# Solving the Schrödinger equation of a planar model $\mathrm{H}_{4}$ molecule 

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#### Abstract

The Schrödinger equation of a planar model $\mathrm{H}_{4}$ molecule was solved with the free complement (FC) - local Schrödinger equation (LSE) theory using the direct local sampling (DLS) method. Although this molecule is often used to examine the intrinsic weakness of the Hartree-Fock related theory, the present FC-LSE-DLS theory successfully produced accurate solutions of the Schrödinger equation at any geometries of this molecule. We mapped the two-dimensional potential energy surfaces and revealed that the ground state has a dissociation channel to a couple of $\mathrm{H}_{2}$ molecules but the two excited states have local minimums constructing $\mathrm{H}_{4}$ molecule.


## 1. Introduction

$\mathrm{H}_{4}$ molecule is a simple four-electron system but such hydrogen clusters and related compounds are key molecules in astrochemistry for the material composition in interstellar clouds [1-9]. The quan-tum-mechanical potential energy surfaces (PES) of not only the ground but also excited states of these molecules should be significant for understanding the hydrogen-reaction chemistry in space.

In quantum chemistry, $\mathrm{H}_{4}$ molecule has been often used to examine new developing theories since this is a simple 4-electron system but includes the strong especially static electron correlations. The HartreeFock based molecular orbital (MO) theory has the intrinsic weakness for this molecule and most of the single-reference theories break down for this simple system due to its strong diradical characters. For doing precise computations of this molecule, several interesting new-type theories different from the conventional quantum chemistry were proposed [10-22]. For instance, whereas ordinary nonvariational coupledcluster theories produce unphysical behaviours in the PES (see Sec. III), Paldus, Piecuch et al. [12] reported the Hilbert-space coupled-cluster theory and Voorhis and Head-Gordon [15] examined the variational coupled-cluster theory compared with the full configuration interaction (CI) method. Recently, Genovese, Meninno and Sorella performed accurate calculations by the Jastrow antisymmetrized geminal power (JAGP) method [19] and produced very precise total energies. Since these reference data are informative and intelligible, we employed them to compare the accuracies with the present results. Further, several newtype theories were also applied to this molecule; a neural-network approach FermiNet [20], the exact two-body expansion by a reduced
density matrix analog [21], the variational quantum eigensolver - unitary coupled-cluster theory for quantum computer [22], etc.

In this paper we study the $\mathrm{H}_{4}$ molecule with the free complement (FC) - local Schrödinger equation (LSE) - direct local sampling (DLS) theory. First, the FC-LSE-DLS theory must be explained. The free complement (FC) theory is the theory for solving exactly the Schrödinger equation (SE) of atoms and molecules published in 2004 [23,24]. The FC theory is based on the following intermediate equation at order $n$,

$$
\begin{equation*}
\psi_{n+1}=\left[1+C_{n} g\left(H-E_{n}\right)\right] \psi_{n} \tag{1}
\end{equation*}
$$

that leads to the exact solution of the $\mathrm{SE} \psi$ from some approximate wave function $\psi_{0}$. In Eq. (1), $H$ is the Hamiltonian of the system of interest and $g$ is the scaling function of the Scaled Schrödinger equation (SSE) that was introduced to improve the divergence defect of the original SE for the exact variational problem [23]. Eq. (1) can be transformed by extracting the elemental analytical functions $\left\{\phi_{I}\right\}$ as,
$\psi=\sum_{I} c_{I} \phi_{I}$
where $\phi_{I}$ is referred to as a complement (complete element) function. This theory is an exact theory that is different from the conventional quantum chemistry theories. This theory has been developed in several different ways and applied to many basic problems [23-40]. By giving more variational freedoms in Eq. (2) than in Eq. (1), one can efficiently obtain the rapid convergences. To calculate the variables $\left\{c_{I}\right\}$ in Eq. (2), the first choice is to use the variational method with analytical integrations [25,27,34-37]. In the variational framework, very precise calculations were performed for small systems [25,27,34] and the

[^0]variational $s_{i j}$ [36] and $s_{i j}$-assisted $r_{i j}$ theories [37] were also proposed for more general atoms and molecules by relaxing the integration difficulties. When the integral evaluation is impossible, an alternative choice was given as the sampling-based LSE theory $[26,30]$ which is integralfree and applicable to any systems and functions in principle. We proposed this theory to determine the FC wave function that is potentially exact. The LSE theory is similar in spirit to the least-squares local-energy method considered by Frost many years ago [41]. It also has some similarity to the pseudospectral or collocation methods [42-44] that were used for other purposes.

We have applied the FC-LSE theory to first-row atoms and several small organic and inorganic molecules and obtained highly accurate solutions [32,33]. There, we used the efficient antisymmetrization algorithm [29] and also proposed the inter-exchange theory [31] that realizes an order- $N$ theory for big systems. Recently, we introduced the chemical formula theory to construct the cf's according to the chemical locality [32] and the generalized scaling functions to accelerate the convergence to the exact solutions [38]. We also introduced the DLS method based on the inverse transformation method [39,40], which enabled to make the sampling distributions rationally according to a given density function without using the Metropolis algorithm [45,46]. Recently, the FC-LSE-DLS theory was satisfactorily applied to calculate the potential curves of the nine valence states of the $\mathrm{Li}_{2}$ molecule in a Schrödinger-level accuracy [40], giving absolute agreements with the experimental Rydberg-Klein-Rees (RKR) potential energy curves available [47-49].

