

Solving non-Born–Oppenheimer Schrödinger equation for hydrogen molecular ion and its isotopomers using the free complement method

Yuh Hijikata, Hiroyuki Nakashima, and Hiroshi Nakatsuji^{a)}

Quantum Chemistry Research Institute and JST CREST, Kyodai Katsura Venture Plaza 106, Goryo Oohara 1-36, Nishikyo-ku, Kyoto 615-8245, Japan and Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

(Received 30 October 2008; accepted 24 November 2008; published online 8 January 2009)

The Schrödinger equations for the hydrogen molecular ion (H_2^+) and its isotopomers (D_2^+ , T_2^+ , HD^+ , HT^+ , and DT^+) were solved very accurately using the free iterative complement interaction method, which is referred to in short as the free complement (FC) method, in the non-Born–Oppenheimer (non-BO) level, i.e., in the nonrelativistic limit. Appropriate complement functions for both electron and nuclei were generated automatically by the FC procedure with the use of the non-BO Hamiltonian, which contains both electron and nuclear operators on an equal footing. Quite accurate results were obtained not only for the ground state but also for the vibronic excited states. For example, we obtained the ground-state energy of H_2^+ as **−0.597 139 063 123 405 074 834 134 096 025 974 142** a.u., which is variationally the best in literature. The difference in the nuclear spin states of 1S (para) and 3P (ortho) of H_2^+ and some physical expectation values for several of the isotopomers shown above were also examined. The present study is the first application of the FC method to molecular systems with the non-BO Hamiltonian. © 2009 American Institute of Physics. [DOI: [10.1063/1.3048986](https://doi.org/10.1063/1.3048986)]

I. INTRODUCTION

The Born–Oppenheimer (BO) approximation¹ is quite a useful approximation in chemistry because it enables the definition of potential energy surfaces on which the constituent nuclei undergo chemical reactions and molecular vibrations. The BO approximation is good when nuclei are heavy. However, the quantum effects of nuclear motion become significant for light elements and must be considered to reproduce real experimental results to high accuracy,^{2–11} for example, in the proton transfer and proton exchange in chemical and biological reactions, in proton tunneling phenomena, and in detailed analysis of the coupling of the vibrational, rotational, and electronic motions. The exact wave function for the non-BO Hamiltonian couples the vibrational and rotational modes with the electronic wave function and one cannot exactly separate these motions in general: we have to deal with electrons and nuclei efficiently at the same level.

Recently, we have developed the free iterative complement interaction (ICI) method, which is referred to here in short as the free complement (FC) method, as a general method to solve very accurately the Schrödinger equation (SE) and relativistic Dirac–Coulomb equation (DCE).^{12–16} The method has been applied to various atoms and molecules and gave very accurate results,^{17–21} particularly for H_2^+ ,²⁰ the helium atom,^{19,21,22} and the hydrogen molecule.¹⁸ The

applications were not only limited to the ground state but could also be used for excited states²² and also for the three-body helium atomic system with the nucleus in motion.^{22,23} However, it has not yet been applied to a molecular system with the non-BO Hamiltonian. The purpose of this article is to perform non-BO calculations for the hydrogen molecular ion H_2^+ and its isotopomers, the simplest possible molecules, with the FC methodology.

The H_2^+ ion is important as one of the astronomical interstellar molecules.²⁴ In optical physics and electron scattering theories, the dissociation of a hydrogen molecule from two-electron resonance excited states produces the H_2^+ ion, which is a key molecule but unstable and only has a short lifetime.^{25–27} Because the proton is the lightest nucleus, the quantum effect of nuclear motion could be significant for the H_2^+ ion.

