

Potential Energy Curves of the Low-Lying Five $^1\Sigma^+$ and $^1\Pi$ States of a CH^+ Molecule Based on the Free Complement - Local Schrödinger Equation Theory and the Chemical Formula Theory

Hiroyuki Nakashima* and Hiroshi Nakatsuji*

Cite This: <https://doi.org/10.1021/acs.jctc.3c00645>

Read Online

ACCESS |



Metrics & More

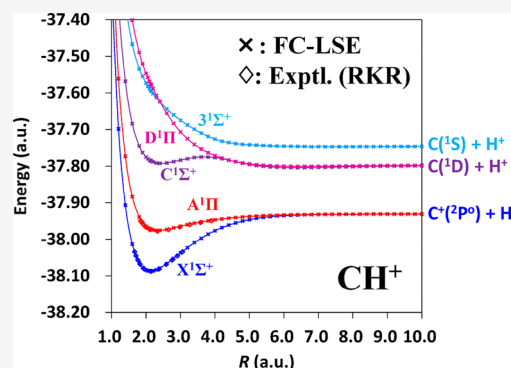


Article Recommendations



Supporting Information

ABSTRACT: The potential energy curves (PECs) of the low-lying five $^1\Sigma^+$ and $^1\Pi$ states ($X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states) of a CH^+ molecule, an important interstellar molecule, were calculated by the free complement (FC) - local Schrödinger equation (LSE) theory with the direct local sampling scheme. The FC wave functions were constructed based on the chemical formula theory (CFT), whose local characters correspond to the covalent dissociations: $\text{C}^+(^2\text{p}^0(\text{s}^2\text{p}^1)) + \text{H}(^2\text{S})$ of the $X^1\Sigma^+$ and $A^1\Pi$ states and the ionic dissociations: $\text{C}(^1\text{D}(\text{s}^2\text{p}^2)) + \text{H}^+$ of the $C^1\Sigma^+$ and $D^1\Pi$ states. All the calculated PECs were obtained with satisfying the chemical accuracy, i.e., error less than 1 kcal/mol, as absolute total energy of the Schrödinger equation without any energy shift. The spectroscopic data calculated from the PECs agreed well with both experimental and other accurate theoretical references. We also analyzed the wave functions using the inverse overlap weights proposed by Gallup et al. with the CFT configurations. For the $X^1\Sigma^+$ and $A^1\Pi$ states, the covalent $\text{C}^+(\text{sp}^2)$ and $\text{C}^+(\text{p}^3)$ configurations played important roles for bond formation. In the small internuclear distances of the $C^1\Sigma^+$, $D^1\Pi$, and $3^1\Sigma^+$ states, the covalent character was also dominant as a result of the electron charge transfer from C to H^+ . Thus, the present FC-LSE results not only are accurate but also can provide chemical understanding according to the CFT.



1. INTRODUCTION

The CH^+ molecule, i.e., methyldiyne cation, is a simple six-electron ionic molecule. It was one of the first molecular ions detected in the interstellar medium by Dunham¹ and identified with the laboratory spectra by Douglas and Herzberg^{2,3} and Adams.⁴ This molecule is also considered one of the significant key molecules in astronomical chemical reactions because it becomes an origin for the formations of various interstellar molecules.^{5–9} A lot of experimental studies in the laboratory phase also have been extensively performed to respond to astronomical requests.^{10–19} Their experimental studies, however, might not be easy since this molecule is highly reactive and unstable in a moderate environment. Reliable quantum-mechanical theoretical studies are therefore also highly required. Most of these theoretical studies have been performed by the quantum chemistry methods based on the Hartree–Fock related molecular orbital (MO) theory.^{20–28} Generally speaking, however, single-reference MO theories have a weakness for describing static correlations in dissociation limits, excited states, etc. Multireference methods, therefore, are required for quantitatively describing the potential energy curves (PECs) of the ground and excited states up to their dissociations, but their multireference wave functions are generally complicated and huge number of configurations would be necessary for accurate results.

Different from ordinary quantum chemistry methods, one of the authors proposed the free complement (FC) theory,²⁹ which leads to the convergence to the exact solutions of the Schrödinger equation (SE) based on the scaled Schrödinger equation (SSE) that eliminates the Coulomb singularities in the Hamiltonian. The local Schrödinger equation (LSE) method was also developed for the applications to general atoms and molecules without any analytical integrations.^{30,31} Various applications of the FC-LSE theory have been performed and numerically proved their reliabilities.^{30–35} Recently, we introduced the general scaling functions³⁶ for efficient improvements of the FC wave functions. The direct local sampling (DLS) scheme³⁷ was also proposed to generate a rational set of sampling points for the LSE method. The DLS scheme does not require any numerical random simulation like Metropolis-related algorithms.^{38,39} This scheme, therefore, should be suitable for describing continuity properties like PECs that

Received: June 14, 2023



ACS Publications

© XXXX American Chemical Society

A

<https://doi.org/10.1021/acs.jctc.3c00645>
J. Chem. Theory Comput. XXXX, XXX, XXX–XXX

require smooth energy connections at different geometries. Actually, in the previous paper,⁴⁰ we have applied the FC theory at this level to the calculations of the PECs of all the nine valence ground and excited states of a Li₂ molecule. The calculated potential curves completely agreed with the experimental Rydberg-Klein-Rees (RKR) potentials^{41–43} within the chemical accuracy, i.e., the error less than 1 kcal/mol as absolute total energy of the Schrödinger equation.

In the present paper, we apply the FC-LSE theory to solving the SE of a CH⁺ molecule and draw the theoretical exact-level accurate PECs as functions of internucleus distances *R* for the ground X¹Σ⁺ and excited C¹Σ⁺, 3¹Σ⁺, A¹Π, and D¹Π states. In our previous letter,³⁷ we reported the single-point calculations of the ¹Σ⁺ symmetry of CH⁺ at the equilibrium distance *R*_{eq} of the ground state. Here, we improve our calculations and discuss the whole PECs from *R*_{eq} to the dissociation limits. Since CH⁺ is an ionic molecule, both covalent and ionic states strongly couple in their electronic structures. We prepare the initial wave functions of the FC theory based on the chemical formula theory (CFT),³⁴ which enable us to construct the wave functions with local descriptions more chemically understandable than the MO theory. The FC-LSE theory based on the CFT can give efficient convergences to the exact solutions with compact forms since the chemistry is local and the electron correlations should also be local without considering static correlations denoted in the MO theory. Thus, the aims in the present study are to calculate the PECs within the chemical accuracy correct as absolute solution of the SE, i.e., no energy shifts are employed in the resultant PECs, and to perform the spectroscopic analysis from the obtained accurate PECs. We also analyze our FC–CFT wave functions to investigate the characters of chemical bonds for all the target states, using the inverse overlap weights (IOW)⁴⁴ by Gallup et al. with grouping the CFT configurations.

2. FC-LSE CALCULATIONS

2.A. Initial Functions Constructed Based on the CFT

Concepts. In the first step of FC theory, one needs to prepare a set of initial functions appropriate for the target states. We employed the CFT to construct the initial functions with local-based valence-bond descriptions to directly reflect the chemical natures.³⁴ One of the important concepts of the CFT is “the molecular states from the atomic states”, and thus, we first consider the atomic quantum states, i.e., molecular dissociation limits. The prior chemical knowledge implies that the X¹Σ⁺ and A¹Π states of a CH⁺ molecule covalently dissociate to the ²P^o(s²p) state of a C⁺ atom and the ²S state of a H atom; we simply denote it as C⁺(²P^o(s²p)) + H(²S). On the other hand, the C¹Σ⁺ and D¹Π states ionically dissociate to C(¹D(s²p²)) + H⁺, and the 3¹Σ⁺ state also ionically dissociates to C(¹S(s²p²)) + H⁺. In ordinary neutral molecules, the states ionically dissociated usually locate on a high-energy region, but those of the present CH⁺ molecule locate on a low-energy region because the ¹D and ¹S states of a neutral C atom are comparably stable to the ²P^o state of a C⁺ atom. One can see these atomic energy levels of C⁺ and C atoms in the Moore’s table and the atomic spectra database given in the National Institute of Standards and Technology (NIST) site.^{45,46}

We construct the wave functions from not only atomic ground but also excited states according to the CFT following the Brillouin theorem. Therefore, we prepared the initial functions of a CH⁺ molecule in the FC theory from the atomic states of C⁺ and C atoms: C⁺(²P^o(s²p)), C⁺(²D(sp²)), C⁺(²P^o(p³)), C(¹D-

(s²p²)), C(¹S(s²p²)), C(¹P^o(sp³)), C(¹D(p⁴)), and C(¹S(p⁴)). For the ¹Σ⁺ symmetry of the X¹Σ⁺, C¹Σ⁺, and 3¹Σ⁺ states, we employed the following initial functions classified into six groups (eqs 1a–1f):

$$\text{Cov}(s^2p): C^+({}^2P^o(s^2p)) \cdot H({}^2S) \\ \psi_0^{(1)} = A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2s_{in,C} 2s_{out,C})(\alpha\beta - \beta\alpha) \cdot \left(\frac{2p_{x,C}^{(1)} 1s_H}{2p_{y,C}^{(1)} 1s_H} \right) (\alpha\beta - \beta\alpha) \right], \quad (1a)$$

$$\text{Cov}(sp^2): C^+({}^2D(sp^2)) \cdot H({}^2S) \\ \psi_0^{(2)} = A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot \left(\frac{2p_{x,C}^{(2)} 2p_{y,C}^{(2)}}{2p_{y,C}^{(2)} 2p_{z,C}^{(2)} + 2p_{z,C}^{(2)} 2p_{x,C}^{(2)}} \right) (\alpha\beta - \beta\alpha) \cdot (2s_{out,C} 1s_H)(\alpha\beta - \beta\alpha) \right], \quad (1b)$$

$$\text{Cov}(p^3): C^+({}^2P^o(p^3)) \cdot H({}^2S) \\ \psi_0^{(3)} = A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(3)} 2p_{y,C}^{(3)} + 2p_{z,C}^{(3)} 2p_{z,C}^{(3)})(\alpha\beta - \beta\alpha) \cdot \left(\frac{2p_{x,C}^{(3)} 1s_H}{2p_{x,C}^{(3)} 1s_H} \right) (\alpha\beta - \beta\alpha) \right], \quad (1c)$$

$$\text{Ion}(s^2p^2): C({}^1D(s^2p^2), {}^1S(s^2p^2)) \cdot H^+ \\ \psi_0^{(4)} = A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2s_{in,C} 2s_{out,C})(\alpha\beta - \beta\alpha) \cdot \left(\frac{2p_{x,C}^{(4)} 2p_{y,C}^{(4)}}{2p_{y,C}^{(4)} 2p_{z,C}^{(4)} + 2p_{z,C}^{(4)} 2p_{x,C}^{(4)}} \right) (\alpha\beta - \beta\alpha) \right], \quad (1d)$$

$$\text{Ion}(sp^3): C({}^1P^o(sp^3)) \cdot H^+ \\ \psi_0^{(5)} = A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(5)} 2p_{y,C}^{(5)} + 2p_{z,C}^{(5)} 2p_{z,C}^{(5)})(\alpha\beta - \beta\alpha) \cdot \left(\frac{2s_{out,C} 2p_{x,C}^{(5)}}{2s_{out,C} 2p_{y,C}^{(5)}} \right) (\alpha\beta - \beta\alpha) \right], \quad (1e)$$

$$\text{Ion}(p^4): C({}^1D(p^4), {}^1S(p^4)) \cdot H^+ \\ \psi_0^{(6)} = A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot \left(\frac{(2p_{x,C}^{(6)} 2p_{y,C}^{(6)})(2p_{y,C}^{(6)} 2p_{z,C}^{(6)} + 2p_{z,C}^{(6)} 2p_{x,C}^{(6)})}{(2p_{y,C}^{(6)} 2p_{y,C}^{(6)})(2p_{y,C}^{(6)} 2p_{z,C}^{(6)})} \right) (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \right]. \quad (1f)$$