The purpose of the present letter is to solve the SE of a $\mathrm{H}_{4}$ molecular system accurately with the FC-LSE-DLS theory and examine its intrinsic theoretical ability. In Sec. II, we specify the calculations of the FC-LSE-
given in Sec. IV.

## 2. FC-LSE-DLS calculations of a $\mathrm{H}_{4}$ molecule

In the present study, we employed the model planar geometries with the restrictions of square or rectangle. Fig. 1 shows their definitions. The coordinates of Fig. 1a are taken from Ref. [15], where $R$ is defined as the distance between the center of quadrangle and each hydrogen and $\theta$ is the angle of two diagonal lines. The coordinates of Fig. 1b are taken from Ref. [19], where $R_{x}$ and $R_{y}$ are defined as simple horizontal $x$ and vertical $y$ lengths between two hydrogen atoms. Corresponding to these geometries, we first prepared a set of initial functions for progressing the FC theory for the totally spatial symmetric singlet states, given by

$$
\begin{align*}
& \psi_{0}^{(\mathrm{Cov}, 1)}=A\left[\left(H_{1 s, A} H_{1 s, B}\right)(\alpha \beta-\beta \alpha) \cdot\left(H_{1 s, C} H_{1 s, D}\right)(\alpha \beta-\beta \alpha)\right] \\
& \psi_{0}^{(\mathrm{Cov}, 2)}=A\left[\left(H_{1 s, A} H_{1 s, C}\right)(\alpha \beta-\beta \alpha) \cdot\left(H_{1 s, B} H_{1 s, D}\right)(\alpha \beta-\beta \alpha)\right] \\
& \psi_{0}^{(\mathrm{Ion}, 1)}=A\left[\left(H_{1 s, A} H_{1 s, A}\right) \alpha \beta \cdot\left(H_{1 s, C} H_{1 s, D}\right)(\alpha \beta-\beta \alpha)\right]+(\text { symmetrized }) \\
& \psi_{0}^{(\mathrm{Ion}, 2)}=A\left[\left(H_{1 s, A} H_{1 s, A}\right) \alpha \beta \cdot\left(H_{1 s, B} H_{1 s, D}\right)(\alpha \beta-\beta \alpha)\right]+(\text { symmetrized }) \\
& \psi_{0}^{(\operatorname{Cov}(2 s), 1)}=A\left[\left(H_{1 s, A} H_{2 s, B}\right)(\alpha \beta-\beta \alpha) \cdot\left(H_{1 s, C} H_{1 s, D}\right)(\alpha \beta-\beta \alpha)\right]+(\text { symmetrized }) \\
& \psi_{0}^{(\mathrm{Cov}(2 s), 2)}=A\left[\left(H_{1 s, A} H_{2 s, C}\right)(\alpha \beta-\beta \alpha) \cdot\left(H_{1 s, B} H_{1 s, D}\right)(\alpha \beta-\beta \alpha)\right]+(\text { symmetrized }) \tag{3}
\end{align*}
$$

where $A$ denotes the four-electron antisymmetrizer and $\alpha$ and $\beta$ denote the spin coordinates. '(symmetrized)' represents the additional terms to satisfy the spatial symmetries: $\mathrm{A}_{1 \mathrm{~g}}$ in $\mathrm{D}_{4 \mathrm{~h}}$ for the square geometries and $A_{g}$ in $D_{2 h}$ for the rectangle geometries. We employed the simplest hydrogen-type 1 s and 2 s atomic orbitals for each center, given by
$H_{1 s, A}=\exp \left(-\alpha_{1 s} r_{A}\right), \quad H_{1 s, B}=\exp \left(-\alpha_{1 s} r_{B}\right), \quad H_{1 s, C}=\exp \left(-\alpha_{1 s} r_{C}\right), \quad H_{1 s, D}=\exp \left(-\alpha_{1 s} r_{D}\right)$
$H_{2 s, A}=r_{A} \exp \left(-\alpha_{2 s} r_{A}\right), \quad H_{2 s, B}=r_{B} \exp \left(-\alpha_{2 s} r_{B}\right), \quad H_{2 s, C}=r_{C} \exp \left(-\alpha_{2 s} r_{C}\right), \quad H_{2 s, D}=r_{D} \exp \left(-\alpha_{2 s} r_{D}\right)$

DLS theory for the present $\mathrm{H}_{4}$ molecule. We employ the local-based wave function according to the chemical formula theory [32] different from a molecular-orbital-based delocalized picture. In Sec. III, we first examine the accuracies of the present FC-LSE-DLS calculations by comparing with the reference data. We further calculate the twodimensional (2D) PES of the ground and two totally symmetric singlet excited states in the square and rectangle planar geometries. These are model geometries but the computed results might be useful for understanding hydrogen-cluster chemistry. Lastly, the concluding remarks are
(a)