In the BO approximation, the exact form of the wave function of H_2^+ was proposed by Wind²⁸ in elliptic coordinates, but there is no exact solution for the non-BO Hamiltonian because of the existence of the proton-proton two-body correlation with the electron-proton correlations. H_2^+ is a typical three-body Coulomb system, such as the helium atom and the positronium-negative ion (Ps^-). However, it should have a quite different nature from that of helium and Ps^- , although their Hamiltonians have the same form except for the differences in the charges and masses of the particles. High precision calculations of H_2^+ with the non-BO Hamiltonian were performed by several authors.^{29–36} In particular, Cassar and Drake³² reported in 2004 very accurate results with the double exponent basis set expressed as

^{a)}Author to whom correspondence should be addressed. Electronic mail: h.nakatsuji@qcri.or.jp.

$$\psi = \sum_{p=1}^2 \sum_{i,j=0}^{\Omega_1} \sum_{k=\Omega_{\text{low}}}^{\Omega_{\text{high}}} c^{(p,i,j,k)} r_1^i r_2^j R^k \exp(-\alpha^{(p)} r_1 - \beta^{(p)} r_2 - \gamma^{(p)} R) \cdot Y_{L,M}^{l_1,l_2}(\mathbf{r}_1, \mathbf{r}_2) \pm (1 \leftrightarrow 2), \quad (1)$$

where the interparticle coordinates (r_1, r_2, R) were employed with the distances of one proton to the electron, the other proton to the electron, and proton to proton, respectively, and $Y_{L,M}^{l_1,l_2}(\mathbf{r}_1, \mathbf{r}_2)$ are the vector-coupled spherical harmonics with quantum numbers (L, M, l_1, l_2) for the spatial angular momentum derived by Schwartz.³⁷ The other parameters shown in Eq. (1) were given in their paper.³² In their basis function, the R coordinate, $\exp(-\gamma R)$, and very high powers of R^k were introduced, in which Ω (maximum number of k) was a very large number around 40 and γ was optimized around 20.³² They concluded that these forms and numbers would be essential to well represent the vibronic motions of nuclei. Actually, as expected from the BO approximation, the proton-proton distance should be steadily fixed at the equilibrium position of the vibration (for example, almost 2.0 a.u. for the 1S state). The function $R^{40} \exp(-20R)$ has a maximum peak at $R=2.0$ (a.u.) and the shape of the function resembles the Gaussian function, which is the exact wave function of the harmonic oscillator. Although their basis functions showed very rapid convergence to the exact solution, it is difficult to handle and generalize their functions for general molecules because their functions are too arbitrary and complicated.

Recently, Li *et al.*³³ reported the most accurate calculations of H_2^+ with a large number of basis functions (8381 functions), which are written as

$$\psi = \sum_{(i,j,k)} c^{(i,j,k)} r_1^i r_2^j R^k \exp(-\alpha^{(p)} r_1 - \gamma^{(p)} R) \cdot Y_{L,M}^{l_1,l_2}(\mathbf{r}_1, \mathbf{r}_2) \pm (1 \leftrightarrow 2), \quad (2)$$

where R^k also has very high power ($k \geq 35$), similar to the calculations by Cassar and Drake.³³ They used eight different blocks for the nonlinear parameters of $\alpha^{(p)}$ and $\gamma^{(p)}$ to accelerate convergence.³³ The ground-state energy they reported was correct to over 30 digits in accuracy.

Employing the Slater function not only for the r coordinates but also for the R coordinate may cause some arguments. The Slater-type function $\exp(-\gamma R)$ might be appropriate from the cusp condition for the two protons, but the probability of two-proton collision is expected to be much smaller than that of electron-proton collision. This function would also describe the asymptotic behavior when $R \rightarrow \infty$

and has the benefit of easy integration. However, from a simple intuition based on the BO description of the nuclear motion (vibration), it would be physical, at first approximation, to use the Gaussian function $\exp(-\gamma(R-R_e)^2)$, where R_e is a nonlinear variational parameter that should become close to the value of the equilibrium distance in the BO picture. For this reason, we want to employ the Gaussian function $\exp(-\gamma(R-R_e)^2)$ in our initial function for the FC calculations. It is familiar to chemists and so can be easily extended to more complicated systems.

