporating the average anisotropy into the interaction potential,⁶⁴ instead of the effective isotropic one used until now. This is possible using the present fit because it treats very accurately the asymptotic charge-induced dipole and quadrupole interactions. Work in this direction is currently in progress.

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APPENDIX: H_2^+ , H_2 , AND H_3^+ MATRIX ELEMENTS

1. H_2^+

For this mono-electronic system, the two eigenstates are expressed in the minimum basis set used in the DIM and TRIM treatment as

$$^2\Sigma_g(R_{jk}) = \frac{1}{\sqrt{2}}[s_j(1) + s_k(1)]|\alpha\rangle,$$

$$^2\Sigma_u(R_{jk}) = \frac{1}{\sqrt{2}}[s_j(1) - s_k(1)]|\alpha\rangle,$$

where $|\alpha\rangle$ is the spin function (with $m_s = \pm 1/2$), and the indexes j, k refer to the nuclei involved. The eigenvalues associated to these states are denoted as $V_g^+(R_{jk})$ and $V_u^+(R_{jk})$, respectively.

Thus the matrix elements between the basis set functions are in turn obtained as

$$\begin{aligned} \langle s_j(1)|H_{jk}^+(1)|s_j(1)\rangle &= \langle s_k(1)|H_{jk}^+(1)|s_k(1)\rangle \\ &= [V_g^+(R_{jk}) + V_u^+(R_{jk})]/2 \equiv \Sigma^+(R_{ij}), \end{aligned}$$

$$\begin{aligned} \langle s_j(1)|H_{jk}^+(1)|s_k(1)\rangle &= \langle s_k(1)|H_{jk}^+(1)|s_j(1)\rangle \\ &= [V_g^+(R_{jk}) - V_u^+(R_{jk})]/2 \equiv \Delta^+(R_{ij}). \end{aligned}$$

2. H₂

The ground singlet and triplet states considered ($\Phi^{SM}(R_{jk})$) for this system, expressed in the minimum basis set considered, are expressed as

$$\begin{aligned}\Phi^{00}(R_{jk}) &= \frac{1}{\sqrt{2}}[|s_j^\alpha(1)s_k^\beta(2)| - |s_j^\beta(1)s_k^\alpha(2)|], \\ \Phi^{10}(R_{jk}) &= \frac{1}{\sqrt{2}}[|s_j^\alpha(1)s_k^\beta(2)| + |s_j^\beta(1)s_k^\alpha(2)|], \\ \Phi^{11}(R_{jk}) &= |s_j^\alpha(1)s_k^\alpha(2)|, \\ \Phi^{11}(R_{jk}) &= |s_j^\beta(1)s_k^\beta(2)|,\end{aligned}\quad (\text{A1})$$

where $|s_j^\alpha(1)s_k^\beta(2)|$ are Slater determinants of spin orbitals $s_j^\alpha(1)$. The eigenvalues associated to these functions are denoted by $V_{1\Sigma}(R_{jk})$ and $V_{3\Sigma}(R_{jk})$ for singlet and triplets, respectively. Thus, the matrix elements needed in the DIM treatment take the form

$$\begin{aligned}\langle \Phi^{00}(R_{jk}) | H_{jk}(1,2) | \Phi^{00}(R_{jk}) \rangle &= V_{1\Sigma}(R_{jk}) = \langle s_j^\alpha(1)s_k^\beta(2) | H_{jk}(1,2) | s_j^\alpha(1)s_k^\beta(2) \rangle \\ &\quad + \langle s_k^\alpha(1)s_j^\beta(2) | H_{jk}(1,2) | s_j^\alpha(1)s_k^\beta(2) \rangle, \\ \langle \Phi^{10}(R_{jk}) | H_{jk}(1,2) | \Phi^{10}(R_{jk}) \rangle &= V_{3\Sigma}(R_{jk}) = \langle s_j^\alpha(1)s_k^\beta(2) | H_{jk}(1,2) | s_j^\alpha(1)s_k^\beta(2) \rangle \\ &\quad - \langle s_k^\alpha(1)s_j^\beta(2) | H_{jk}(1,2) | s_j^\alpha(1)s_k^\beta(2) \rangle, \\ \langle \Phi^{11}(R_{jk}) | H_{jk}(1,2) | \Phi^{11}(R_{jk}) \rangle &= V_{3\Sigma}(R_{jk}) = \langle s_j^\alpha(1)s_k^\alpha(2) | H_{jk}(1,2) | s_j^\alpha(1)s_k^\alpha(2) \rangle \\ &\quad - \langle s_k^\alpha(1)s_j^\alpha(2) | H_{jk}(1,2) | s_j^\alpha(1)s_k^\alpha(2) \rangle, \\ \langle \Phi^{1-1}(R_{jk}) | H_{jk}(1,2) | \Phi^{1-1}(R_{jk}) \rangle &= V_{3\Sigma}(R_{jk}) = \langle s_j^\beta(1)s_k^\beta(2) | H_{jk}(1,2) | s_j^\beta(1)s_k^\beta(2) \rangle \\ &\quad - \langle s_k^\beta(1)s_j^\beta(2) | H_{jk}(1,2) | s_j^\beta(1)s_k^\beta(2) \rangle.\end{aligned}\quad (\text{A2})$$

The following definitions have been introduced to simplify the notation in the main text:

$$\begin{aligned}\Delta(R_{ij}) &= [V_{1\Sigma}(R_{ij}) - V_{3\Sigma}(R_{ij})]/2, \\ \Sigma_1(R_{ij}) &= [3V_{1\Sigma}(R_{ij}) + V_{3\Sigma}(R_{ij})]/4, \\ \Sigma_3(R_{ij}) &= [V_{1\Sigma}(R_{ij}) + 3V_{3\Sigma}(R_{ij})]/4.\end{aligned}\quad (\text{A3})$$