(b)


Fig. 1. Definitions of the coordinates of square and rectangle model geometries in the present study of a $\mathrm{H}_{4}$ molecule. The coordinates of (a) are taken from Ref. [15], where $R$ is defined as the distance between the center of quadrangle and each hydrogen and $\theta$ is the angle of two diagonal lines. The coordinates of (b) are from Ref. [19], where $R_{x}$ and $R_{y}$ are defined as simple horizontal $\times$ and vertical $y$ lengths between two hydrogen atoms.
with $\alpha_{1 \mathrm{~s}}=1.0$ and $\alpha_{2 \mathrm{~s}}=0.5$. In Eq. (3), $\psi_{0}^{(\mathrm{Cov}, 1)}$ and $\psi_{0}^{(\mathrm{Cov}, 2)}$ show a couple of independent covalent terms with different singlet couplings. $\psi_{0}^{(\text {Ion,1) }}$ and $\psi_{0}^{(\text {Ion,2) }}$ represent the ionic contributions corresponding to $\psi_{0}^{(\operatorname{Cov}, 1)}$ and $\psi_{0}^{(\operatorname{Cov}, 2)}$, respectively. $\psi_{0}^{(\operatorname{Cov}(2 \mathrm{~s}), 1)}$ and $\psi_{0}^{(\operatorname{Cov}(2 \mathrm{~s}), 2)}$ are introduced to describe the PES for the excited states accurately. Thus, different from an ordinary MO theory, we employed the local-picture initial functions according to the chemical formula theory proposed before [32]. These guarantee the dissociation limits of four hydrogen atoms and are suitable for describing the PES and chemical reactions. We use the same form of the initial functions given by Eq. (3) for all the present calculations at all the adopted geometries.

We employed the scaling functions in the scaled SE [23,24,38], given by
$g_{i A}=r_{i A} \quad$ and $\quad g_{i j}=\operatorname{Ei}\left(-\gamma_{1} r_{i j}-\gamma_{2}\right)-\operatorname{Ei}\left(-\gamma_{2}\right)$
for the electron-nucleus and electron-electron cases, respectively, where $r_{i A}$ denotes the distance between electron $i$ and nucleus $A$ and $r_{i j}$ between electrons $i$ and $j$. In Eq. (5), we used the parameters: $\gamma_{1}=$ 0.00121 and $\gamma_{2}=0.000238$ which were the roughly optimized values for a helium atom in Ref. [38].

Starting from this set of the initial functions and the scaling functions, the FC theory was applied up to order $n$ and collected the cf's whose number is denoted as dimension $M$. By the FC theory, so-called inter terms: one-electron $r_{i_{A} B}$ terms and two-electron $r_{i_{A} j_{B}}$ terms are naturally generated, where $i_{A}$ represents the electron $i$ belongs to the center $A$ of the Slater orbital in Eq. (4). Therefore, $r_{i_{A} B}$ represents the
distance from the electron $i_{A}$ to another atom $B$ and $r_{i_{A} j_{B}}$ represents the electron-electron distance whose two electrons belong to different centers. The former works as a kind of polarization and also for the improvement of the coalescence condition at another atomic center. The latter also works for describing the polarization and the electro-n-electron correlations in the chemical bond. The former is a oneelectron function but out of common in ordinary quantum chemistry. The FC theory, however, generates them from the theoretical point of view and implies their importance in the exact-level solutions. After generating cf's, their unknown variables were calculated by the HS method of the LSE theory [30].

The sampling points were produced by the recently developed DLS method [39]. We employed a $N$-electron density $\Gamma^{(N)}=\psi_{0}^{2}$ of the ground state with $9 \times 10^{6}$ sampling points at each molecular geometry. The coordinates of each electron were distributed by the conditional probability of $\Gamma^{(N)}$. As a result, most probability was found that each electron equally located on each atom one by one due to the locality and Pauli's exclusion principle. For any geometry in the present study, the sampling points are constructed in the same style and this enables to compute the smooth PES in spite of a sampling-type procedure.

