



# Benchmark potential energy curve for collinear H<sub>3</sub>

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## ABSTRACT

A benchmark-quality potential energy curve is reported for the H<sub>3</sub> system in collinear nuclear configurations. The electronic Schrödinger equation is solved using explicitly correlated Gaussian (ECG) basis functions using an optimized fragment initialization technique that significantly reduces the computational cost. As a result, the computed energies improve upon recent orbital-based and ECG computations. Starting from a well-converged basis set, a potential energy curve with an estimated sub-parts-per-billion relative precision is generated for a series of nuclear configurations using an efficient ECG rescaling approach.

## 1. Introduction

This paper is dedicated to the memory of Professor Kuchitsu. The authors did not know Professor Kuchitsu in person, but have learned about his fundamental work on gas-electron diffraction [1] as part of their undergraduate studies, and later, used in their own research [2] molecular structural parameters taken from Kozu Kuchitsu's work [3,4]. The present contribution to the Kuchitsu Special Issue is about a triatomic system, H<sub>2</sub> + H, which, at some point and with further development, may become relevant to Professor Kuchitsu's contribution to the photodissociation dynamics study of triatomics [5].

The simplest chemical reaction H<sub>2</sub> + H → H + H<sub>2</sub>—including its isotopologues—is possibly one of the most exhaustively studied chemical processes [6]. Furthermore, the H<sub>3</sub> system has qualitatively interesting features: a shallow van-der-Waals minimum for collinear nuclear structures and a conical intersection for equilateral triangular configurations. These features impose challenges when investigating the quantum dynamics of the system and require a high-level description of the electronic structure. The first potential energy surface (PES) for collinear H<sub>3</sub> was obtained by Liu in 1973 [7]. Since then, several full-dimensional surfaces have been published [8–14] and refined [15–21] using increasingly accurate quantum chemical methods. More recently, a multireference configuration interaction (MRCI) PES was developed, using a hierarchy of correlation consistent basis sets followed by extrapolation to the complete basis set (CBS) limit [22] with an estimated  $\mu E_h$  level of precision. This complete configuration interaction (CCI) surface has been the most accurate full-dimensional PES of H<sub>3</sub>, and it was used to resolve long-standing discrepancy of experimental and

theoretical thermal rate constants [23].

The first computation for this system using explicitly correlated Gaussian (ECG) basis functions was performed by Cafiero and Adamowicz [24]. They determined the stationary points of the PES by the simultaneous minimization of the energy with respect to both the nonlinear parameters of the basis functions and the nuclear configuration using analytic gradients. Nevertheless, using only 64 basis functions, they obtained an energy,  $-1.673\,467\,E_h$ , which is above the dissociation threshold,  $E(\text{H}_2) + E(\text{H}) = -1.674\,475\,714\,E_h$ .

In later work, Pavanello, Tung, and Adamowicz carried out methodological developments to improve the convergence of the ECG wave function and energy, and to reduce the computational cost for polyatomic, *i.e.*, H<sub>3</sub><sup>+</sup> and H<sub>3</sub>, systems. Their efforts resulted in the most precise non-relativistic energy for H<sub>3</sub>, so far, near the equilibrium structure [25].

The aim of the present letter is to explore and take the achievable precision further for H<sub>3</sub>, a simple prototype for poly-electronic and poly-atomic molecular systems, using explicitly correlated Gaussian functions.

## 2. Method

The Schrödinger equation (in atomic units) with  $N_{\text{nuc}}$  nuclei clamped at the  $\mathbf{R}$  configuration and  $n_p$  electrons,

$$H\psi(\mathbf{r}; \mathbf{R}) = E(\mathbf{R})\psi(\mathbf{r}; \mathbf{R}) \quad (1)$$

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$$H = \frac{1}{2} \sum_{i=1}^{n_p} \mathbf{p}_i^2 - \sum_{a=1}^{N_{\text{nuc}}} \sum_{i=1}^{n_p} \frac{Z_a}{r_{ia}} + \sum_{i<j}^{n_p} \frac{1}{r_{ij}} + \sum_{a<b}^{N_{\text{nuc}}} \frac{Z_a Z_b}{R_{ab}}, \quad (2)$$

is solved for the ground state of  $\text{H}_3$ . The wave function is written as sum of antisymmetrized product of spatial and spin functions,

$$\psi(\mathbf{r}; \mathbf{R}) = \mathcal{A} \sum_{n=1}^{N_b} c_n \phi_n(\mathbf{r}; \mathbf{A}_n, \mathbf{s}_n) \chi(\vartheta_n). \quad (3)$$