Recently, Bubin and co-workers³⁴⁻³⁶ studied charge asymmetry and some other interesting properties of HD^+ and HT^+ over a wide range of vibrational states with the explicitly correlated Gaussian function method.

In this paper, we report the FC calculations to obtain not only the ground state but also the vibronic excited states of H_2^+ . We also examine the difference of the nuclear spin states of 1S (ortho) and 3P (para). Further, we report the calculations for the isotopomers of H_2^+ , i.e., D_2^+ , T_2^+ , HD^+ , HT^+ , and DT^+ . Some physical expectation values are also reported and discussed.

II. FORMULATION AND COMPUTATIONS

We want to solve the Schrödinger equation for the hydrogen molecule ion and its isotopomers with the non-BO Hamiltonian. The non-BO Hamiltonian for a general atomic or molecular system is written as

$$H = - \sum_i \frac{1}{2m_e} \nabla_i^2 - \sum_A \frac{1}{2m_A} \nabla_A^2 + \sum_i \sum_A \frac{Z_e Z_A}{r_{iA}} + \sum_i \sum_{i < j} \frac{Z_e Z_e}{r_{ij}} + \sum_A \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}, \quad (3)$$

where i and A denote electrons and nuclei, m_e and m_A are their masses, and Z_e and Z_A are their charges, respectively. Recently, Harris³⁸ derived a useful expression for the kinetic operator of a few-body problem. After the center-of-mass motion is separated out, the Hamiltonian can be expressed by the interparticle coordinates (r_1, r_2, R) with angular factors. We introduce here the (s, t, R) coordinates, instead of the interparticle coordinate, for the present three-body systems, that is,

$$s = r_1 + r_2, \quad t = r_1 - r_2. \quad (4)$$

This coordinate set is equivalent to the (s, t, u) coordinate set for the helium atom used by Hylleraas.^{19,39} The Hamiltonian of the present system is written in atomic units as

$$H = - \frac{1}{2m_1} \left\{ \frac{\partial^2}{\partial s^2} + \frac{4}{(s+t)} \frac{\partial}{\partial s} + \frac{\partial^2}{\partial t^2} + \frac{4}{(s+t)} \frac{\partial}{\partial t} + \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} + 2 \frac{\partial^2}{\partial s \partial t} + \frac{2(R^2 + st)}{R(s+t)} \frac{\partial^2}{\partial t \partial R} + \frac{2(R^2 + st)}{R(s+t)} \frac{\partial^2}{\partial R \partial s} \right\} - \frac{2l_1}{m_1(s+t)} \left(\frac{\partial}{\partial s} + \frac{\partial}{\partial t} \right) - \frac{l_1 - \hat{L}^{+-}}{m_1 R} \frac{\partial}{\partial R} - \frac{1}{2m_2} \left\{ \frac{\partial^2}{\partial s^2} + \frac{4}{(s-t)} \frac{\partial}{\partial s} + \frac{\partial^2}{\partial t^2} - \frac{4}{(s-t)} \frac{\partial}{\partial t} + \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} - 2 \frac{\partial^2}{\partial s \partial t} - \frac{2(R^2 - st)}{R(s-t)} \frac{\partial^2}{\partial t \partial R} - \frac{2(R^2 - st)}{R(s-t)} \frac{\partial^2}{\partial R \partial s} \right\} - \frac{2l_2}{m_2(s-t)} \left(\frac{\partial}{\partial s} - \frac{\partial}{\partial t} \right) - \frac{l_2 - \hat{L}^{+-}}{m_2 R} \frac{\partial}{\partial R} - \frac{1}{2m_3} \left\{ \frac{4(s^2 - R^2)}{(s^2 - t^2)} \frac{\partial^2}{\partial s^2} + \frac{8s}{(s^2 - t^2)} \frac{\partial}{\partial s} \right\}$$