## 3. Results and discussions

### 3.1. Examination of the accuracies of the FC-LSE-DLS calculations

We first performed the FC-LSE-DLS calculations up to order $n=3$ with dimension $M=8497$. at the geometries defined in Fig. 1a with the fixed $R=3.2843$ a.u. $(=1.70 \AA$ ) and changing $\theta$ from 70 to 110 degree (70-90 and 90-110 are symmetric each other). The results for the
ground state are summarized in Table 1 with the absolute total energies and H-square errors defined by $\langle\psi|(H-E)^{2}|\psi\rangle$. The H -square error is a good measure of the exactness of the wave function [30]: if this quantity is zero for any set of sampling points, the wave function is exact as the solution of the Schrödinger equation. Table 1 also summarizes the reference data for comparison: the full CI results of the double-zeta plus polarization (DZP) Gaussian basis by Voorhis and Head-Gordon [15] and the Hartree-Fock, non-variational coupled-cluster singles and doubles (CCSD), and full CI results of the large Slater-type CVB2 basis calculated by the MOLPRO program package [50]. Fig. 2 shows the plots of these energies with respect to the angle $\theta$. As shown in Table 1, the Hsquare errors were very small less than 0.00003 for all of $\theta$. It implies that the calculated results were sufficiently highly accurate and in the essentially exact level. In the reference calculations, the single-reference MO theories failed even with the present simple 4-electron system due to the large error for describing the static electron correlation. For instance, the potential energy curve of the Hartree-Fock theory with CVB2 basis set was considerably high and had a strange cusp at $\theta=90$ degree. Such a discontinuity of the first derivative in the potential energy curve should never be seen in the nature. Thus, the Hartree-Fock theory breaks down and its wave function does not work as a good reference for the successive correlated theories. Actually, the potential energy curve of the HF-CCSD theory with CVB2 basis showed an unphysical lower energy region and also a strange cusp around $\theta=90$ degree, which reflects the fault of the Hartree-Fock wave function. On the other hand, the full CI results were reasonable but their total energies with DZP basis were much higher than those of our calculations, though those of the full CI with CVB2 basis were much improved. Table 1 also shows the energy differences $\Delta E$ between the full-CI (CVB2)

Table 1
FC-LSE-DLS calculations of a $\mathrm{H}_{4}$ molecule with the FC order $n=3$ and dimension $M=8497$ at the geometries defined in Fig. 1a with the fixed $R=3.2843$ a.u. and changing $\theta$ from 90 to 70 degree, compared with the reference data of the full CI method with DZP basis set by Ref. [15] and the Hartree-Fock, CCSD, and full CI methods with CVB2 basis set. The results at $\theta$ from 90 to 110 degree are symmetrically same as those at $\theta$ from 90 to 70 degree.

| $\theta$ (degree) | FC-LSE |  | Full CI(DZP) [15] | Hartree-Fock (CVB2) | $\begin{aligned} & \text { CCSD } \\ & \text { (CVB2) } \end{aligned}$ | Full CI (CVB2) |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Energy (a.u.) | H-square error | Energy (a.u.) |  |  | Energy (a.u.) | $\Delta E: E_{\text {full CI }}-E_{\mathrm{FC}-L S E-D L S}$ $(\mathrm{kcal} / \mathrm{mol})^{\mathrm{a}}$ |
| 90.0 | $-2.01533880$ | 0.00001449 | -2.001 978 | -1.735 934 | -2.022 071 | -2.014 183 | 0.702 |
| 89.9 | -2.015 35981 | 0.00001931 |  | $-1.736406$ | -2.021 964 | -2.014 184 | 0.694 |
| 89.8 | $-2.01536287$ | 0.00001916 |  | -1.736 879 | -2.021 858 | -2.014 186 | 0.698 |
| 89.7 | -2.015 36744 | 0.00001959 |  | -1.737 353 | -2.021 754 | -2.014 191 | 0.700 |
| 89.6 | -2.015 37551 | 0.00001941 |  | -1.737828 | -2.021 651 | -2.014 197 | 0.705 |
| 89.5 | -2.015 38419 | 0.00001892 | -2.001 998 | -1.738 303 | -2.021 550 | -2.014 205 | 0.707 |
| 89.3 | $-2.01540660$ | 0.00001860 |  | $-1.739255$ | -2.021 354 | -2.014 227 | 0.708 |
| 89.0 | -2.015 45362 | 0.00001850 | -2.002 057 | -1.740 688 | -2.021 073 | -2.014 273 | 0.705 |
| 88.5 | -2.015 57306 | 0.00001813 |  | -1.743 090 | -2.020 641 | -2.014 385 | 0.708 |
| 88.0 | -2.015 73733 | 0.00001890 | -2.002 291 | -1.745 510 | -2.020 258 | -2.014 541 | 0.710 |
| 87.5 | -2.015 93862 | 0.00001923 |  | -1.747948 | -2.019 925 | -2.014 739 | 0.712 |
| 87.0 | -2.016 18542 | 0.00001964 |  | -1.750 405 | -2.019 647 | -2.014 979 | 0.714 |
| 86.5 | -2.016 47388 | 0.00001877 |  | -1.752882 | -2.019 426 | -2.015 257 | 0.715 |
| 86.0 | -2.016 79971 | 0.00001876 |  | -1.755 378 | -2.019 264 | -2.015 574 | 0.727 |
| 85.5 | -2.017 16346 | 0.00001965 |  | -1.757895 | -2.019 163 | -2.015 928 | 0.720 |
| 85.0 | -2.017 56133 | 0.00001999 | -2.003 838 | $-1.760433$ | -2.019 125 | -2.016 317 | 0.737 |
| 84.0 | -2.018 45835 | 0.00002274 |  | $-1.765573$ | -2.019 242 | -2.017 195 | 0.787 |
| 83.0 | -2.019 48706 | 0.00002375 |  | -1.770 803 | -2.019 615 | -2.018 199 | 0.781 |
| 82.0 | -2.020 63783 | 0.00002474 |  | $-1.776128$ | -2.020 235 | -2.019 325 | 0.810 |
| 81.0 | -2.021 91138 | 0.00002261 |  | -1.781552 | -2.021 087 | -2.020 568 | 0.823 |
| 80.0 | -2.023 26096 | 0.00001701 | -2.008 733 | -1.787 078 | -2.022 151 | -2.021 927 | 0.843 |
| 79.0 | -2.024 80923 | 0.00002285 |  | -1.792711 | -2.023 410 | -2.023 401 | 0.864 |
| 78.0 | $-2.02643160$ | 0.00002423 |  | -1.798 455 | -2.024 848 | -2.024 993 | 0.879 |
| 77.0 | -2.028 18659 | 0.00002440 |  | -1.804 315 | -2.026 453 | -2.026 706 | 0.906 |
| 76.0 | -2.030 06588 | 0.00002460 |  | -1.810 293 | -2.028 216 | -2.028 543 | 0.937 |
| 75.0 | -2.032 06863 | 0.00002529 |  | -1.816 395 | -2.030 135 | -2.030 510 | 0.962 |
| 74.0 | -2.034 21789 | 0.00002710 |  | -1.822 624 | -2.032 207 | -2.032 611 | 0.984 |
| 73.0 | -2.036 49744 | 0.00002787 |  | -1.828 985 | -2.034 433 | -2.034 854 | 1.005 |
| 72.0 | -2.038 93767 | 0.00002835 |  | -1.835 481 | -2.036 816 | -2.037 245 | 1.044 |
| 71.0 | -2.041 52797 | 0.00002597 |  | -1.842 117 | -2.039 361 | -2.039 790 | 1.072 |
| 70.0 | -2.044 25744 | 0.00002241 | -2.029 083 | -1.848896 | -2.042 073 | -2.042 497 | 1.086 |