In the following equations, the spin degree of freedom is explicitly shown if it is directly relevant to the equations. The spatial basis functions,  $\phi_n$ , are expressed with floating ECG functions,

$$\phi_n(\mathbf{r}; \mathbf{A}_n, \mathbf{s}_n) = \exp[-(\mathbf{r} - \mathbf{s}_n)^T \underline{\mathbf{A}}_n (\mathbf{r} - \mathbf{s}_n)], \quad (4)$$

where  $\underline{\mathbf{A}}_n = \mathbf{A}_n \otimes \mathbf{I}_3$ ,  $\mathbf{A}_n \in \mathbb{R}^{n_p \times n_p}$  is the exponent matrix,  $\otimes \mathbf{I}_3$  means direct product with the  $3 \times 3$  unit matrix, and  $\mathbf{r}, \mathbf{s} \in \mathbb{R}^{3n_p}$  are the coordinate vectors of the electrons and the Gaussian centers, respectively.  $\mathcal{A}$  is the anti-symmetrization operator, and  $\mathbf{A}$  is parameterized in the  $\mathbf{A} = \mathbf{L}^T \mathbf{L}$  Cholesky-form, with an  $\mathbf{L}$  lower-triangular matrix, to ensure positive definiteness of  $\mathbf{A}$  and square integrability of the basis functions. The  $\text{A}_1$  symmetry (in the  $C_{\infty v}$  point group) of the ground-state wave function is realized by constraining the Gaussian centers to the  $z$  axis.

The  $\chi(\vartheta_n)$  three-particle spin function corresponding to the doublet multiplicity of the ground-state is obtained as a linear combination of the two possible couplings of the elementary, one-electron spin functions  $\sigma(i)_{\frac{1}{2}, \pm \frac{1}{2}}$  to a doublet state [26],

$$\begin{aligned} \chi \left( \vartheta_n \right) &= d_1 \left( \vartheta_n \right) \left[ \left[ \sigma(1)_{\frac{1}{2}} \sigma(2)_{\frac{1}{2}} \right]_{1,0} \sigma(3)_{\frac{1}{2}} \right]_{\frac{1}{2}, \frac{1}{2}} \\ &+ d_2 \left( \vartheta_n \right) \left[ \left[ \sigma(1)_{\frac{1}{2}} \sigma(2)_{\frac{1}{2}} \right]_{0,0} \sigma(3)_{\frac{1}{2}} \right]_{\frac{1}{2}, \frac{1}{2}}, \end{aligned} \quad (5)$$

where the square brackets denote angular momentum coupling, using the Clebsch–Gordan coefficients  $\langle j_1, m_{j_1}, j_2, m_{j_2} | J, M_J \rangle$ . For example, coupling two spin-1/2 particles to a singlet function is labelled as

$$\begin{aligned} &\left[ \sigma(1)_{\frac{1}{2}} \sigma(2)_{\frac{1}{2}} \right]_{0,0} \\ &= \left\langle \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2} \middle| 0, 0 \right\rangle \sigma(1)_{\frac{1}{2}, \frac{1}{2}} \sigma(2)_{\frac{1}{2}, -\frac{1}{2}} \\ &+ \left\langle \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \middle| 0, 0 \right\rangle \sigma(1)_{\frac{1}{2}, -\frac{1}{2}} \sigma(2)_{\frac{1}{2}, \frac{1}{2}} \\ &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \end{aligned} \quad (6)$$

Considering the normalization condition as well, the doublet three-electron spin functions can be parameterized by a single  $\vartheta_n$  parameter as

$$d_1(\vartheta_n) = \sin \vartheta_n \quad \text{and} \quad d_2(\vartheta_n) = \cos \vartheta_n, \quad (7)$$

and  $\vartheta_n$  is optimized together with the nonlinear parameters of the basis set. Although the non-relativistic Hamiltonian, Eq. (2), is spin independent, during the course of the variational solution of Eq. (1), optimization of  $\vartheta_n$  (and the linear combination coefficients of the two possible spin functions, Eq. (5)), provides an additional flexibility for the basis set.