Here, the molecular axis is set to the *x* axis. We employed the in–out correlations for the 1s and 2s orbitals and the double-ζ 2p orbitals for C atom, where we abbreviate the descriptions by tensor product forms. *A* denotes the antisymmetrization operator, and *α* and *β* denote the spin terms corresponding to *S_z* = 1/2 and −1/2, respectively. Atomic orbitals used here were given by

$$\begin{aligned} 1s_{in,C} &= N_{1s,in,C} \exp(-\alpha_{1s,in,C} r_C) \\ 1s_{out,C} &= N_{1s,out,C} \exp(-\alpha_{1s,out,C} r_C) \\ 2s_{in,C} &= N_{2s,in,C}^{(1)} \exp(-\alpha_{2s,in,C}^{(1)} r_C) + d_{2s,in,C} N_{2s,in,C}^{(0)} \exp(-\alpha_{2s,in,C}^{(0)} r_C) \\ 2s_{out,C} &= N_{2s,out,C}^{(1)} \exp(-\alpha_{2s,out,C}^{(1)} r_C) + d_{2s,out,C} N_{2s,out,C}^{(0)} \exp(-\alpha_{2s,out,C}^{(0)} r_C) \\ 2p_{x,C}^{(1)} &= N_{2p,x,C}^{(1)} \exp(-\alpha_{2p,x,C}^{(1)} r_C) \quad 2p_{y,C}^{(1)} = N_{2p,y,C}^{(1)} \exp(-\alpha_{2p,y,C}^{(1)} r_C) \\ 2p_{z,C}^{(1)} &= N_{2p,z,C}^{(1)} \exp(-\alpha_{2p,z,C}^{(1)} r_C) \\ 2p_{x,C}^{(2)} &= N_{2p,x,C}^{(2)} \exp(-\alpha_{2p,x,C}^{(2)} r_C) \quad 2p_{y,C}^{(2)} = N_{2p,y,C}^{(2)} \exp(-\alpha_{2p,y,C}^{(2)} r_C) \\ 2p_{z,C}^{(2)} &= N_{2p,z,C}^{(2)} \exp(-\alpha_{2p,z,C}^{(2)} r_C) \\ 1s_H &= N_{1s,H} \exp(-\alpha_{1s,H} r_H) \end{aligned} \quad (2)$$

where *N* represents the normalization factor of each orbital and *r_C* and *r_H* are the radial distances from the C and H nuclei, respectively. The parameters of the orbital exponents and coefficients used were (α_{1s,in,C}, α_{1s,out,C}, α_{2s,in,C}⁽¹⁾, α_{2s,in,C}⁽⁰⁾, d_{2s,in,C}⁽⁰⁾, α_{2s,out,C}⁽¹⁾, α_{2s,out,C}⁽⁰⁾, d_{2s,out,C}⁽⁰⁾, α_{2p,x,C}⁽¹⁾, α_{2p,y,C}⁽¹⁾, α_{2p,z,C}⁽¹⁾, α_{1s,H}) = (6.5978, 4.7456, 2.0363, 3.7586, −0.248955, 1.3148, 4.7236, −0.0178340, 2.0258, 1.1261, 1.0).

In eq 1a, the first three terms, named Cov(*s*²p), Cov(*sp*²), and Cov(*p*³), dissociate to C⁺ and H, i.e., belong to the covalent group, and the latter three terms, named Ion(*s*²p²), Ion(*sp*³), and Ion(*p*⁴), dissociate to C and H⁺, i.e., belong to the ionic group. The main configuration of the X¹Σ⁺ state is eq 1a (covalent), and those of the C¹Σ⁺ and 3¹Σ⁺ states are eq 1d (ionic). Equations 1b and 1e at dissociations correspond to C⁺(*sp*²) and C(*sp*³) with one-electron atomic excitations to the vacant p-orbitals from C⁺(*s*²p) and C(*s*²p²), respectively. Equations 1c and 1f, i.e., C⁺(*p*³) and C(*p*⁴), correspond to the two-electron atomic excitations to the vacant p-orbitals from

$C^+(s^2p)$ and $C(s^2p^2)$, respectively. We did not include the opposite ionic terms: $C^{2+}H^-$ since its electronic states locate a quite high-energy region and should not be important for the present lower electronic states of a CH molecule. We also introduced the configurations with the alternative spin eigenfunctions of the valence four electrons all for eq 1a, i.e., the following both spin singlet eigenfunctions were used for electrons 3 to 6,

$$\begin{aligned}\Theta_1 &= (\alpha(3)\beta(4) - \beta(3)\alpha(4)) \cdot (\alpha(5)\beta(6) - \beta(5)\alpha(6)) \\ \Theta_2 &= (\alpha(3)\beta(5) - \beta(3)\alpha(5)) \cdot (\alpha(4)\beta(6) - \beta(4)\alpha(6))\end{aligned}\quad (3)$$

Since the different orbitals are assigned to the 2s and 2p electrons, Θ_2 remains as an independent function. They are important to include spin polarization effects and guarantee correct bond dissociations.⁴⁷

Similarly, the initial functions for the $^1\Pi$ symmetry are given as follows and are also classified into six groups (eqs 4a–4f):

$$\text{Cov}(s^2p): C^+(^2P^o(s^2p)) - H(^2S) \\ \psi_0^{(1)} = A \left[(1s_{inC} 1s_{outC})(\alpha\beta - \beta\alpha) \cdot (2s_{inC} 2s_{outC})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{yC}^{(1)} 1s_H \\ 2p_{yC}^{(2)} 1s_H \end{pmatrix} (\alpha\beta - \beta\alpha) \right], \quad (4a)$$

$$\text{Cov}(sp^2): C^+(^2D(sp^2)) - H(^2S) \\ \psi_0^{(2)} = A \left[(1s_{inC} 1s_{outC})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{yC}^{(1)} 2p_{xC}^{(2)} \\ 2p_{yC}^{(2)} 2p_{xC}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \cdot (2s_{outC} 1s_H)(\alpha\beta - \beta\alpha) \right], \quad (4b)$$

$$\text{Cov}(p^3): C^+(^2P^o(p^3)) - H(^2S) \\ \psi_0^{(3)} = A \left[(1s_{inC} 1s_{outC})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{xC}^{(1)} 2p_{xC}^{(2)} \\ 2p_{yC}^{(1)} 2p_{yC}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{yC}^{(1)} 1s_H \\ 2p_{yC}^{(2)} 1s_H \end{pmatrix} (\alpha\beta - \beta\alpha) \right], \quad (4c)$$

$$\text{Ion}(s^2p^2): C(^2S^o(s^2p^2)) - H^+ \\ \psi_0^{(4)} = A \left[(1s_{inC} 1s_{outC})(\alpha\beta - \beta\alpha) \cdot (2s_{inC} 2s_{outC})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{yC}^{(1)} 2p_{xC}^{(2)} \\ 2p_{yC}^{(2)} 2p_{xC}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \right], \quad (4d)$$

$$\text{Ion}(sp^3): C(^1P^o(sp^3)) - H^+ \\ \psi_0^{(5)} = A \left[(1s_{inC} 1s_{outC})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{yC}^{(1)} 2p_{xC}^{(2)} \\ 2p_{yC}^{(2)} 2p_{xC}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2s_{outC} 2p_{yC}^{(1)} \\ 2s_{outC} 2p_{yC}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \right], \quad (4e)$$

$$\text{Ion}(p^4): C(^1D(p^4)) - H^+ \\ \psi_0^{(6)} = A \left[(1s_{inC} 1s_{outC})(\alpha\beta - \beta\alpha) \cdot (2p_{yC}^{(1)} 2p_{yC}^{(2)})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{yC}^{(1)} 2p_{xC}^{(2)} \\ 2p_{yC}^{(2)} 2p_{xC}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \right]. \quad (4f)$$

Here, the molecular axis is set to the x axis and the direction of the π orbital is set to the y axis. We used the same atomic orbitals as those given by eq 2.

The main configuration of the $A^1\Pi$ state is eq 4a (covalent), and that of the $D^1\Pi$ state is eq 4d (ionic). From a symmetry reason, there is no channel of the ionic dissociation to $C(^1S(s^2p^2))$ that appears in the $^1\Sigma^+$ symmetry. Similar to the $^1\Sigma^+$ case, eqs 4b and 4e, i.e., $C^+(sp^2)$ and $C(sp^3)$, represent the one-electron atomic excitations to the vacant p-orbitals from $C^+(s^2p)$ and $C(s^2p^2)$, respectively. Equations 4c and 4f, i.e., $C^+(p^3)$ and $C(p^4)$, correspond to the two-electron atomic excitations from $C^+(s^2p)$ and $C(s^2p^2)$. We used both spin singlet eigenfunctions given by eq 3 for electrons 3 to 6 the same as the $^1\Sigma^+$ case.