[^1]

Fig. 2. Potential energy curves of the FC-LSE-DLS calculations of a $\mathrm{H}_{4}$ molecule with the FC order $n=3$ and dimension $M=8497$ at the geometries defined in Fig. 1 a with the fixed $R=3.2843 \mathrm{a} . \mathrm{u}$. and changing $\theta$ from 70 to 110 degree. Those of the reference calculations are also plotted for comparison. The left graph is large scaling and the right is enlarged drawing.
and the FC-LSE-DLS. $\Delta E$ were always positive, i.e. the full-CI (CVB2) total energies were still higher than our results. At $\theta=90$ degree, the energy of full-CI (CVB2) was $\Delta E=0.702 \mathrm{kcal} / \mathrm{mol}$ higher than that of the FC-LSE-DLS, but $\Delta E$ became large as decreasing $\theta$ and became 1.086 $\mathrm{kcal} / \mathrm{mol}$ at $\theta=70$ degree. This implies that even the full CI method with quite large basis set cannot always describe the correct shape of the potential energy curve. The full CI method is exact when the basis set space is complete, but there is no systematic way to approach to the exact. On the other hand, the FC-LSE-DLS theory was successful to provide essentially exact results with accurate and smooth potential energy curves at any geometry of $\theta$.

We next compared the present calculations with other recent accurate calculations of the JAGP method by Genovese, Meninno and Sorella [19]. They employed the geometries defined in Fig. 1b. They provided the total energies by the JAGP method compared with the complete active space ( $\operatorname{CAS}(4,4)$ ) and full CI results with the fixed $R_{y}=2.4$ a.u. and changing several $R_{x}$. We performed the FC-LSE-DLS calculations at the same geometries to check the convergences at the FC orders $n=0$ to 3 with dimensions $M=6,96,1064$, and 8497 , respectively, and the results are summarized in Table 2 and the reference data are given in Table 3. In Tables 2 and 3, the energy differences from the most accurate energies by the FC-LSE-DLS of $n=3$ were denoted as $\Delta E$ at each geometry. At all the geometry, as increasing the order $n$, both total energies and H -square errors converged rapidly and smoothly. The energies of the FC-LSE-DLS theory at $n=3$ were lowest and best among any reference values. For instance, at $R_{x}=2.4$, the energy and H-square error of the FC-LSE-DLS theory at $n=3$ were -2.11317123 a.u. and 0.00046588 , whose energies by JAGP(cc-pVTZ) and JAGP were $-2.1084 \pm 0.0003$ and $-2.1125 \pm 0.0002$ and $\Delta E$ were 2.994 and $0.421 \mathrm{kcal} / \mathrm{mol}$ higher, respectively. The latter method was also very accurate but the FC-LSE-DLS energies were further lower than them and our results were always accurate regardless of the geometries. Moreover, due to the local picture of the wave functions, the freedom (dimension) to achieve these accurate solutions was not so large even compared to other references and, if one applies the cf selection scheme etc. [36,37], more compact and understandable wave function would be constructed without loos of accuracy.
3.2. $2 D$ potential energy surfaces of the ground and excited states on the restriction of the model planar square or rectangle geometries