## 2.1. Optimized fragment initialization

The starting basis function parameters are usually generated in a pseudo-random manner, retaining those functions from a trial set that provide the lowest energy expectation value. This generation procedure is followed by extensive refinement of the parameterization based on the variational principle [26]. By increasing the number of electrons, the dimensionality of the parameter space, and hence, the optimization cost increases. To keep the computational cost low, it is useful to consider that the interaction between the electrons of the hydrogen molecule and the electron of the hydrogen atom is weak in the van-der-Waals well or if the two ‘fragments’ are not too close, in general. If the interaction is not too strong, then a  $\psi_I$  initial approximation for the wave function can be written as the product of the wave functions optimized for the ‘fragments’ (atom and molecule for the present example):

$$\begin{aligned} \psi_I^{\text{H}_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \psi^{\text{H}_2}(\mathbf{r}_1, \mathbf{r}_2) \psi^{\text{H}}(\mathbf{r}_3) \\ &= \sum_{k,l} c_{kl} \phi_k^{\text{H}_2}(\mathbf{r}_1, \mathbf{r}_2) \phi_l^{\text{H}}(\mathbf{r}_3), \end{aligned} \quad (8)$$

which corresponds to an initial parameterization of the three-electron basis set with

$$A_{kl}^I = \begin{pmatrix} \mathbf{A}_k^{\text{H}_2} & 0 \\ 0 & \mathbf{A}_l^{\text{H}} \end{pmatrix}, \quad (9)$$

and the 3-electron  $s$  vectors include the  $s$  vectors shifted according to the configuration of the ‘fragments’ in  $\text{H}_3$ :

$$s_{kl}^I = \begin{pmatrix} s_k^{\text{H}_2} + \mathbf{R}_{\text{CM}}^{\text{H}_2} \\ s_l^{\text{H}} + \mathbf{R}^{\text{H}} \end{pmatrix}, \quad (10)$$

where  $\mathbf{R}_{\text{CM}}^{\text{H}_2}$  is the center of mass of the protons in  $\text{H}_2$ .

This procedure is reminiscent of the monomer contraction method that was first introduced in Ref. [27] for the helium dimer, although there are a few differences. First, we use the fragment (or monomer) basis set only to initialize the many(three)-electron basis, and we run repeated refinement cycles [28,29] using the Powell method [30] for this initial basis. Second, retaining the full direct-product basis optimized for  $\text{H}_2$  and separately for H would be computationally very demanding, so instead, we truncate the direct-product basis according to the following strategy.

The ground-state wave function of the  $\text{H}_2$  molecule was expanded over 1200 ECG functions, yielding  $-1.174475714 E_h$  for the ground state energy, which—compared to the most accurate value obtained by Pachucki  $-1.1744757142204434(5) E_h$  [31]—is converged to a fraction of a  $nE_h$ . The wave function of the hydrogen atom was represented with 10 optimized Gaussian functions, resulting in  $-0.499999332 E_h$  (in comparison with the exact value,  $-0.5 E_h$ ) ground-state energy. Inclusion of all possible combinations of the  $\text{H}_2$  and H basis functions would result in a gigantic, 12 000-term expansion. Such a long expansion would be prohibitively expensive to extensively optimize (refine), and it is unnecessary to have so many functions for reaching a  $1 : 10^9$  (ppb) precision. To reduce the direct-product basis, it would be possible to perform competitive selection over the large basis space or to order (and then truncate) the basis functions based on their importance in lowering the energy [26]. In the present work, we used a very simple construct that does not require any computation: we have generated a set of 1200 functions by appending each  $\text{H}_2$  basis function from the 1200 set with a single H function. Out of the 10 H functions, we have picked one based on the basis index, *i.e.*,

$$\begin{aligned}
& \{ \phi_{10n+i}^{\text{H}_2} \phi_i^{\text{H}}; n = 0, 1, \dots, 119, i = 1, 2, \dots, 10 \} \\
& = \{ \phi_1^{\text{H}_2} \phi_1^{\text{H}}, \phi_2^{\text{H}_2} \phi_2^{\text{H}}, \dots, \phi_{10}^{\text{H}_2} \phi_{10}^{\text{H}}, \\
& \quad \phi_{11}^{\text{H}_2} \phi_1^{\text{H}}, \phi_{12}^{\text{H}_2} \phi_2^{\text{H}}, \dots, \phi_{20}^{\text{H}_2} \phi_{10}^{\text{H}}, \\
& \quad \dots \\
& \quad \phi_{1191}^{\text{H}_2} \phi_1^{\text{H}}, \phi_{1192}^{\text{H}_2} \phi_2^{\text{H}}, \dots, \phi_{1200}^{\text{H}_2} \phi_{10}^{\text{H}} \}.
\end{aligned} \quad (11)$$