2.B. Application of the FC Theory. Starting from the initial functions given in section 2.A, the FC theory was applied for leading the exact solutions of the SE.²⁹ In the FC theory, the wave function ψ_n at order n is generated by a following recursive formula

$$\psi_n = [1 + C_n g(H - E_{n-1})] \psi_{n-1} \quad (5)$$

where H is the Hamiltonian of the system, E_{n-1} and ψ_{n-1} are the energy and wave function at order $n - 1$, and C_n is the simplest variational coefficient at order n . g is a scaling function in the SSE, and we employed

$$g = \sum_{i=1}^N \sum_{A=1}^{N_A} r_{iA} + \sum_{i < j}^N (g_{ij}^{(1)} + g_{ij}^{(2)}) \quad (6)$$

with

$$g_{ij}^{(1)} = 1 - \exp(-\gamma^{(1)} r_{ij}) \quad (7)$$

and

$$g_{ij}^{(2)} = Ei(-\gamma_1^{(2)} r_{ij} - \gamma_2) - Ei(-\gamma_1^{(2)}) \quad (8)$$

where N and N_A are the numbers of electrons and nuclei; i.e., $N = 6$ and $N_A = 2$ for the present CH^+ molecule. r_{iA} denotes the distance between electron i and nucleus A and r_{ij} between electrons i and j . In eq 6, we employed an ordinary linear r_{iA} function for the one-electron part but employed two different kinds of g functions for the two-electron part: exponential type (eq 7) and exponential integral (Ei) type (eq 8) since different types of dual g functions would efficiently cover the variational space and accelerate convergences. In eqs 7 and 8, we used the parameters $\gamma^{(1)} = 0.378$, $\gamma_1^{(2)} = 0.00121$, and $\gamma_2^{(2)} = 0.00238$, which were the values roughly optimized with a helium atom at $n = 3$ in ref 36.

The right side of eq 5 can be transformed by extracting the basic analytical functions $\{\phi_l\}$ and expressed by a linear expansion as

$$\psi = \sum_{l=1}^M c_l \phi_l \quad (9)$$

where we call ϕ_l complement (complete element) function (cf). M is the number of cfs, called dimension. When generating $\{\phi_l\}$, we employed the potential-alone method defined in ref 36.

As described in our previous paper,³⁷ the FC theory generates not only the ordinary intra terms: one-electron r_{iA} and two-electron $r_{iA} r_{iA'}$ but also the inter terms: one-electron r_{iAB} and two-electron $r_{iA} r_{iA'}$ where i_A represents the electron i belonging to the center A . The center of each orbital is determined from the exponent center of each orbital in each initial function. These inter terms are not shown in ordinary quantum chemistry but work as a polarization and coalescence term between different atoms.

We generated the cfs by applying the FC theory up to order $n = 3$, but only applying up to order $n = 2$ for the initial functions of $\text{Cov}(sp^2)$, $\text{Cov}(p^3)$, $\text{Ion}(sp^3)$, and $\text{Ion}(p^4)$ in eq 1a or 4a. They may importantly work for chemical bond creations especially in a small R region but less important than the main $\text{Cov}(s^2p)$ and $\text{Ion}(s^2p^2)$ configurations. To reduce computational costs further, we discarded the cfs including the inter terms between 1s electrons in C and H atoms since they are mostly separated and independent from each other. The dimensions of the resultant cfs were $M = 24870$ and 26808 for the $^1\Sigma^+$ and $^1\Pi$ symmetries, respectively.

2.C. Generation of Sampling Points by the DLS Scheme. After generating cfs, the HS method of the LSE theory³¹ was performed to calculate the coefficients in eq 9 with the sampling points produced by the DLS scheme.³⁷ The DLS scheme is a straightforward and deterministic sampling-point generation method, as the sampling-point distribution obeys a given density function. We used the N -electron DLS scheme and employed $|\psi_0^{(I)}|^2$ of eq 1a or 4a ($I = 1$ to 6) evenly as a density function used in the DLS scheme. This is rather appropriate to calculate the coefficients of the cfs from each initial function

equally. For instance, even at the dissociation limit of the $X^1\Sigma^+$ state, whose dominant configuration is $\text{Cov}(s^2p)$, the sampling points from the ionic terms are necessary to determine the ionic cf's coefficients. Otherwise, the computations become numerically failed or unstable. Although we employed only the initial functions as a density function of the DLS scheme, it was almost enough because important chemical natures were mostly included in the initial functions by the CFT.

2.D. Analysis Scheme Using the Inverse Overlap Weights with Grouping the CFT Configurations. The cf's generated by the FC theory based on the CFT have local characters and something connected to chemical understanding. However, since the cf's are nonorthogonal with large overlaps each other, the coefficients $\{c_i\}$ themselves in eq 9 are not simply used to interpret the importance of each cf. In the modern valence bond theory, several procedures have been suggested to measure the weights for nonorthogonal basis sets. One of the simplest ways is called the Chirgwin-Coulson weight (or Mulliken weight),⁴⁸ i.e., $w_I = \sum c_I c_J S_{IJ}$, where S is the overlap matrix $S_{IJ} = \langle \phi_I | \phi_J \rangle$. This weight, however, sometimes becomes negative especially for the case having strong overlaps. The other methods were known as the Löwdin weight using the symmetric orthogonalization of S matrix⁴⁹ and the IOW suggested by Gallup and Norbeck using the inverse S matrix.⁴⁴ For the purpose of measuring the contribution of each basis function, the latter method would be adequate. However, one needs to calculate the inverse S matrix and it may often cause an numerical unstableness especially when basis functions have large overlaps.

In the present study, our purpose is not to investigate the importance of all the cf's in detail but to understand the chemical natures corresponding to the local CFT structures. Since the cf's are assigned to one of the original initial functions, one can classify the calculated FC wave function into six groups defined in eq 1a or 4a as given by

$$\begin{aligned} \psi &= \sum_{I=1}^{M^{(1)}} c_I^{(1)} \phi_I^{(1)} + \sum_{I=1}^{M^{(2)}} c_I^{(2)} \phi_I^{(2)} + \sum_{I=1}^{M^{(3)}} c_I^{(3)} \phi_I^{(3)} + \sum_{I=1}^{M^{(4)}} c_I^{(4)} \phi_I^{(4)} \\ &\quad + \sum_{I=1}^{M^{(5)}} c_I^{(5)} \phi_I^{(5)} + \sum_{I=1}^{M^{(6)}} c_I^{(6)} \phi_I^{(6)} \\ &= \psi^{(1)} + \psi^{(2)} + \psi^{(3)} + \psi^{(4)} + \psi^{(5)} + \psi^{(6)} \end{aligned} \quad (10)$$

where $\phi_I^{(k)}$, $c_I^{(k)}$, and $M^{(k)}$ denote the cf, its coefficient, and the number of cf's belong to $\psi_0^{(k)}$, respectively. $\psi^{(k)}$ represents the part of the wave function of group k ; i.e., $k = 1$: $\text{Cov}(s^2p)$, $k = 2$: $\text{Cov}(sp^2)$, $k = 3$: $\text{Cov}(p^3)$, $k = 4$: $\text{Ion}(s^2p^2)$, $k = 5$: $\text{Ion}(sp^3)$, and $k = 6$: $\text{Ion}(p^4)$. For these classified $\psi^{(k)}$, we evaluate the IOWs: w_k by Gallup et al., given by

$$w_k = \frac{N_G}{[G^{-1}]_{kk}} \quad (11)$$

where G is the overlap matrix for $\psi^{(k)}$, i.e., $G_{kl} = \langle \psi^{(k)} | \psi^{(l)} \rangle$, and N_G is a normalization factor, i.e., $N_G^{-1} = \sum_k 1/[G^{-1}]_{kk}$. In the present case, G is just a 6-dimensional nonsingular matrix and its inverse matrix is easily and safely evaluated. These amplitudes can be recognized as a direct indicator to measure the importance of the CFT configurations and would directly lead to a chemical understanding. Such a grouping scheme of the IOW might be useful even for general nonorthogonal systems by defining groups appropriately.

3. RESULTS AND DISCUSSION

3.A. FC-LSE Calculations of C^+ and C Atoms. To construct the molecular wave functions according to CFT, it is necessary to first examine the atomic quantum states. As discussed in section 2, the dissociation limits of the present target states of a CH^+ molecule are the $2P^o(s^2p)$ state of a C^+ atom and the $1D(s^2p^2)$ and $1S(s^2p^2)$ states of a C atom. Therefore, we performed the atomic FC-LSE calculations of these states with the equivalent computational conditions of CH^+ denoted in section 2. In addition, we computed the $4P(sp^2)$ of C^+ and the $3P(s^2p^2)$ and $5S(sp^3)$ states of C because their states are important for building chemical bonds of ordinary organic molecules.

Table 1 summarizes the calculated FC-LSE results at order $n = 3$ with the H-square errors,³¹ absolute total energies, and energy differences ΔE from the estimated exact energies. The exact absolute ground-state energy of $C^+(2P^o(s^2p))$ is estimated as $-35.431\,03$ a.u.^{50,51} and that of $C(3P(s^2p^2))$ as $-37.845\,0$ a.u.⁵¹ From the experimental excitation energies in refs 45, 46 and the absolute energy of $C(3P(s^2p^2))$, the absolute energies of $C(1D(s^2p^2))$ and $C(1S(s^2p^2))$ are estimated as $-37.798\,559$, and $-37.746\,364$ a.u., respectively. The exact energies of $H(2S)$ and H^+ are -0.5 and 0 a.u., respectively. Therefore, the exact absolute energies of the dissociation limits of CH^+ : $C^+(2P^o(s^2p)) + H(2S)$, $C(1D(s^2p^2)) + H^+$, and $C(1S(s^2p^2)) + H^+$ are estimated as $-37.931\,03$, $-37.798\,559$, and $-37.746\,364$ a.u., respectively. For all the calculated states of C^+ and C atoms, $|\Delta E|$ show less than 1 kcal/mol, i.e., satisfying the chemical accuracies as absolute total energy of the SE. The H-square errors were mostly less than 0.05, which indicated their sufficient accuracies of the calculated wave functions. In the literature of accurate calculations,^{52–55} the explicitly correlated Gaussian (ECG) methods provided very accurate variational energies,^{54,55} but their applications would be limited to small systems. The calculations of the diffusion Monte Carlo (DMC) method by Needs et al. also gave the accurate total energies of both ground states of C^+ and C atoms.⁵² Gálvez et al. systematically reported the excited states of a C atom also by the DMC method,^{50,53} but their total energies did not satisfy chemical accuracies. We compared the calculated excitation energies with the experimental atomic energy levels provided in the NIST site⁴⁶ and agreed very well each other where the absolute differences $|\Delta EX|$ were less than 0.03 eV. Thus, in the atomic calculations, i.e., as the dissociation limits, the present FC-LSE solutions of the ground and target excited states of C^+ and C atoms were satisfactorily accurate, correct as the dissociation limits of a CH^+ molecule. They can be reasonably used in CFT for the CH^+ molecular calculations.