$$-\frac{4(l^2 - R^2)}{(s^2 - t^2)} \frac{\partial^2}{\partial t^2} - \frac{8t}{(s^2 - t^2)} \frac{\partial}{\partial t} \left\} - \frac{2(l_1 + \hat{L}^{+-})}{m_3(s+t)} \left(\frac{\partial}{\partial s} + \frac{\partial}{\partial t} \right) - \frac{2(l_2 + \hat{L}^{+-})}{m_3(s-t)} \left(\frac{\partial}{\partial s} - \frac{\partial}{\partial t} \right) + \frac{Z_1 Z_2}{R} + \frac{2Z_2 Z_3}{s-t} + \frac{2Z_1 Z_3}{s+t}, \quad (5)$$

where m_1 , m_2 , and m_3 are the masses of one nucleus, the other nucleus, and an electron (equal to unity in atomic units), respectively. Similarly, $Z_1(=+1)$ and $Z_2(=+1)$ represent the charge of each nucleus and $Z_3(=-1)$ represents the charge of the electron, respectively. The operators \hat{L}^{+-} and \hat{L}^{+-} operate on the solid spherical harmonics $Y_{L,M}^{l_1,l_2}$ as follows:³⁸

$$\hat{L}^{-+} Y_{L,M}^{l_1,l_2} = \sqrt{\frac{(L-l_2)(L-l_1+1)(2l_1+1)}{2l_2+3}} Y_{L,M}^{l_1-1,l_2+1}, \quad (6)$$

$$\hat{L}^{+-} Y_{L,M}^{l_1,l_2} = \sqrt{\frac{(L-l_1)(L-l_2+1)(2l_2+1)}{2l_1+3}} Y_{L,M}^{l_1+1,l_2-1}. \quad (7)$$

Next, let us briefly introduce the FC method.^{12–16} The ICI method is based on the idea that the exact wave function would be expressed by a function of the Hamiltonian $f(H)$ applied to some function ψ_0 as

$$\psi_{\text{exact}} = f(H) \psi_0 \quad (8)$$

because, in the SE, the exact wave function is an output, together with an energy, and the Hamiltonian is an input. As one such expression, we introduced the simplest ICI (SICI) wave function based on the scaled Schrödinger equation as

$$\psi_{n+1} = [1 + C_n g(H - E_n)] \psi_n. \quad (9)$$

The g function was introduced to prevent the singularity difficulty intrinsic to the Coulombic systems. This SICI is guaranteed to converge to the exact wave function as the iteration proceeds.^{12–16} To accelerate the convergence and to introduce a simpler method, we introduce the FC method.^{13,14} In the FC method, we collect all linearly independent functions $\{\phi_i\}$, $i=1, 2, \dots, M_n$ from the right-hand side of Eq. (9) and give an independent coefficient to each as

$$\psi_{n+1} = \sum_{i=1}^{M_n} c_i \phi_i. \quad (10)$$

In the present calculations, the coefficients $\{c_i^{(n)}\}$ are variationally determined. We call n (the iteration cycle) “order” and M_n (the number of independent functions) “dimension” of order n .

Thus, our wave function explicitly includes the Hamiltonian of the system itself. When we apply the ICI method to the non-BO calculations, the Hamiltonian contains operators of the nuclear coordinates as well as the electron coordinates. As a result, by the Hamiltonian itself, the ICI formalism can generate the appropriate functions automatically for nuclear motions such as vibrations and rotations together with electron motions. This is an important advantage of the FC formalism for obtaining very accurate wave functions for both electronic and nuclear motions.

Before starting the ICI process, we must first fix the two degrees of freedom in Eq. (9), i.e., the scaling function g and the initial function ψ_0 . The g function we employed is

$$g = -\frac{1}{V_{Ne}} + \frac{1}{V_{NN}} = \frac{s^2 - t^2}{4sZ} + R, \quad (11)$$