The spin basis functions defined in Eq. (5), were initialized by coupling the two electrons initially localized on the H<sub>2</sub> fragment to a singlet state, *i.e.*,  $d_1(\vartheta_n) = 0$  and  $d_2(\vartheta_n) = 1$  corresponding to  $\vartheta_n = 0$  ( $n = 1, 2, \dots, 1200$ ) in Eqs. (5)–(7). All non-linear parameters, including  $\vartheta_n$ , of the initial basis set were excessively optimized in repeated refinement cycles (Fig. 1). The optimized fragment-based initialization of the basis set, described in this section, allowed saving several weeks (months) of computer time in comparison with Ref. [32] (see also Section 3).

## 2.2. Gaussian-center scaling

Independent variational optimization of the basis set at many points along the PEC (or over the PES) would make the computations very computationally intensive. Kołos and Wolniewicz [33] noted already in 1964 that for a sufficiently large basis set, the  $A_k$  exponents are insensitive to small displacements of the nuclear coordinates. In 1997, Cencek and Kutzelnigg proposed a scaling technique to generate a good initial ECG (re) parameterization for the electronic basis set of diatomics upon small nuclear displacements [34]. They noted that their approach can be generalized beyond diatomics. Pavanello and Adamowicz implemented rescaling the ECG centers (to have a good starting basis set) of H<sub>3</sub><sup>+</sup> upon small nuclear displacements to generate a series of points to represent the 3D PES [32,35–37]. Upon a small  $\Delta R_a$  displacement of the coordinates of the *a*th nucleus,

$$\mathbf{R}_a' = \mathbf{R}_a + \Delta \mathbf{R}_a, \quad (12)$$

the  $s_i \in \mathbb{R}^3$  ECG centers corresponding to the *i*th electron were transformed as

$$s_i' = s_i + \Delta s_i, \quad (13)$$

where  $\Delta s_i$  is expressed as a function of the  $\Delta R_a$  nuclear displacement,

$$\Delta s_i = \frac{1}{W_i} \sum_{a=1}^{N_{\text{ nuc}}} w_{ia} \Delta \mathbf{R}_a \quad (14)$$

with  $W_i = \sum_{a=1}^{N_{\text{ nuc}}} w_{ia}$ . The  $w_{ia}$  ‘weight’ is a function constructed based on simple arguments. It is chosen to be the distance of the  $s_i$  center and the *a*th nucleus,  $|s_i - \mathbf{R}_a|$  and it is expected to have good limiting properties.

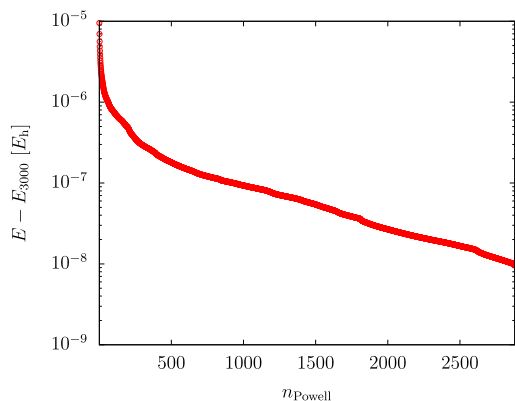


Fig. 1. Convergence of the ground-state energy of H<sub>2</sub>...H during the course of the Powell refinement cycles ( $n_{\text{Powell}}$ ) of  $N_b = 1200$  basis functions initialized using basis functions optimized for the fragments, Eq. (11).  $R_{\text{H}_2} = 1.4$  bohr and  $R_{\text{H}_2 \dots \text{H}} = 6.442$  bohr,  $E_{3000} = -1.674\,561\,687 E_h$ . (See also Table 1.)

First, it must vanish if the  $s_i$  center is very (infinitely) far from the displaced nucleus,  $\lim_{|s_i - \mathbf{R}_a| \rightarrow \infty} w_{ia} = 0$ . Second, the closer the  $s_i$  center to the  $\mathbf{R}_a$  nucleus position, the  $\Delta R_{ia}$  displacement has a larger contribution, *i.e.*, larger  $w_{ia}$  weight, to the  $\Delta s_i$  change.