3.B. Potential Energy Curves of a CH^+ Molecule by the FC-LSE Theory. Next, we performed FC-LSE calculations of a CH^+ molecule for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states. Table 2 summarizes the converging behavior of the FC-LSE calculations as increasing order n with the H-square error, absolute total energies, and vertical excitation energies at $R = R_{\text{eq}} = 2.137$ a.u., i.e., the equilibrium distance of the ground $X^1\Sigma^+$ state. A similar table was also given in our previous paper,³⁷ but the previous one shows only the results of the $1^1\Sigma^+$ states and the construction method of the cf's in the present case is improved to describe the PECs accurately. In the $X^1\Sigma^+$ state, the total energies of the FC calculations rapidly approached the estimated exact energy as increasing order n . ΔE , i.e., the energy difference between the calculated energy and the estimated exact energy,

Table 1. FC-LSE Calculations of a C⁺ Atom: ²p^o and ⁴p States and a C Atom: ³p, ¹D, ¹S, and ⁵S^o States at Order $n = 3$, Compared to the Experimental Estimated Exact Energies and Excitation Energies and the Theoretical Results by the DMC and ECG Methods

State	FC-LSE				energy (reference) (a.u.)				excitation energy (eV)	
	M^a	H-square error ^b	energy (a.u.)	ΔE (kcal/mol) ^c	estimated exact energy (a.u.) ^{d,e}	DMC (Needs et al.) ^f	DMC (Gálvez et al.) ^{g,h}	ECG ^{i,j}	FC-LSE	ΔEX^k Exptl. (NIST) ^l
C ⁺ atom										
² p ^o (² p)	6806	0.031 910	-37.430 769	0.164	-37.431 03 ^d	-37.430 73(4)	-37.410 20(5) ^g	-37.430 880 49(250) ^j		
⁴ p(³ p ²)	3432	0.033 744	-37.234 462	0.397	-37.235 095 ^e				5.342	5.332
C atom										
³ p(³ p ²)	18098	0.038 035	-37.844 313	0.431	-37.845 0 ^d	-37.844 46(6)	-37.835 44(9) ^h	-37.844 906(4) ^j		
¹ D(³ p ²)	13178	0.054 004	-37.797 062	0.939	-37.798 559 ^e		-37.789 66(6) ^h		1.285	1.264
¹ S(³ p ²)	12964	0.021 281	-37.746 269	0.0598	-37.746 364 ^e		-37.738 30(5) ^h		2.668	2.684
⁵ S ^o (³ p ³)	7006	0.016 067	-37.691 495	-0.128	-37.691 291 ^e		-37.690 26(3) ^h	-37.691 751(2) ^j	4.158	4.183

^aNumber of cfs (Dimension). ^bDefined in ref 31. ^cEnergy differences of the FC-LSE energies from the estimated exact energy. Boldface means satisfying chemical accuracy, i.e., $|\Delta E| < 1$ kcal/mol. ^dRefs 50, 51. ^eEstimated by the absolute ground-state energies plus the NIST experimental excitation energies (the value of the lowest J state was used). ^fRef 52. ^gRef 50. ^hRef 53. ⁱRef 54. ^jref 55. ^kDifference of the excitation energy from the experimental excitation energies. Boldface means $|\Delta EX| < 0.03$ eV. NIST experimental excitation energies (the value of the lowest J state was used) ⁴⁶ with converted eV units.

was 0.481 kcal/mol for the X¹ Σ^+ state, thus satisfying the chemical accuracy as absolute solution. Note that the exact energy $-38.087\,598$ a.u. at R_{eq} was estimated from the atomic energies of the C⁺(²p^o(²p))^{30,51} and H(¹S) atoms and the experimental dissociation energy D_e .¹⁷ We also compared the total energies with the other accurate theoretical computations by the multireference CI (MRCI) method with the large basis set.²⁶ ΔE of this reference was 34.685 kcal/mol, i.e., whose absolute energy was much higher than the estimated exact energy. The vertical excitation energies from the X¹ Σ^+ state to the C¹ Σ^+ , 3¹ Σ^+ , A¹ Π , and D¹ Π states were 8.201, 13.415, 3.111, and 13.896 eV at order $n = 3$, respectively, and they agreed well with the MRCI references; 8.198, 13.375, 3.093, and 13.773 eV, respectively.

Table 3 summarizes the numerical data of the PECs for the X¹ Σ^+ , C¹ Σ^+ , 3¹ Σ^+ , A¹ Π , and D¹ Π states with the H-square error and absolute total energies by FC-LSE theory at several specific points of R . The comparisons with the experimental RKR potentials¹⁴ and the PECs by the MRCI method²⁶ were also provided, where the RKR and MRCI data were interpolated by a spline fitting from the originally given data. Here, ΔE : [FC-LSE]-[RKR] denotes the energy difference of the FC-LSE from the RKR potential, ΔE : [MRCI]-[RKR] shows the energy difference between the MRCI and the RKR potential, and ΔE : [MRCI]-[FC-LSE] shows that between the MRCI and the FC-LSE. Detailed numerical data of the PECs are given in Supporting Information by Tables S1 to S4 for the X¹ Σ^+ , C¹ Σ^+ , and 3¹ Σ^+ , A¹ Π , and the D¹ Π states, respectively.

For the X¹ Σ^+ state, the RKR potentials were only available between $R = 1.667$ and 3.055 a.u.¹⁴ The estimated exact energy given in Table 2 was used to estimate the absolute total energy of the RKR potential at $R_{eq} = 2.137$ a.u. $|\Delta E$: [FC-LSE]-[RKR]| were always less than 1 kcal/mol satisfying chemical accuracies at all R where the RKR data were available. On the other hand, $|\Delta E$: [MRCI]-[RKR]| values were about 34 kcal/mol higher than the RKR data. In both cases of the FC-LSE and MRCI methods, ΔE slightly increased as increasing R between $R = 1.667$ and 3.055 a.u. At the dissociation limit: C⁺(²p^o(²p)) + H(¹S), ΔE of the FC-LSE from the estimated exact energy was also less than 1 kcal/mol satisfying the chemical accuracy, and that of the MRCI was still about 34 kcal/mol higher.

For the C¹ Σ^+ and 3¹ Σ^+ states, since there are no RKR references available to our knowledge for these states, only the H-square error and total energies of the FC-LSE are given in Table 3 and Table S2 compared to the MRCI energies. Similar to the X¹ Σ^+ case, the total energies of the MRCI were almost shifted above about 34 kcal/mol from the FC-LSE energies, and their largest differences appeared at R less than 1.8 a.u. in the 3¹ Σ^+ state: 36–41 kcal/mol. The dissociation limits of the C¹ Σ^+ and 3¹ Σ^+ states were C(¹D(³p²)) + H⁺ and C(¹S(³p²)) + H⁺, respectively; the FC-LSE PECs correctly dissociate to these atomic states as absolute energy.

For the A¹ Π state, the experimental RKR potential is available, where the experimental adiabatic excitation energy¹⁴ $T_e = 24118.726$ cm⁻¹ was used to determine the absolute total energy of the RKR potential of this state. In the region where the RKR data were available between $R = 1.840$ and 3.895 a.u., $|\Delta E$: [FC-LSE]-[RKR]| were less than 1 kcal/mol from $R = 2.8$ to 3.6 a.u. but slightly larger than 1 kcal/mol from $R = 2.0$ to 2.4 a.u. $|\Delta E$: [MRCI]-[RKR]| were again about 34 kcal/mol higher than the RKR data similar to the X¹ Σ^+ state and they were also slightly larger in the small R region around $R = 2.0$ to 2.4 a.u. The shapes of the PECs of the FC-LSE and MRCI methods, therefore, were

Table 2. Convergence of the FC-LSE Calculations for the Ground $X^1\Sigma^+$ State and the Excited $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ States of a CH^+ Molecule at the Equilibrium Geometry of $X^1\Sigma^+$, i.e., $R_{\text{eq}} = 2.137$ a.u., Compared to the Experimental Estimated Exact Energy of the $X^1\Sigma^+$ State and the Theoretical Results by the MRCI Method

n^a	M^b	$X^1\Sigma^+$ state			$C^1\Sigma^+$ state			$3^1\Sigma^+$ state		
		H-square error ^c	energy (a.u.)	ΔE (kcal/mol) ^d	H-square error ^c	energy (a.u.)	vertical excitation energy (eV)	H-square error ^c	energy (a.u.)	vertical excitation energy (eV)
0	20	(variational) ^e	−37.892 731	122.281	(variational) ^e	−37.559 296	9.073	(variational) ^e	−37.234 240	17.918
1	690	1.265 060	−38.062 894	15.502	1.615 676	−37.750 682	8.496	2.509 006	−37.526 412	14.598
2	9138	0.167 132	−38.085 179	1.518	0.270 448	−37.782 707	8.231	0.520 470	−37.586 925	13.558
3	24870	0.049 269	−38.086 831	0.481	0.141 880	−37.785 450	8.201	0.161 012	−37.593 832	13.415
Estimated exact energy ^f			−38.087 598							
MRCI ^g			−38.032 324	34.685			8.198			13.375

n^a	M^b	$A^1\Pi$ state			$D^1\Pi$ state		
		H-square error ^c	Energy (a.u.)	Vertical excitation energy (eV)	H-square error ^c	Energy (a.u.)	Vertical excitation energy (eV)
0	22	(variational) ^e	−37.770 698	3.321	(variational) ^e	−37.279 817	16.678
1	814	1.393 049	−37.944 092	3.233	2.017 605	−37.503 206	15.230
2	11076	0.221 027	−37.970 386	3.124	0.520 611	−37.569 208	14.040
3	26808	0.101 993	−37.972 499	3.111	0.340 655	−37.576 160	13.896
MRCI ^g			−37.918 660	3.093		−37.526 176	13.773

^aOrder of the FC theory. At order $n = 3$, only applying $n = 2$ for the initial functions of eqs 1b,c,e,f. ^bNumber of cf's (Dimension). ^cDefined in ref 31. ^dEnergy differences of the FC-LSE or reference energies from the estimated exact energy. Boldface means satisfying chemical accuracy, i.e., $|\Delta E| < 1$ kcal/mol. ^eVariational calculations with analytical integrations. ^fEstimated from the atomic energies of the $\text{C}^+(^2\text{P}^\circ)^{50,51}$ and H atoms and the experimental dissociation energy D_e given in ref 17. ^gRef 26, where the energies at R_{eq} were interpolated by a spline fitting. Absolute total energies of the excited states were calculated using the excitation energies.

similar to each other. Therefore, the experimental RKR data may have some differences from theoretical PECs on the Born–Oppenheimer (BO) approximation. The dissociation limit of this state is $\text{C}^+(^2\text{P}^\circ(\text{s}^2\text{p})) + \text{H}(\text{S})$ the same as the $X^1\Sigma^+$ state, and the PEC of the FC-LSE correctly dissociates to this atomic state as absolute energy.