Next, we computed the 2D potential energy surfaces by the FC-LSEDLS theory at $n=3$ with $M=8497$ in the model planar geometry assumed the square or rectangle restrictions for the ground and two totally symmetric singlet excited states. Figs. 3 to 5 show the PES for these states, respectively, to the $R_{x}$ and $R_{y}$ coordinates defined in Fig. 1b with coloured contour graphs. In Fig. 3 for the ground state, the rightupper position represents four dissociated ground-state $\mathrm{H}(1 \mathrm{~s})$ atoms, whose total energy is $(-0.5) \times 4=-2.0$ a.u. In the ground sate, two hydrogen molecules: $2 \mathrm{H}_{2}$ are constructed as the lowest energy pass. Thus, a molecular $\mathrm{H}_{4}$ is not formed at least with the present model geometries. In Fig. 4 for the first excited state, the right-upper position is same as the ground state, i.e. $4 \mathrm{H}(1 \mathrm{~s})$. In this state, there was an energy minimum constructing a molecular $\mathrm{H}_{4}$ at the square geometry: $R_{x}=R_{y}$ $=2.22596$ a.u. with the energy: -2.04195883 a.u., whose minimum position was computed using the 2D spline interpolation from the calculated discrete PES. This minimum was $26.3 \mathrm{kcal} / \mathrm{mol}$ more stable than the dissociated four $\mathrm{H}(1 \mathrm{~s})$ atoms, but $192.64 \mathrm{kcal} / \mathrm{mol}$ less stable than the two $\mathrm{H}_{2}$ molecules. Thus, if the system absorbs the light and is excited to this state, an $\mathrm{H}_{4}$ excited-state molecule is weakly constructed and then two $\mathrm{H}_{2}$ molecules are formed after the detransition to the ground state. In Fig. 5 for the second excited state, the right-upper position shows the dissociation of $3 \mathrm{H}(1 \mathrm{~s})+\mathrm{H}(2 \mathrm{~s})$, i.e. one of the four hydrogen atoms becomes the $2 s$ excited state, whose total energy is $(-0.5) \times 3+(-0.125)=-1.625$ a.u. The PES of this state has a complicated shape because of several state repulsions. Interestingly, there were the local minimums at the rectangle (symmetry-broken) geometry, $R_{x}=$ 1.84196 and $R_{y}=2.54364$ a.u. and vice versa with the energy: -1.888 09529 a.u., whose minimum position was also obtained using the 2D spline interpolation. This local minimum is $165.09 \mathrm{kcal} / \mathrm{mol}$ lower than the dissociated $3 \mathrm{H}(1 \mathrm{~s})+\mathrm{H}(2 \mathrm{~s})$ state. The global minimum pass, however, was to generate two $\mathrm{H}_{2}$ molecules, which should be one in the ground state: $\mathrm{H}(1 \mathrm{~s})-\mathrm{H}(1 \mathrm{~s})$ but the other in the excited state: $\mathrm{H}(1 \mathrm{~s})-\mathrm{H}(2 \mathrm{~s})$.
Table 2
 the FC-LSE-DLS theory at $n=3 ; E_{\text {target }}-E_{\text {FC-LSE-DLS }(n=3)}$.

| $R_{x}$ (a.u.) | $n=0, M=6$ |  |  | $n=1, M=96$ |  |  | $n=2, M=1064$ |  |  | $n=3, M=8497$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Energy (a.u.) | $\Delta E(\mathrm{kcal} / \mathrm{mol})$ | H-square error | Energy (a.u.) | $\Delta E(\mathrm{kcal} / \mathrm{mol})$ | H -square error | Energy (a.u.) | $\Delta E(\mathrm{kcal} / \mathrm{mol})$ | H -square error | Energy (a.u.) | H-square error |
| 1.8 | -2.103 56425 | 59.925 | 0.33667413 | -2.179 21484 | 12.453 | 0.16589359 | -2.197 70240 | 0.852 | 0.01561630 | -2.199 06070 | 0.00078470 |
| 2.188 | -2.059 97505 | 44.850 | 0.24485555 | -2.114 93643 | 10.361 | 0.13743012 | -2.130 45050 | 0.626 | 0.01202738 | -2.13144800 | 0.00059514 |
| 2.4 | -2.053 86012 | 37.218 | 0.19551245 | -2.097 69290 | 9.713 | 0.11362179 | -2.112 01599 | 0.725 | 0.00924674 | -2.113 17123 | 0.00046588 |
| 2.646 | -2.072 64212 | 33.858 | 0.18517730 | -2.114 45659 | 7.619 | 0.12168011 | -2.125 58869 | 0.634 | 0.01094133 | -2.126 59848 | 0.00040550 |
| 3.0 | -2.109 58612 | 28.367 | 0.18473897 | -2.146866 36 | 4.974 | 0.17016377 | -2.153 99237 | 0.502 | 0.01554597 | -2.154 79245 | 0.00032409 |