These conditions allow several possible choices for the weight function. For example, Coulomb-like weights were used in Ref. [32]

$$w_{ia}^{\text{C}} = \frac{1}{|s_i - \mathbf{R}_a|}. \quad (15)$$

After some experimentation with different possible functions, and inspired by the picture that the weight function can be intuitively defined as if there was some attraction between the centers and the nuclear positions by a central field, a Yukawa-like weight function appears to be a good choice

$$w_{ia}^{\text{Y}} = \frac{e^{-\mu|s_i - \mathbf{R}_a|}}{|s_i - \mathbf{R}_a|}, \quad (16)$$

where the parameter  $\mu \in \mathbb{R}^+$  was set to unity in this work. For small nuclear displacements, a parameterization rescaled with Yukawa weights (with  $\mu = 1$ ) provided an energy lower than rescaling with Coulomb weights, Eq. (15).

The rescaling technique with the Yukawa weight function was used to generate the PEC corresponding to the H atom approaching the H<sub>2</sub> molecule with a proton-proton distance fixed at  $R_{\text{H}_2} = 1.4$  bohr. The  $R_{\text{H}_2 \dots \text{H}}$  distance of the hydrogen atom was measured from the center of mass of the H<sub>2</sub> fragment. The starting value was  $R_{\text{H}_2 \dots \text{H}} = 6.442$  bohr, for which an initial basis set was generated using the optimized fragment initialization (Section 2.1) and the representation was improved through several Powell refinement [30] cycles of the non-linear parameters (Fig. 1). Then, initial basis sets were generated by making small  $\Delta R_{\text{H}_2 \dots \text{H}} = \pm 0.1$  bohr displacements, rescaling the centers according to Eq. (14) with Yukawa weights, Eq. (16), followed by 5 entire basis refinement cycles (that took 4 h) before the next step was taken along the series of the nuclear configurations (the positive and the negative displacement series were run in parallel). All computations have been carried out using the QUANTEN computer program [29,38–40].

The energies (Fig. 2) and optimized basis set parameters are deposited in the Supplementary Material.

## 3. Results and discussion

We have carried out extensive single-point computations for the near-equilibrium geometry in the van-der-Waals well with  $R_{\text{H}_2}^{(0)} = 1.4$  bohr and  $R_{\text{H}_2 \dots \text{H}}^{(0)} = 6.442$  bohr first reported in Ref. [24]. This structure is close to

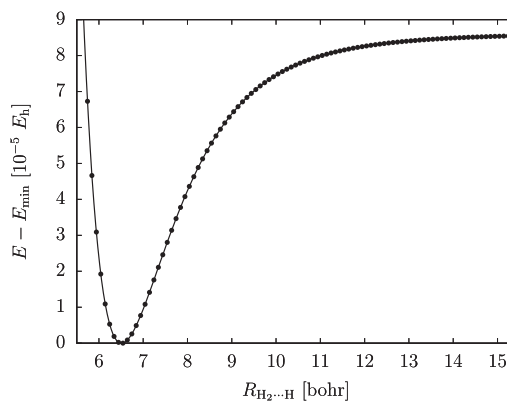


Fig. 2. Potential energy cut of the H<sub>3</sub> system converged in the present work with an estimated sub-ppm precision. Along the curve, the geometry of the H<sub>2</sub> unit is fixed at  $R_{\text{H}_2} = 1.4$  bohr. The lowest-energy datapoint corresponds to  $E_{\text{min}} = -1.674\,561\,899 E_h$  and  $R_{\text{min}} = 6.542$  bohr.

the equilibrium geometry obtained with carefully conducted orbital-based computations [22] (Table 2). The energy of Ref. [24] computed with a small ECG basis is inaccurate, but later, large-scale computations were reported in Ref. [25].

At this geometry, the best energy obtained from the present work with 1200 ECGs (constructed by the initial fragment initialization, Section 2.1, followed by  $n_{\text{Powell}} = 3000$  Powell refinement cycles of the entire basis set) is  $-1.674561687 E_h$  (upper part of Table 1). Table 1 also shows the computed energy values for smaller basis sets that allow assessment of the convergence and extrapolation to the complete basis set (CBS) limit [41].