For the $D^1\Pi$ state, the RKR data are not available. Similar to the other states, the total energies of the MRCI were shifted above the FC-LSE energies, but their differences were slightly smaller than those of the other states: 31–34 kcal/mol. The dissociation limit of this state is also ionic to $\text{C}(\text{D}(\text{s}^2\text{p}^2)) + \text{H}^+$ same as the $C^1\Sigma^+$ state and the FC-LSE results correctly dissociate to this atomic state as absolute energy.

Figure 1 illustrates the PECs of the RKR (left), FC-LSE (center), and the MRCI (right) for all of the target states: $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states. The RKR potentials were only available for the $X^1\Sigma^+$ and $A^1\Pi$ states only around the equilibrium distances of these states.¹⁴ The FC-LSE PECs are plotted at more R points than those given in Tables S1 to S4. The PECs of FC-LSE and RKR are located on the same energy level. On the other hand, the PECs of the MRCI were about 34 kcal/mol higher for all of the states, but the relative shapes of the FC-LSE and MRCI PECs were similar. However, when examining precisely in kcal/mol, the differences between the FC-LSE and MRCI were not completely constant but slightly fluctuated from 31 to 41 kcal/mol especially in the small R region.

Figure 2 illustrates the overlapped graphs of the FC-LSE and RKR¹⁴ PECs. To make the comparison between their PECs clearer, we also showed an enlarged graph only for the $X^1\Sigma^+$ and $A^1\Pi$ states where the RKR potentials are available. Thus, the PECs of the FC-LSE show almost perfect correspondence with the RKR for both $X^1\Sigma^+$ and $A^1\Pi$ states without any energy shift. As discussed above, however, the differences between the FC-LSE and RKR PECs around $R = 2.0$ to 2.4 a.u. for the $A^1\Pi$ state were slightly larger than the case around $R = 2.8$ to 3.6 a.u.

The PEC of the $X^1\Sigma^+$ state has an ordinary shape with the bounded energy minimum at $R_{\text{eq}} = 2.137$ a.u., but the $C^1\Sigma^+$ state has two minimums around $R = 2.4$ and 6.4 a.u., respectively. The first minimum is metastable since its energy is higher than the dissociation limit and the second minimum is slightly lower than the dissociation limit, but its depth is very shallow and this state is considered almost dissociative. The PEC of the $A^1\Pi$ state also has a bound energy minimum, but its binding depth is considerably smaller than that of the $X^1\Sigma^+$ state. There are also very shallow minimums around $R = 7.4$ and 6.4 a.u. for the $3^1\Sigma^+$ and $D^1\Pi$ states, respectively, but they are considered as a dissociative curve.

3.C. Spectroscopic Analysis from the PECs. Next, we performed the spectroscopic analysis from the PECs calculated by FC-LSE theory. We first fitted the PECs with eight extended Morse potentials and performed the Dunham's analysis.^{56,57} We computed the equilibrium distance: R_{eq} (Å), vibrational frequency: ω_e (cm^{-1}), absolute energy (au) at R_{eq} with the energy difference from the experimental one: ΔE (kcal/mol), adiabatic excitation energy: T_e (eV), and dissociation energy: D_e (kcal/mol) for each state and summarized their results in Table 4. Note that these quantities depend on fitting and analysis procedures.

For the ground $X^1\Sigma$ state, R_{eq} was 1.1298 Å, which was quite close to those of both the experiment: 1.1309 Å¹⁴ and the MRCI calculation: 1.130 Å.²⁶ ω_e was 2855.21 cm^{-1} , which was also close to the experimental one: 2857.560 cm^{-1} and slightly larger than that of the MRCI: 2851 cm^{-1} . The absolute energies and ΔE at R_{eq} were already discussed in section 3.B and Table 2. D_e was 97.965 kcal/mol, which was also close to the experimental one: 98.248 kcal/mol¹⁷ and that of the MRCI: 97.860 kcal/mol.

Since the $C^1\Sigma^+$ state is not stably bound, the experimental data of the spectroscopic quantities are not available. On the other hand, since there is a local energy minimum in the PEC, R_{eq} , ω_e , and T_e can be computed theoretically. However, we did not discuss ω_e of the $C^1\Sigma^+$ state since ω_e corresponding to a

Table 3. Numerical Data of the PECs by the FC-LSE Theory for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ States of a CH^+ Molecule at Several Specific Points of R at Order $n = 3$ with Dimension $M = 24870$ and 26808 for the $1^1\Sigma^+$ and $1^1\Pi$ Symmetries, Respectively^a

R (a.u.) ^b	$X^1\Sigma^+$ state				$C^1\Sigma^+$ state				$3^1\Sigma^+$ state			
	FC-LSE		FC-LSE		FC-LSE		FC-LSE		FC-LSE		FC-LSE	
	H-square error ^c	energy (a.u.)	ΔE^d [FC-LSE] - [RKR] ^e (kcal/mol)	ΔE^f [MRCI] - [RKR] ^e (kcal/mol)	ΔE^g [MRCI] - [FC-LSE] (kcal/mol)	H-square error ^c	energy (a.u.)	ΔE^g [MRCI] - [FC-LSE] (kcal/mol)	H-square error ^c	energy (a.u.)	ΔE^g [MRCI] - [FC-LSE] (kcal/mol)	H-square error ^c
1.2	0.071 185	-37.698 534		35.491	0.178 053	-37.350 912	35.250	0.606 652	-37.131 360	41.087		
1.8	0.054 310	-38.064 414	-0.185	34.531	0.145 096	-37.745 052	34.583	0.308 127	-37.534 381	36.028		
2.137	0.049 269	-38.086 831	0.481	34.204	0.141 880	-37.785 450	34.135	0.161 012	-37.593 832	33.275		
2.4	0.046 455	-38.078 905	0.632	34.119	0.141 540	-37.792 408	34.067	0.121 499	-37.624 564	32.859		
2.8	0.042 663	-38.052 420	0.607	34.133	0.133 267	-37.787 632	33.550	0.090 386	-37.660 544	33.483		
3.6	0.036 978	-37.997 058		34.037	0.098 787	-37.774 855	32.896	0.061 009	-37.710 022	33.908		
4.0	0.034 807	-37.976 384		33.998	0.081 476	-37.776 772	33.215	0.055 074	-37.726 566	33.903		
5.0	0.028 706	-37.946 061		34.055	0.063 852	-37.795 406	33.881	0.042 942	-37.741 895	33.982		
7.0	0.025 315	-37.932 158		34.079	0.064 327	-37.803 162	34.094	0.039 734	-37.746 810	34.892		
10.0	0.025 997	-37.930 925		34.123	0.061 075	-37.798 717	34.088	0.032 095	-37.746 361	35.007		
∞		-37.930 769 ^b	0.164	34.297		-37.797 062 ^f	34.449		-37.746 269 ^f	35.247		
R (a.u.) ^b	$A^1\Pi$ state				$D^1\Pi$ state				$D^1\Pi$ state			
	FC-LSE		FC-LSE		FC-LSE		FC-LSE		FC-LSE		FC-LSE	
	H-square error ^c	energy (a.u.)	ΔE^d [FC-LSE] - [RKR] ^e (kcal/mol)	ΔE^f [MRCI] - [RKR] ^e (kcal/mol)	ΔE^g [MRCI] - [FC-LSE] (kcal/mol)	H-square error ^c	energy (a.u.)	ΔE^g [MRCI] - [FC-LSE] (kcal/mol)	H-square error ^c	energy (a.u.)	ΔE^g [MRCI] - [FC-LSE] (kcal/mol)	H-square error ^c
1.2	0.231 998	-37.560 944			33.418	0.841 301	-37.035 441	31.696				
1.8	0.132 077	-37.938 976			33.636	0.401 219	-37.489 050	31.266				
2.137	0.101 993	-37.972 499	1.344	35.129	33.785	0.340 655	-37.576 160	31.365				
2.4	0.086 173	-37.975 670	1.134	34.998	33.864	0.261 213	-37.623 877	31.849				
2.8	0.069 944	-37.968 760	0.944	34.805	33.861	0.164 073	-37.683 702	32.693				
3.6	0.053 148	-37.952 459	0.674	34.549	33.875	0.092 617	-37.753 129	33.492				
4.0	0.048 758	-37.946 715			33.885	0.081 744	-37.771 175	33.596				
5.0	0.041 208	-37.937 512			33.846	0.075 901	-37.793 772	33.693				
7.0	0.037 703	-37.931 771			33.969	0.077 500	-37.800 229	33.948				
10.0	0.036 594	-37.930 658			33.947	0.078 370	-37.797 737	34.038				
∞		-37.930 769 ^b	0.164	34.297	34.133		-37.797 062 ^f	34.449				

^aThey are compared to the RKR and MRCI results. More detailed tables are given in Tables S1 to S4 in Supporting Information. ^bInternuclear distance between C and H. ^cDefined in ref 31. ^dEnergy differences of the FC-LSE energies from the experimental RKR energies. Boldface means satisfying chemical accuracy, i.e., $|\Delta E| < 1$ kcal/mol. ^eRKR potential data (relative energies) were extracted from ref 14 and interpolated by a spline fitting. The absolute total energy of the RKR potential at $R_{eq} = 2.137$ a.u. of $X^1\Sigma^+$ was estimated as given in footnote f in Table 2. ^fEnergy differences of the MRCI reference energies, interpolated by a spline fitting, of ref 26 from the experimental RKR energies. ^gEnergy differences of the MRCI reference energies, interpolated by a spline fitting, of ref 26 from the FC-LSE energies. ^hAtom energy of the ground state of $C^+(2p^2)$ shown in Table 1 and that of $H(2s)$: -0.5 a.u. ⁱAtom energy of the ground state of $C(1D)$ shown in Table 1. ^jAtom energy of the ground state of $C(1S)$ shown in Table 1.