3. H₃⁺

The expression of singlet ($S=0$) and triplet ($S=1$) eigenfunctions of H₃⁺ is formally obtained in a DIM treatment. For this purpose, an initial basis set is first constructed formed by three functions, similar to those used for H₂⁺ in Eq. (3), with well defined total spin SM_S as

$$\tilde{\Psi}_i^{S0} = \frac{1}{\sqrt{2}}[\tilde{A}s_j^\alpha(1)s_k^\beta(2) - (-1)^S \tilde{A}s_j^\beta(1)s_k^\alpha(2)],$$

$$\tilde{\Psi}_i^{S=1, M_S=+1} = \tilde{A}s_j^\alpha(1)s_k^\alpha(2), \quad (\text{A4})$$

with $j > i, k > j$ and where the tilde is introduced to distinguish the functions and antisymmetrization operators from the case of H₂⁺.

In this basis, the matrix elements of the triatomic H₃⁺ Hamiltonian, denoted by $\hat{H}_{ijk}^+$, are given by

$$\begin{aligned}\langle \tilde{\Psi}_{i'}^{S0} | \hat{H}_{ijk}^+ | \tilde{\Psi}_i^{S0} \rangle &= H_{i'i}^{S0}(R_{ij}, R_{jk}, R_{ki}) \\ &= \langle s_{j'}^\alpha(1)s_k^\beta(2) | \hat{H}_{ijk}^+ | s_j^\alpha(1)s_k^\beta(2) \rangle \\ &\quad + (-1)^S \langle s_{k'}^\beta(1)s_j^\alpha(2) | \hat{H}_{ijk}^+ | s_j^\alpha(1)s_k^\alpha(2) \rangle, \\ \langle \tilde{\Psi}_{i'}^{11} | \hat{H}_{ijk}^+ | \tilde{\Psi}_i^{11} \rangle &= H_{i'i}^{11}(R_{ij}, R_{jk}, R_{ki}) \\ &= \langle s_{j'}^\alpha(1)s_k^\alpha(2) | \hat{H}_{ijk}^+ | s_j^\alpha(1)s_k^\alpha(2) \rangle \\ &\quad - \langle s_{k'}^\alpha(1)s_j^\alpha(2) | \hat{H}_{ijk}^+ | s_j^\alpha(1)s_k^\alpha(2) \rangle.\end{aligned}\quad (\text{A5})$$

These matrix elements are the ones needed in Eq. (14) and are obtained by solving the secular equation

$$\mathbf{HC} = \mathbf{CE} \rightarrow \mathbf{H} = \mathbf{CEC}^+, \quad (\text{A6})$$

where $\mathbf{H}$ is the 3×3 Hamiltonian matrix, $\mathbf{E}$ is the diagonal matrix with the eigenvalues, and $\mathbf{C}$ are the matrices with the coefficients. This equation can be rewritten in a more explicit form as

$$H_{i'i}^{SS} = \sum_j C_{i'j}^S E_j^S C_{ji}^S. \quad (\text{A7})$$

The following definitions are made to simplify the notation:

$$\begin{aligned}\Sigma_{i'i}(R_{ij}, R_{jk}, R_{ki}) &= (H_{i'i}^0 + H_{i'i}^1)/2 = \langle s_{j'}s_{k'} | H_{ijk}^+ | s_j s_k \rangle, \\ \Delta_{i'i}(R_{ij}, R_{jk}, R_{ki}) &= (H_{i'i}^0 - H_{i'i}^1)/2 = \langle s_{k'}s_{j'} | H_{ijk}^+ | s_j s_k \rangle, \\ \Sigma_{i'i}^1(R_{ij}, R_{jk}, R_{ki}) &= (H_{i'i}^0 + 3H_{i'i}^1)/4 \\ &= \langle s_{j'}s_{k'} | H_{ijk}^+ | s_j s_k \rangle - \langle s_{k'}s_{j'} | H_{ijk}^+ | s_j s_k \rangle/2, \\ \Delta_{i'i}^1(R_{ij}, R_{jk}, R_{ki}) &= (-H_{i'i}^0 + 3H_{i'i}^1)/4 \\ &= \langle s_{j'}s_{k'} | H_{ijk}^+ | s_j s_k \rangle/2 - \langle s_{k'}s_{j'} | H_{ijk}^+ | s_j s_k \rangle, \\ \Delta_{i'i}^0(R_{ij}, R_{jk}, R_{ki}) &= (3H_{i'i}^0 - H_{i'i}^1)/4 \\ &= \langle s_{j'}s_{k'} | H_{ijk}^+ | s_j s_k \rangle/2 + \langle s_{k'}s_{j'} | H_{ijk}^+ | s_j s_k \rangle, \\ \Sigma_{i'i}^0(R_{ij}, R_{jk}, R_{ki}) &= (3H_{i'i}^0 + H_{i'i}^1)/4 \\ &= \langle s_{j'}s_{k'} | H_{ijk}^+ | s_j s_k \rangle + \langle s_{k'}s_{j'} | H_{ijk}^+ | s_j s_k \rangle/2,\end{aligned}\quad (\text{A8})$$

where (R_{ij}, R_{jk}, R_{ki}) refers to the internuclear distances

among the ijk nuclei, defined in a cyclic way for the triatomic system, i.e., $i, j, k = 1, 2, 3$ with $j > i, k > j$. Note, however, that when used in the TRIM the subindexes of the matrix elements refer to the 3×3 matrix of the triatomic DIM Hamiltonian, while the subindexes of the radial coordinates can then be i, j, k, l, m to denote the five nuclei of H_5^+ .

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