Direct comparison with Ref. [25] requires further computation, because the extensively optimized energy reported in Ref. [25] appears to belong to a 6.442 bohr distance of the hydrogen atom not from the center of nuclear mass of the  $H_2$  unit, but from the closer proton of  $H_2$ . We think that this nuclear structure was used in Ref. [25], because we obtain good agreement for the energies when we perform the computation at this geometry, shown in the lower part of Table 1, corresponding to  $R_{H_2}^{(0)} = 1.40$  bohr and  $R_{H_2 \dots H} = R_{H_2 \dots H}^{(0)} + R_{H_2}^{(0)}/2 = 6.442$  bohr + 0.700 bohr = 7.142 bohr.

We also note that the best energy value of Ref. [25] computed in 6 months (using 12 CPU cores) was reproduced in this work (corresponding to the structure given in footnote <sup>b</sup> of Table 1) using the optimized fragment initialization technique (Section 2.1) followed by a few Powell refinement cycles in 4 days. The computational benefit of the optimized fragment technique is significant in comparison with a computation [25] constructed from ‘scratch’ immediately for the three-particle problem.

Then, we continued the extensive refinement of the basis parameterization based on the variational principle, and the best result after 3 months computation (using 12 CPU cores) is reported in Table 1. The generation of the points along the PEC was started from this well-optimized parameterization by  $\Delta R_{H_2 \dots H} = \pm 0.1$  bohr increments/decrements (running in parallel) using the rescaling technique (Section 2.1), followed by 5 Powell refinement cycles at every step (before the next step was taken). The entire PEC generation took 13 days using 12 CPU cores.

Finally, it is relevant to compare the ECG energies with the best orbital-based results underlying the CCI PES. For this reason, we have used a single rescaling step from the starting optimized parameterization (upper part of Table 1) to the  $R_{H_2}^{(0)} = 1.4$  bohr and  $R_{H_2 \dots H}^{(0)} = 6.51205$  bohr structure, which was determined to be the global minimum

**Table 1**

Convergence of the non-relativistic, ground-state energy of  $H_3$  near the van-der-Waals equilibrium structure at  $R_{H_2} = 1.4$  bohr and  $R_{H_2 \dots H} = 6.442$  bohr taken from Ref. [24].

$N_b$	Ansatz	$n_{\text{Powell}}$	$E [E_h]$
$R_{H_2} = 1.40$ bohr, $R_{H_2 \dots H} = 6.442$ bohr : <sup>a</sup>			
600	$\{\psi_{10n+i}^{H_2}, \psi_i^{H_1}\}$	2000	-1.674 560 470
800	$\{\psi_{10n+i}^{H_2}, \psi_i^{H_1}\}$	2000	-1.674 561 379
1000	$\{\psi_{10n+i}^{H_2}, \psi_i^{H_1}\}$	2000	-1.674 561 583
1200	$\{\psi_{10n+i}^{H_2}, \psi_i^{H_1}\}$	3000	-1.674 561 687
[Extrapolation to $N_b \rightarrow \infty$ :			-1.674 561 75(3)]
$R_{H_2} = 1.40$ bohr, $R_{H_2 \dots H} = 7.142$ bohr : <sup>b</sup>			
1000	Ref. [25] <sup>c</sup>		-1.674 547 421 00
1200	$\{\psi_{10n+i}^{H_2}, \psi_i^{H_1}\}$	3000	-1.674 547 750

<sup>a</sup>  $R_{H_2} = 1.4$  bohr,  $R_{H_2 \dots H} = 6.442$  bohr, measured from the nuclear center of mass (NCM) of the  $H_2$  unit.

<sup>b</sup>  $R_{H_2} = 1.4$  bohr,  $R_{H_2 \dots H} = 7.142$  bohr (measured from the NCM of the  $H_2$  unit), and corresponds to a 6.442 bohr distance measured from the nearer proton in the  $H_2$  unit.

<sup>c</sup> Geometry <sup>a</sup> is claimed in Ref. [25], but it appears to be <sup>b</sup>. The difference amounts to whether the distance of the hydrogen atom is measured from the NCM or the nearer proton.

structure at the MRCI/aug-cc-pV6Z level [22]. The parameter rescaling, with a negligible computational cost, was followed by 5 Powell refinement cycles that took 4 h. Table 2 shows the energy values reported for the MRCI computations corresponding to the aug-cc-pVXZ ( $X = D, T, Q, 5, 6$ ) and the ‘modified’ correlation consistent aug-mcc-pVXZ ( $X = D, T, Q, 5, 6, 7$ ) basis sets [22,19]. The ECG energy is already  $74 \mu E_h$  lower, than the best MRCI value corresponding to the largest (aug-mcc-pV7Z) basis set. Furthermore, we can confirm the estimated  $\mu E_h$  precision of the CBS extrapolated energy from the mcc basis, whereas the extrapolated energy based on the regular correlation consistent basis is slightly lower than our current best estimate [22].