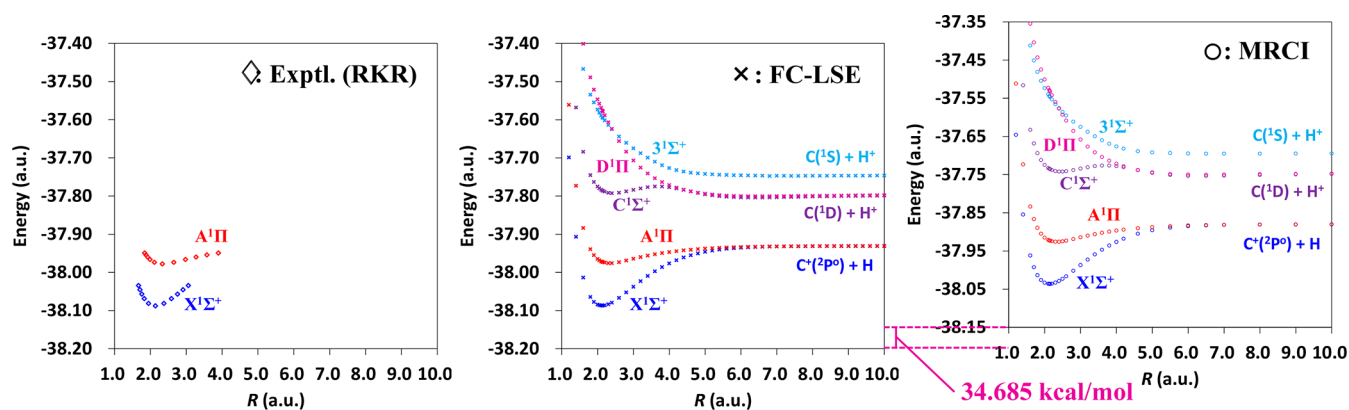


Figure 1. PECs for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states of a CH^+ molecule by the experimental RKR potentials (left),¹⁴ the FC-LSE theory (center), and the MRCI method (right).²⁶

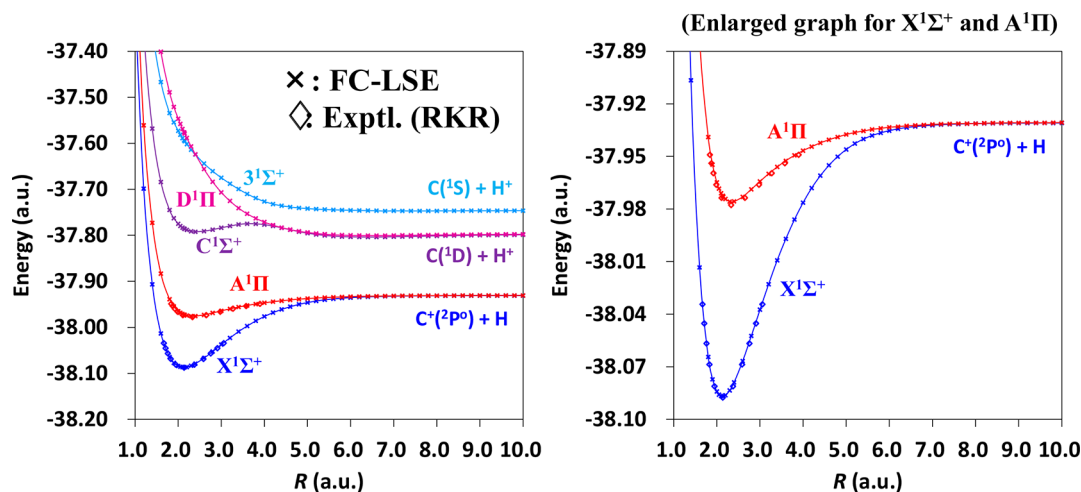


Figure 2. PECs overlapped with the FC-LSE results and the experimental RKR potentials¹⁴ for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states of a CH^+ molecule. Right-side figure shows the enlarged graph for the $X^1\Sigma^+$ and $A^1\Pi$ states.

Table 4. Some Spectroscopic Data Associated to the PECs of the FC-LSE Theory for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ States of a CH^+ Molecule, Compared to Those Quantities by the Experiments and the MRCI Method

state	method	equilibrium distance R_{eq} (Å)	vibrational frequency ω_e (cm ⁻¹)	absolute energy (a.u.) at R_{eq}	ΔE^b (kcal/mol)	adiabatic excitation energy T_e (eV)	dissociation energy D_e (kcal/mol)
$X^1\Sigma^+$	FC-LSE (this work) ^c	1.1298	2855.21	-38.086 831	0.481		97.965
	Exptl. ^d	1.1308843	2857.560	-38.087 598			98.248 ^e
	MRCI ^f	1.130	2851	-38.032 324	34.685		97.860
$C^1\Sigma^+$	FC-LSE (this work) ^c	1.2970	^g	-37.793 097		7.9929	Dissociative
	MRCI ^f	1.296	^g	-37.738 249		8.0022	
$3^1\Sigma^+$							Dissociative
$A^1\Pi$	FC-LSE (this work) ^c	1.2404	1825.26	-37.975 756	1.224	3.0225	28.264
	Exptl. ^d	1.235053	1864.402	-37.977 706		2.9903	29.460 ^e
	MRCI ^f	1.239	1819	-37.921 896	35.021	3.0049	28.569
$D^1\Pi$							Dissociative

^aCalculated with the absolute energies of the $X^1\Sigma^+$ state and the adiabatic excitation energies. ^bEnergy differences of the FC-LSE or reference energies from the estimated exact energy given in the footnote f in Table 2. ^cResults at order $n = 3$. ^dRef 14. ^eRef 17. ^fRef 26. ^gWe do not discuss this quantity since it may be sensitive to fitting and/or analysis methods.

complicated PEC might be more sensitive to fitting or analysis methods. The FC-LSE values of R_{eq} and T_e were 1.2970 Å and 7.9929 eV, respectively, and they were close to the MRCI values: 1.296 and 8.0022 eV. D_e could not be computed due to the dissociative character of this state.

For the $A^1\Pi$ state, R_{eq} by the FC-LSE was 1.2404 Å, which was slightly larger than the experimental value: 1.235053 Å with 0.005 difference, but almost quite close to the MRCI case: 1.239 Å. ω_e by the FC-LSE was 1825.26 cm⁻¹, which was also moderately close to the MRCI case: 1819 cm⁻¹ with a 6 cm⁻¹

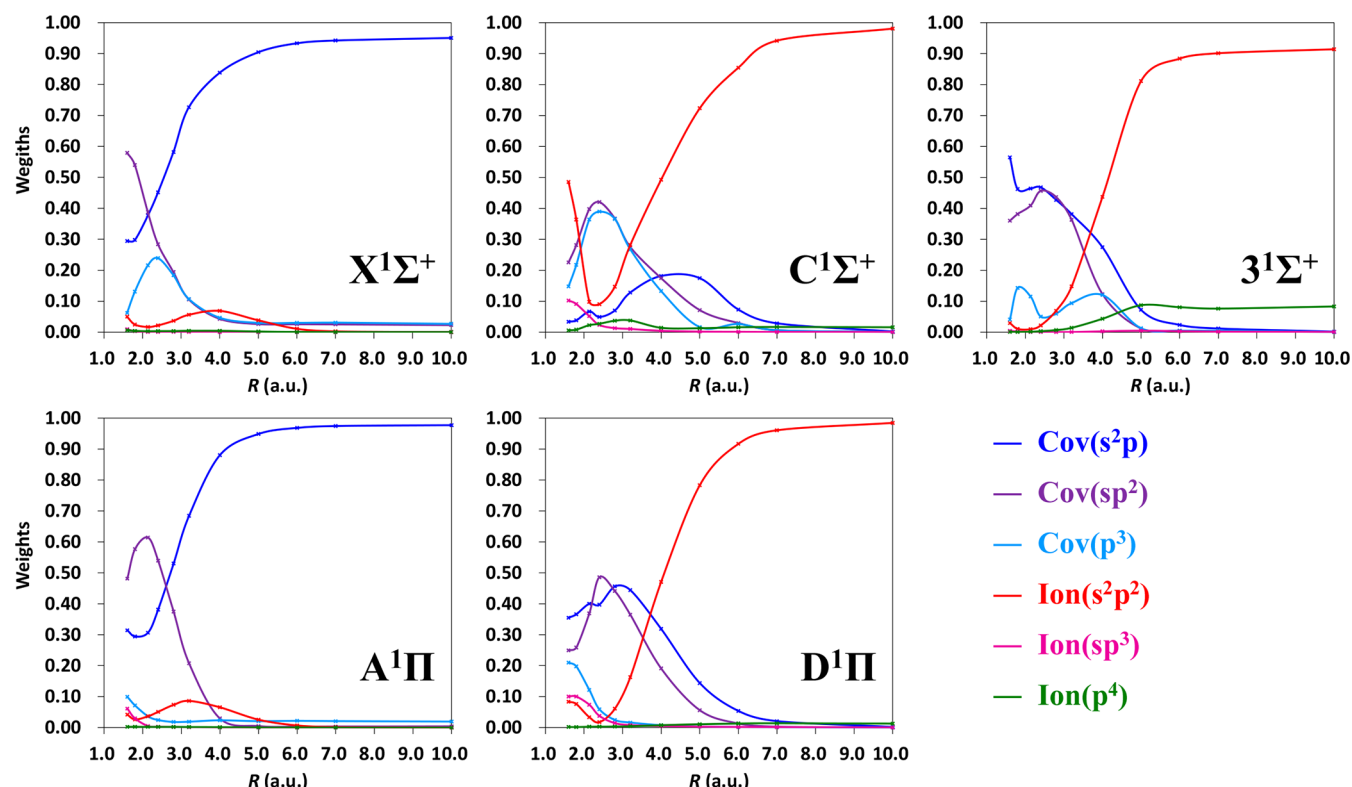


Figure 3. Rough plots of the inverse overlap weights (IOW) w_k in eq 11 of six CFT groups defined in eq 1a or 4a for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states of a CH^+ molecule, analyzed from the calculated FC-LSE wave functions at order $n = 3$.

difference, but about 39 cm^{-1} smaller than the experimental one: 1864.402 cm^{-1} . ΔE values of the absolute energy at R_{eq} were 1.224 and 35.021 kcal/mol for the FC-LSE theory and the MRCI method, respectively. Thus, the latter one was far from the correct absolute energy. The former one was slightly overestimated from the experimental one because the experimental results may include some physical effects beyond the BO approximation of theoretical calculations as discussed in section 3.B. T_e by the FC-LSE was 3.0225 eV, which was almost close to the experimental one: 2.9903 eV and the MRCI case: 3.0049 eV. Similarly, D_e was 28.264 kcal/mol and almost identical with the experiment: 29.460 kcal/mol and the MRCI case: 28.569 kcal/mol.

Referring to Table 4 again, we note that the agreements between the FC-LSE and the experiments are impressively accurate, when both data exist, in comparison with those seen in the comparisons of the conventional quantum chemistry calculations with the experiments. No spectroscopic data were calculatable for the $3^1\Sigma^+$ and $D^1\Pi$ states, since the PECs of these states were repulsive.

3.D. Analysis of the Wave Functions Using the Inverse Overlap Weights with Grouping the CFT Configurations.