Table 3



| $R_{x}$ (a.u.) | FC-LSE ( $n=3, M=8497$ ) |  | JAGP(cc-pVTZ) ${ }^{\text {a }}$ |  | JAGP ${ }^{\text {b }}$ |  | CAS $(4,4)^{\text {b }}$ |  | Full CI ${ }^{\text {b }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Energy (a.u.) | H -square error | Energy (a.u.) | $\Delta E(\mathrm{kcal} / \mathrm{mol})$ | Energy (a.u.) | $\Delta E(\mathrm{kcal} / \mathrm{mol})$ | Energy (a.u.) | $\Delta E(\mathrm{kcal} / \mathrm{mol})$ | Energy (a.u.) | $\Delta E(\mathrm{kcal} / \mathrm{mol})$ |
| 1.8 | -2.199 06070 | 0.00078470 | $-2.1953 \pm 0.0003$ | 2.360 |  |  |  |  |  |  |
| 2.188 | -2.131 44800 | 0.00059514 |  |  | $-2.1307 \pm 0.0001$ | 0.469 | $-2.13033 \pm 0.00010$ | 0.702 | -2.129 7 | 1.097 |
| 2.4 | -2.113 17123 | 0.00046588 | $-2.1084 \pm 0.0003$ | 2.994 | $-2.1125 \pm 0.0002$ | 0.421 | $-2.11193 \pm 0.00005$ | 0.779 | -2.1114 | 1.111 |
| 2.646 | -2.126 59848 | 0.00040550 |  |  | $-2.1257 \pm 0.0001$ | 0.564 | $-2.12558 \pm 0.00003$ | 0.639 | -2.124 8 | 1.129 |
| 3.0 | -2.154 79245 | 0.00032409 | $-2.1504 \pm 0.0003$ | 2.756 |  |  |  |  |  |  |

[^2]b See Table 2 of Ref. [19].


Fig. 3. Potential energy surface of the FC-LSE-DLS theory as a colored contour graph for the ground state of a $\mathrm{H}_{4}$ molecule with the FC order $n=3$ and dimension $M=8497$ at the model planar geometry assumed the square or rectangle restrictions.


Fig. 4. Potential energy surface of the FC-LSE-DLS theory as a colored contour graph for the first totally symmetric singlet excited state of a $\mathrm{H}_{4}$ molecule with the FC order $n=3$ and dimension $M=8497$ at the model planar geometry assumed the square or rectangle restrictions.

## 4. Concluding remarks

In the present study, we performed accurate FC-LSE-DLS calculations for the $\mathrm{H}_{4}$ system using the DLS sampling method within the restricted square or rectangular model geometries. We first compared our calculations with the reference data by the Hartree-Fock, CCSD, full CI, CAS, and JAGP methods. Single-reference and/or non-variational theories based on the MO theory failed to describe the present simple fourelectron system due to the strong static electron correlations. On the other hand, the present FC-LSE-DLS calculations were always successful at any geometries without any complexity because of the local descriptions of the wave function based on the chemical formula theory. The obtained ground-state energies were very accurate and lowest among the existing reference data.


Fig. 5. Potential energy surface of the FC-LSE-DLS theory as a colored contour graph for the second totally symmetric singlet excited state of a $\mathrm{H}_{4}$ molecule with the FC order $n=3$ and dimension $M=8497$ at the model planar geometry assumed the square or rectangle restrictions.

We further investigated the 2D PES of the ground and two totally symmetric singlet excited states. On the restricted model planar geometries, the channel of the creation of two $\mathrm{H}_{2}$ molecules was most stable in the ground state, but there were the energy minimums constructing a $\mathrm{H}_{4}$ molecule at the square geometry in the first excited state and the rectangle symmetry-broken geometry in the second excited state. Thus, we are extending the present approach to study other $\mathrm{H}_{\mathrm{n}}$ systems for astronomical interests.

## Data availability

The data that support the findings of this study are available within the article.

## CRediT authorship contribution statement

Hiroyuki Nakashima: Methodology, Software, Validation, Formal analysis, Writing - original draft, Writing - review \& editing, Visualization. Hiroshi Nakatsuji: Methodology, Software, Validation, Formal analysis, Writing - original draft, Writing - review \& editing, Visualization.

## 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.

## Data availability

No data was used for the research described in the article.