#### 4. Summary, conclusion, and outlook

In summary, we have computed a benchmark-quality one-dimensional segment of the Born–Oppenheimer potential energy surface of the  $H_3$  system for a series of collinear nuclear configurations. The electronic energies are estimated to be converged on the sub-parts-per-million level.

The depth of the van-der-Waals well was predicted to be  $86(1)\mu E_h$  at the  $R_{H_2} = 1.4015$  bohr and  $R_{H_2 \dots H} = 6.51205$  bohr geometry in MRCI computations underlying the currently most precise potential energy surface of  $H_3$  [22]. The variational computations reported in this work and using a (relatively small) explicitly correlated Gaussian basis set confirm this value and improve upon its precision by two orders of magnitude,  $86.54(3)\mu E_h$ . In order to achieve a similar precision for non-collinear nuclear structures, which have a lower order or no point-group symmetry, it will be necessary to use a larger basis set, which is certainly feasible.

Regarding the broader context of this work, (non-) adiabatic perturbation theory [42–46] combined with leading-order relativistic and quantum electrodynamics (QED) corrections [47,48] are expected to provide a state-of-the-art theoretical description for this system. This framework has already been extensively used and tested for the lightest diatomic molecules [49,40]. For the ground-electronic state of the  $H_2$  molecule, the effect of the non-adiabatic-relativistic coupling has also been evaluated and was found to be non-negligible [50]. In this direction, the computation of a precise representation of the electronic wave function is a necessary first step that was demonstrated in this work to be feasible. The adiabatic [51,52], non-adiabatic and (regularized) relativistic and QED corrections can be evaluated at a couple of points using currently existing procedures [46,53,40,54]. At the same time, for a

**Table 2**

Comparison of energies of various *ab initio* computations. The equilibrium geometry, determined at the MRCI/aug-cc-pV6Z is  $R_{H_2} = 1.4015$  bohr and  $R_{H_2 \dots H} = 6.51205$  bohr [22].

Source	$E [E_h]$
aug-cc-pVDZ <sup>a</sup>	-1.664 339
aug-cc-pVTZ <sup>a</sup>	-1.672 540
aug-cc-pVQZ <sup>a</sup>	-1.673 902
aug-cc-pV5Z <sup>a</sup>	-1.674 332
aug-cc-pV6Z <sup>a</sup>	-1.674 445
aug-mcc-pVTZ <sup>a</sup>	-1.672 553
aug-mcc-pVQZ <sup>a</sup>	-1.673 917
aug-mcc-pV5Z <sup>a</sup>	-1.674 298
aug-mcc-pV6Z <sup>a</sup>	-1.674 430
aug-mcc-pV7Z <sup>a</sup>	-1.674 488
MBE <sup>cc</sup> (3,4 CBS) <sup>b</sup>	-1.674 566
MBE <sup>mcc</sup> (6,7 CBS) <sup>c</sup>	-1.674 562
Present work ( $N_b = 1200$ ) <sup>d</sup>	-1.674 562 264

<sup>b, c</sup> Ref. [22]: extrapolated CBS energy corresponding to the aug-cc-pVXZ ( $X = 3, 4$ ) and aug-mcc-pVXZ ( $X = 6, 7$ ) basis sets, respectively.

<sup>a</sup> Ref. [22]: MRCI energy.

<sup>d</sup> Rescaled from the basis set optimized for the  $(R_{H_2}^{(0)}, R_{H_2 \dots H}^{(0)})$  structure in Table 1 followed by 1000 Powell refinement cycles.

complete description of a polyatomic system like  $H_3$ , these corrections must be computed over hundreds or thousands of nuclear configurations. This requires a fully automated evaluation and error control of all corrections, which may be especially challenging for the singular terms in the relativistic and QED expressions, and this requires further methodological and algorithmic developments that is left for future work.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cplett.2022.139734>.

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