According to the scheme given in section 2.D, we computed the IOWs of the calculated FC-LSE wave functions at order $n = 3$ with grouping the CFT configurations. Table S5 in Supporting Information summarizes the numerical values of the weights of six CFT groups in eq 1a or 4a, i.e., $\text{Cov}(s^2p)$, $\text{Cov}(sp^2)$, $\text{Cov}(p^3)$, $\text{Ion}(s^2p^2)$, $\text{Ion}(sp^3)$, and $\text{Ion}(p^4)$, for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states at several points of R . Figure 3 shows rough plots of them. Note that since these weights are not physical observables, there were a few points that lost smoothness due to the sampling randomness.

For the ground $X^1\Sigma$ state, the IOW of $\text{Cov}(s^2p)$ was 95.0% at $R = 10.0$ a.u. due to the covalent dissociation. Approaching the equilibrium distance R_{eq} , the weight of $\text{Cov}(s^2p)$ was rapidly decreasing, and on the other hand, those of $\text{Cov}(sp^2)$ and $\text{Cov}(p^3)$ increased. At $R_{\text{eq}} = 2.137$ a.u., they were 37.7%, 38.8%, and 21.6% for the $\text{Cov}(s^2p)$, $\text{Cov}(sp^2)$, and $\text{Cov}(p^3)$ groups, respectively. It implies that the chemical bond of the ground $X^1\Sigma$ state consists of only covalent forms. The local atomic excited configurations, $\text{Cov}(sp^2)$ and $\text{Cov}(p^3)$, were important for creating chemical bonds with the main $\text{Cov}(s^2p)$ configuration. The ionic configurations were always small except for the intermediate region where only the $\text{Ion}(s^2p^2)$ structure contributed with the weight 6.8% at $R = 4.0$ a.u.

For the $C^1\Sigma^+$ state that ionically dissociates, the most dominant amplitude at $R = 10.0$ a.u. was 98.1% of $\text{Ion}(s^2p^2)$. Around the local minimum $R_{\text{eq}} = 2.4$ a.u.; however, the weight of $\text{Ion}(s^2p^2)$ became only 9.0%. Here, the weight of $\text{Cov}(s^2p)$ was also quite small: 4.9%, and the most dominant ones were rather $\text{Cov}(sp^2)$ and $\text{Cov}(p^3)$, i.e., the covalent excited configurations. The PEC of this state has an energy barrier around $R = 4.0$ a.u. In this intermediate region, the weight of $\text{Cov}(s^2p)$ temporarily increased to 18.1%. Thus, the electronic structures of this state drastically changed from dissociation to equilibrium with a charge-transfer-type bond creation from C to C^+ .

For the $3^1\Sigma^+$ state, the most dominant amplitude at $R = 10.0$ a.u. was 91.4% of $\text{Ion}(s^2p^2)$ the same as the $C^1\Sigma^+$ state. The weight of $\text{Ion}(s^2p^2)$, however, was rapidly decreasing with decreasing R . On the other hand, those of $\text{Cov}(s^2p)$ and $\text{Cov}(sp^2)$ increased in the small R region. This tendency was slightly different from that of the $C^1\Sigma^+$ case, where the weight of $\text{Cov}(s^2p)$ was small in this region. Since the PEC of this state is monotonically repulsive, no further drastic changes were observed.

For the $A^1\Pi$ state, the tendency was similar to the $X^1\Sigma^+$ state because the dissociation limit of this state is $C^+(^2P^o(s^2p)) + H(^1S)$, the same as the $X^1\Sigma^+$ state. The weight of $Cov(s^2p)$ at $R = 10.0$ a.u., therefore, was 97.7%, but it was rapidly decreasing with decreasing R . Instead, near the equilibrium distance R_{eq} , the weight of $Cov(sp^2)$ became large and it was 54.0% at $R = 2.4$ a.u., but that of $Cov(p^3)$ was little different from the $X^1\Sigma^+$ case. From this reason, the chemical bond of the $A^1\Pi$ state would be smaller than that of the $X^1\Sigma^+$ state.

The situation of the $D^1\Pi$ state was also quite similar to that of the $3^1\Sigma^+$ case since the PECs of both states are repulsive. The weight of $Ion(s^2p^2)$ at $R = 10.0$ a.u. was 98.5% and it rapidly decreased as decreasing R . The dominant contributions in the small R region were $Cov(s^2p)$ and $Cov(sp^2)$, the same as the $3^1\Sigma^+$ case.

3.E. Computational Costs of the Present FC-LSE Calculations. Finally, we briefly summarize the computational costs of the present FC-LSE calculations. We mainly used the superparallel computers with the 3000 cores at the Institute of Molecular Sciences (IMS), Okazaki, Japan. A single-point present FC-LSE calculation consists of the following steps: (a) generating FC wave functions,²⁹ (b) generating sampling points by the DLS scheme,³⁷ (c) LSE calculations by the HS method and diagonalization,^{30,31} and (d) analysis of the wave function given in section 2.D. For the $^1\Sigma^+$ symmetry ($M = 24870$, $X^1\Sigma^+$, $C^1\Sigma^+$, and $3^1\Sigma^+$ states) and the $^1\Pi$ symmetry ($M = 26808$, $A^1\Pi$ and $D^1\Pi$ states), these steps at a single point $R = 2.137$ a.u. took (a) 18.3 and 32.5 min, (b) 51.5 and 64.3 min, (c) 92.6 and 102.3 min, and (d) 2.4 and 2.9 min, respectively, i.e., totally, 164.8 min (2.7 h) and 202.0 min (3.4 h), respectively. Time consuming steps are steps (b) and (c), but they were efficiently parallelized due to the sampling scheme.

4. CONCLUSIONS

We performed the FC-LSE calculations with the DLS scheme for the ground $X^1\Sigma^+$ and four low-lying excited $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states of a CH^+ molecule. We constructed the initial functions according to the CFT. The $X^1\Sigma^+$ and $A^1\Pi$ states show covalent dissociations to the $C^+(^2P^o(s^2p)) + H(^1S)$. The $C^1\Sigma^+$ and $D^1\Pi$ states ionically dissociate to $C(^1D(s^2p^2)) + H^+$, and the $3^1\Sigma^+$ state also ionically dissociates to $C(^1S(s^2p^2)) + H^+$. All the PECs were smoothly and very accurately calculated up to the dissociation limits with not only their relative shapes but also their absolute energies satisfying chemical accuracies. When compared with the experimental RKR potentials available only for the $X^1\Sigma^+$ and $A^1\Pi$ states around R_{eq} , the PECs of the FC-LSE theory almost completely overlapped with the RKR potentials without any energy shift. They also relatively agreed with the energy-shifted MRCI PECs for all the target states. By the spectroscopic analysis from the PECs, the equilibrium distance R_{eq} , the vibrational frequency ω_e , the adiabatic excitation energy T_e , and the dissociation energy D_e of the target states showed good agreement with the experimental and MRCI reference data.

To analyze the chemical bonds of the target states, we also computed the IOWs by Gallup et al. with grouping the CFT configurations. At sufficiently large R , the largest amplitudes corresponded to the atomic states of the dissociation limits. On the other hand, in small R regions, i.e., bonding regions, the most dominant configurations drastically changed in all the target states and especially covalent excited configurations were crucially important for chemical bonds. These tendencies

imply the importance of the CFT concept “from atomic states to molecular states”.

Thus, the present study numerically proved, together with the previous study for the nine valence states of the Li_2 molecule,⁴⁰ that the FC-LSE theory using the DLS scheme could calculate the accurate PECs correct as absolute energy within chemical accuracies with chemically understandable compact wave functions based on the CFT. The present CH^+ is one of the most important molecules in astrochemistry and the present FC-LSE theory would be also applicable to various studies where reliable and accurate quantum mechanical theoretical calculations are required.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.3c00645>.

Numerical data of the PECs by the FC-LSE theory for the $X^1\Sigma^+$, $C^1\Sigma^+$, $3^1\Sigma^+$, $A^1\Pi$, and $D^1\Pi$ states of a CH^+ molecule, compared to the experimental RKR potentials and those by the reference theoretical calculations by the MRCI method. Numerical data of the IOW analysis. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Hiroyuki Nakashima – Quantum Chemistry Research Institute, Kyoto 606-8305, Japan; orcid.org/0000-0002-3758-5159; Email: h.nakashima@qcri.or.jp

Hiroshi Nakatsuji – Quantum Chemistry Research Institute, Kyoto 606-8305, Japan; orcid.org/0000-0002-8162-3220; Email: h.nakatsuji@qcri.or.jp

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jctc.3c00645>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the computer centers of the Research Center for Computational Science, Okazaki, Japan for their generous supports and encouragements to our research project (Project: 22-IMS-C012). We also used partially the computational resources of the SQUID at the Cybermedia Center, Osaka University, Osaka, Japan through the HPCI System Research Project (Project ID: hp220091). This work was also supported by JSPS KAKENHI grant numbers 22H02045 and 23H01930.

■ REFERENCES

- (1) Dunham, T. Interstellar neutral potassium and neutral calcium. *Publ. Astron. Soc. Pac.* **1937**, *49*, 26.
- (2) Douglas, A. E.; Herzberg, G. Note on CH^+ in interstellar space and in the laboratory. *Astrophys. J.* **1941**, *94*, 381.
- (3) Douglas, A. E.; Herzberg, G. Band spectrum and structure of the CH^+ molecule; identification of three interstellar lines. *Can. J. Res. A* **1942**, *20*, 71.
- (4) Adams, W. S. Some results with the COUDÉ spectrograph of the Mount Wilson observatory. *Astrophys. J.* **1941**, *93*, 11.
- (5) Solomon, P. M.; Klemperer, W. The formation of diatomic molecules in interstellar clouds. *Astrophys. J.* **1972**, *178*, 389.
- (6) Cosby, P. C.; Helm, H.; Moseley, J. T. Observation of predissociated levels of CH^+ . *Astrophys. J.* **1980**, *235*, 52.