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## References

[1] T. Oka, Phys. Rev. Lett. 45 (1980) 531.
[2] T. Oka, Rev. Mod. Phys. 64 (1992) 1141.
[3] B.J. McCall, T.R. Geballe, K.H. Hinkle, T. Oka, Science 279 (1998) 1910.
[4] Y. Morisawa1, M. Fushitani, Y. Kato, H. Hoshina, Z. Simizu, S. Watanabe, Y. Miyamoto, Y. Kasai, K. Kawaguchi, T. Momose, Astrophys. J. 642 (2006) 954.
[5] S. Weinreb, A.H. Barrett, M.L. Meeks, J.C. Henry, Nature 200 (1963) 829.
[6] E. Herbst, W. Klemperer, Astrophys. J. 185 (1973) 505.
[7] T. Hama, N. Watanabe, Chem. Rev. 113 (2013) 8783.
[8] G. Vidali, Chem. Rev. 113 (2013) 8762.
[9] E. Roueff, F. Lique, Chem. Rev. 113 (2013) 8906.
[10] J.B. Anderson, Int. J. Quantum Chem. 15 (1979) 109.
[11] J.P. Finley, R.K. Chaudhuri, K.F. Freed, J. Chem. Phys. 103 (1995) 4990.
[12] J. Paldus, P. Piecuch, L. Pylypow, B. Jeziorski, Phys. Rev. A 47 (1993) 2738.
[13] K. Kowalski, K. Jankowski, Phys. Rev. Lett. 81 (1998) 1195.
[14] K. Jankowski, K. Kowalski, J. Chem. Phys. 111 (1999) 2952.
[15] T.V. Voorhis, M. Head-Gordon, J. Chem. Phys. 113 (2000) 8873.
[16] M. Nakano, T. Minami, H. Fukui, R. Kishi, Y. Shigeta, B. Champagne, J. Chem. Phys. 136 (2012), 024315.
[17] H.G.A. Burton, A.J.W. Thom, J. Chem. Theory Comput. 12 (2016) 167.
[18] K. Gasperich, M. Deible, K.D. Jordan, J. Chem. Phys. 147 (2017), 074106.
[19] C. Genovese, A. Meninno, S. Sorella, J. Chem. Phys. 150 (2019), 084102.
[20] D. Pfau, J.S. Spencer, A.G.D.G. Matthews, W.M.C. Foulkes, Phys. Rev. Res. 2 (2020), 033429.
[21] D.A. Mazziotti, Phys. Rev. A 102 (2020), 030802.
[22] Q. Guo, P. Chen, Front. Phys. 9 (2021), 735321.
[23] H. Nakatsuji, Phys. Rev. Lett. 93 (2004), 030403.
[24] H. Nakatsuji, Phys. Rev. A 72 (2005), 062110.
[25] H. Nakashima, H. Nakatsuji, J. Chem. Phys. 127 (2007), 224104.
[26] H. Nakatsuji, H. Nakashima, Y. Kurokawa, A. Ishikawa, Phys. Rev. Lett. 99 (2007), 240402.
[27] H. Nakashima, H. Nakatsuji, Phys. Rev. Lett. 101 (2008), 240406.
[28] H. Nakatsuji, Acc. Chem. Res. 45 (2012) 1480.
[29] H. Nakashima, H. Nakatsuji, J. Chem. Phys. 139 (2013), 044112.
[30] H. Nakatsuji, H. Nakashima, J. Chem. Phys. 142 (2015), 084117.
[31] H. Nakatsuji, H. Nakashima, J. Chem. Phys. 142 (2015), 194101.
[32] H. Nakatsuji, H. Nakashima, J. Chem. Phys. 149 (2018), 114105.
[33] H. Nakatsuji, H. Nakashima, J. Chem. Phys. 149 (2018), 114106.
[34] Y.I. Kurokawa, H. Nakashima, H. Nakatsuji, Phys. Chem. Chem. Phys. 21 (2019) 6327.
[35] H. Nakatsuji, H. Nakashima, J. Chem. Phys. 150 (2019), 044105.
[36] H. Nakatsuji, H. Nakashima, Y.I. Kurokawa, Phys. Rev. A 101 (2020), 062508.
[37] H. Nakashima, H. Nakatsuji, Phys. Rev. A 102 (2020), 052835.
[38] H. Nakatsuji, H. Nakashima, Y.I. Kurokawa, J. Chem. Phys. 156 (2022), 014113.
[39] H. Nakatsuji, H. Nakashima, Chem. Phys. Lett. 806 (2022), 140002.
[40] H. Nakatsuji, H. Nakashima, J. Chem. Phys. 157 (2022), 094109.
[41] A.A. Frost, R.E. Kellogg, B.M. Gimarc, J.D. Scargle, J. Chem. Phys. 35 (1961) 827.
[42] S.A. Orszag, Studies Applied Math. 50 (1971) 293.
[43] R.A. Friesner, Chem. Phys. Lett. 116 (1985) 39.
[44] W. Yang, A.C. Peet, Chem. Phys. Lett. 153 (1988) 98.
[45] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, E. Teller, J. Chem. Phys. 21 (1953) 1087.
[46] W.K. Hastings, Biometrika 57 (1970) 97.
[47] R. Rydberg, Z. Phys. 73 (1932) 376.
[48] O. Klein, Z. Phys. 76 (1932) 226.
[49] A.L.G. Rees, Proc. Phys. Soc. 59 (1947) 998.
[50] H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schutz, P. Celani, W. Gyorffy, D. Kats, T. Korona, R. Lindh et al., MOLPRO, version 2019.2; J. F. Rico, R. Lopez, G. Ramirez, I. Ema, D. Zorrilla, and K. Ishida, SMILES a package for molecular calculations with Slater functions.


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[^1]:    ${ }^{\text {a }}$ Conversion constant: 1 a.u. $=627.5095 \mathrm{kcal} / \mathrm{mol}$ was used between a.u. and $\mathrm{kcal} / \mathrm{mol}$ for all the data in this paper.

[^2]:    a See Table 1 of Ref. [19].