- (7) Sternberg, A.; Dalgarno, A. Chemistry in dense photon-dominated regions. *Astrophys. J. Suppl. Ser.* **1995**, *99*, 565.
- (8) Godard, B.; Cernicharo, J. A complete model of CH^+ rotational excitation including radiative and chemical pumping processes. *Astron. Astrophys.* **2013**, *550*, A8.
- (9) Oka, T.; Welty, D. E.; Johnson, S.; York, D. G.; Dahlstrom, J.; Hobbs, L. M. Anomalous diffuse interstellar bands in the spectrum of Herschel 36. II. Analysis of radiatively excited CH^+ , CH , and diffuse interstellar bands. *Astrophys. J.* **2013**, *773*, 42.
- (10) Read, S. M.; Vanderslice, J. T.; Jenč, F. Potential Curves for BeH^+ and CH^+ . *J. Chem. Phys.* **1962**, *37*, 205.
- (11) Elander, N.; Oddershede, J.; Beebe, N. H. F. On the $\text{A}^1\Pi\text{-X}^1\Sigma^+$ band system in CH^+ and CD^+ : Theoretical spectroscopic constants and life times. *Astrophys. J.* **1977**, *216*, 165.
- (12) Helm, H.; Cosby, P. C.; Graff, M. M.; Moseley, J. T. Photofragment spectroscopy of CH^+ : Laser excitation of shape. *Phys. Rev. A* **1982**, *25*, 304.
- (13) Hechtfisher, U.; Williams, C. J.; Lange, M.; Linkemann, J.; Schwalm, D.; Wester, R.; Wolf, A.; Zajfman, D. Photodissociation spectroscopy of stored CH^+ ions: Detection, assignment, and close-coupled modeling of near-threshold Feshbach resonances. *J. Chem. Phys.* **2002**, *117*, 8754.
- (14) Hakalla, R.; Kępa, R.; Szajna, W.; Zachwieja, M. New analysis of the Douglas-Herzberg system ($\text{A}^1\Pi\text{-X}^1\Sigma^+$) in the CH^+ ion radical. *Eur. Phys. J. D* **2006**, *38*, 481.
- (15) Hechtfisher, U.; Rostas, J.; Lange, M.; Linkemann, J.; Schwalm, D.; Wester, R.; Wolf, A.; Zajfman, D. Photodissociation spectroscopy of stored CH^+ and CD^+ ions: Analysis of the $\text{b}^3\Sigma^-\text{-a}^3\Pi$ system. *J. Chem. Phys.* **2007**, *127*, 204304.
- (16) Amano, T. The $J = 1-0$ transitions of $^{12}\text{CH}^+$, $^{13}\text{CH}^+$, and $^{12}\text{CD}^+$. *Astrophys. J. Lett.* **2010**, *716*, L1.
- (17) Cho, Y.; Le Roy, R. J. Full empirical potential curves for the $\text{X}^1\Sigma^+$ and $\text{A}^1\Pi$ states of CH^+ from a direct-potential-fit analysis. *J. Chem. Phys.* **2016**, *144*, 024311.
- (18) Chakrabarti, K.; Dora, A.; Ghosh, R.; Choudhury, B. S.; Tennyson, J. R-matrix study of electron impact excitation and dissociation of CH^+ ions. *J. Phys. B: At. Mol. Opt. Phys.* **2017**, *50*, 175202.
- (19) Falgarone, E.; Zwaan, M. A.; Godard, B.; Bergin, E.; Ivison, R. J.; Andreani, P. M.; Bounaud, F.; Bussmann, R. S.; Elbaz, D.; Omont, A.; Oteo, I.; Walter, F. Large turbulent reservoirs of cold molecular gas around high-redshift starburst galaxies. *Nature* **2017**, *548*, 430.
- (20) Saxon, R. P.; Kirby, K.; Liu, B. Excited states of CH^+ : Potential curves and transition moments. *J. Chem. Phys.* **1980**, *73*, 1873.
- (21) Koch, H.; Jensen, H. J. Aa.; Jo/rgensen, P.; Helgaker, T. Excitation energies from the coupled cluster singles and doubles linear response function (CCSDLR). Applications to Be, CH^+ , CO, and H_2O . *J. Chem. Phys.* **1990**, *93*, 3345.
- (22) Kanzler, A. W.; Sun, H.; Freed, K. F. Dipole moments, transition moments, oscillator strengths, radiative lifetimes, and overtone intensities for CH and CH^+ as computed by quasi-degenerate many-body perturbation theory. *Int. J. Quantum Chem.* **1991**, *39*, 269.
- (23) Szalay, P. G.; Müller, T.; Lischka, H. Excitation energies and transition moments by the multireference averaged quadratic coupled cluster (MR-AQCC) method. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2067.
- (24) Temelso, B.; Valeev, E. F.; Sherrill, C. D. A Comparison of one-particle basis set completeness, higher-order electron correlation, relativistic effects, and adiabatic corrections for spectroscopic constants of BH, CH^+ , and NH_3 . *J. Phys. Chem. A* **2004**, *108*, 3068.
- (25) Sauer, S. P. A.; Spirko, V. Effective potential energy curves of the ground electronic state of CH^+ . *J. Chem. Phys.* **2013**, *138*, 024315.
- (26) Biglari, Z.; Shayesteh, A.; Maghari, A. Ab initio potential energy curves and transition dipole moments for the low-lying states of CH^+ . *Comput. Theor. Chem.* **2014**, *1047*, 22.
- (27) Li, Y. Q.; Zhang, P. Y.; Han, K. L. Accurate high level ab initio-based global potential energy surface and dynamics calculations for ground state of CH_2^+ . *J. Chem. Phys.* **2015**, *142*, 124302.
- (28) Guo, L.; Ma, H.; Zhang, L.; Song, Y.; Li, Y. Accurate global potential energy surface for the ground state of CH_2^+ by extrapolation to the complete basis set limit. *RSC Adv.* **2018**, *8*, 13635.
- (29) Nakatsuji, H. Scaled Schrödinger equation and the exact wave function. *Phys. Rev. Lett.* **2004**, *93*, 030403.
- (30) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y.; Ishikawa, A. Solving the Schrödinger equation of atoms and molecules without analytical integration based on the free iterative-complement-interaction wave function. *Phys. Rev. Lett.* **2007**, *99*, 240402.
- (31) Nakatsuji, H.; Nakashima, H. Free-complement local-Schrödinger-equation method for solving the Schrödinger equation of atoms and molecules: Basic theories and features. *J. Chem. Phys.* **2015**, *142*, 084117.
- (32) Nakatsuji, H. Discovery of a general method of solving the Schrödinger and Dirac equations that opens a way to accurately predictive quantum chemistry. *Acc. Chem. Res.* **2012**, *45*, 1480.
- (33) Nakatsuji, H.; Nakashima, H. Solving the Schrödinger equation of molecules by relaxing the antisymmetry rule: Inter-exchange theory. *J. Chem. Phys.* **2015**, *142*, 194101.
- (34) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Solving the Schrödinger equation of atoms and molecules: Chemical-formula theory, free-complement chemical-formula theory, and intermediate variational theory. *J. Chem. Phys.* **2018**, *149*, 114105.
- (35) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Solving the Schrödinger equation of atoms and molecules with the free-complement chemical-formula theory: First-row atoms and small molecules. *J. Chem. Phys.* **2018**, *149*, 114106.
- (36) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Accurate scaling functions of the scaled Schrödinger equation. *J. Chem. Phys.* **2022**, *156*, 014113.
- (37) Nakatsuji, H.; Nakashima, H. Direct local sampling method for solving the Schrödinger equation with the free complement - local Schrödinger equation theory. *Chem. Phys. Lett.* **2022**, *806*, 140002.
- (38) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. Equation of state calculations by fast computing machines. *J. Chem. Phys.* **1953**, *21*, 1087.
- (39) Hastings, W. K. Monte Carlo sampling methods using Markov chains and their applications. *Biometrika* **1970**, *57*, 97.
- (40) Nakatsuji, H.; Nakashima, H. Potential curves of the lower nine states of Li_2 molecule: Accurate calculations with the free complement theory and the comparisons with the SAC/SAC-CI results. *J. Chem. Phys.* **2022**, *157*, 094109.
- (41) Rydberg, R. Graphische darstellung einiger bandenspektroskopischer ergebnisse. *Z. Phys.* **1932**, *73*, 376.
- (42) Klein, O. Zur Berechnung von potentialkurven für zweiatomige moleküle mit hilfe von spektraltermen. *Z. Phys.* **1932**, *76*, 226.
- (43) Rees, A. L. G. The calculation of potential-energy curves from band-spectroscopic data. *Proc. Phys. Soc.* **1947**, *59*, 998.
- (44) Gallup, G. A.; Norbeck, J. M. Population analyses of valence-bond wavefunctions and BeH_2 . *Chem. Phys. Lett.* **1973**, *21*, 495.
- (45) Moore, C. E. Atomic Energy Levels: As Derived from the Analyses of Optical Spectra; National Bureau of Standards, GPO: Washington, D.C., 1952; Vol. I, pp 227.
- (46) See <https://physics.nist.gov/> for NIST Atomic Spectra Database.
- (47) Nakatsuji, H.; Nakashima, H. Free complement s_{ij} -assisted r_{ij} theory applied to the $^2\text{P}^\circ$ and ^4P states of boron atom: Accurate variational calculations with Slater functions; In preparation.
- (48) Chirgwin, B. H.; Coulson, C. A. The electronic structure of conjugated systems. VI. *Proc. R. Soc. A* **1950**, *201*, 196.
- (49) Löwdin, P.-O. On the Non-orthogonality problem connected with the use of atomic wave functions in the theory of molecules and crystals. *J. Chem. Phys.* **1950**, *18*, 365.
- (50) Maldonado, P.; Sarsa, A.; Buendía, E.; Gálvez, F. J. Quantum Monte Carlo ground state energies for the singly charged ions from Li through Ar. *J. Chem. Phys.* **2010**, *133*, 064102.
- (51) Chakravorty, S. J.; Gwaltney, S. R.; Davidson, E. R.; Parpia, F. A.; Fischer, C. F. Ground-state correlation energies for atomic ions with 3 to 18 electrons. *Phys. Rev. A* **1993**, *47*, 3649.

- (52) Seth, P.; Ríos, P. L.; Needs, R. J. Quantum Monte Carlo study of the first-row atoms and ions. *J. Chem. Phys.* **2011**, *134*, 084105.
- (53) Maldonado, P.; Sarsa, A.; Buendía, E.; Gálvez, F. J. Jastrow correlated and quantum Monte Carlo calculations for the low-lying states of the carbon atom. *J. Chem. Phys.* **2011**, *134*, 134102.
- (54) Bubin, S.; Adamowicz, L. Accurate variational calculations of the ground $^2P^{\circ}(1s^22s^22p)$ and excited $^2S(1s^22s2p^2)$ and $^2P^{\circ}(1s^22s^23p)$ states of singly ionized carbon atom. *J. Chem. Phys.* **2011**, *135*, 214104.
- (55) Strasburger, K. Explicitly correlated wave functions of the ground state and the lowest quintuplet state of the carbon atom. *Phys. Rev. A* **2019**, *99*, 052512.
- (56) Dunham, J. L. The Wentzel-Brillouin-Kramers method of solving the wave equation. *Phys. Rev.* **1932**, *41*, 713.
- (57) Dunham, J. L. The energy levels of a rotating vibrator. *Phys. Rev.* **1932**, *41*, 721.