where V_{Ne} and V_{NN} represent nuclear-electronic attraction (with $Z=Z_1=Z_2=+1$) and nuclear-nuclear repulsion potentials, respectively. This g function has the same form as the function we used in the very high accuracy calculations on the helium atom.¹⁹ The choice of ψ_0 is important because it influences the convergence speed. The initial function ψ_0 should be chosen to reflect the physical and chemical natures of the target system. In the present non-BO H_2^+ series, we chose the Gaussian function $\exp(-\gamma(R-R_e)^2)$ for the R coordinate, which would be a physically proper function for the vibrational motion. For the ground states of the homonuclear ions (H_2^+ , D_2^+ , and T_2^+), the initial function ψ_0 we adopted was

$$\begin{aligned} \psi_0 &= (1 + P_{12}) [\exp(-\alpha r_1) \exp(-\alpha r_2) \\ &\quad \times \exp(-\beta(R - R_e)^2) \cdot Y_{L,M}^{l_1,l_2}] \\ &= (1 + P_{12}) [\exp(-\alpha s) \\ &\quad \times \exp(-\beta(R - R_e)^2) \cdot Y_{L,M}^{l_1,l_2}], \end{aligned} \quad (12)$$

where P_{12} represents the permutation operator of two nuclei. α and β are nonlinear variational parameters and R_e is also a variational parameter but we fix it at $R_e=2.0$ from the equilibrium distance of the nuclei of H_2^+ . (L, M, l_1, l_2) of $Y_{L,M}^{l_1,l_2}$ is $(0,0,0,0)$ for the ground states. For H_2^+ , because the proton is a fermion as is the electron, the permutation symmetry of Eq. (12) (a plus sign before P_{12}) corresponds to the singlet state of 1S . We will also calculate the triplet state 3P with ψ_0 given by

$$\begin{aligned} \psi_0 &= (1 - P_{12}) [(1+t) \exp(-\alpha s) \\ &\quad \times \exp(-\beta(R - R_e)^2) \cdot Y_{L,M}^{l_1,l_2}] \end{aligned} \quad (13)$$

with a minus sign before P_{12} and (L, M, l_1, l_2) of $(1,0,1,0)$. The term $(1+t)$ in Eq. (13) is introduced to generate additional spatial antisymmetrized functions including odd powers of t . For the heteronuclear ions (HD^+ , HT^+ , and DT^+), there is no need to symmetrize the wave function and so we use

$$\psi_0 = \exp(-\alpha s) \cdot \exp(-\beta(R - R_e)^2) \cdot Y_{L,M}^{l_1,l_2} \quad (14)$$

for the ground states with $R_e=2.0$ and $Y_{L,M}^{l_1,l_2}$: $(0,0,0,0)$. The FC wave functions generated from the g and ψ_0 of Eqs. (11)–(14) are expressed as

$$\psi = (1 \pm P_{12}) \sum_{(i,j,k)} s^i t^j R^k \exp(-\alpha s) \times \exp(-\beta(R - R_e)^2) \cdot Y_{L,M}^{l_1, l_2} \quad (15)$$

where both i and k run over integers including negative integers and index j runs only over nonnegative integers (only even integers for the ground states of homonuclear H_2^+ , D_2^+ , and T_2^+). For HD^+ , HT^+ , and DT^+ , in addition to the even integers of j , the wave function also involves odd-integer powers of t derived from the heterosymmetric Hamiltonian. In contrast to the helium case,¹⁹ however, the negative powers of s^i are not expected to be crucial for the present H_2^+ systems because although these terms are important for the three-particle collision area, the probability of such collision would be very small for the present systems. In contrast, the negative powers of R^k would be important because the vibrational motion would include anharmonicity in the BO sense, which would be flexibly represented by these terms. Therefore, we neglected the functions including the negative powers of s^i but included the negative powers of R^k . The functional form of Eq. (15) is a new type that has never been applied to the H_2^+ systems.

We will also calculate a few vibronic excited states of the same symmetry as the ground state and 3P state for the H_2^+ case. Actually, the FC variational method can determine not only the ground state but also the excited sequences, because the Hamiltonian contains all of the information, including excited states. The second and third solutions after diagonalization correspond to the first and second excited states, etc. The initial function ψ_0 given in Eqs. (12)–(14) may be enough for a few low lying excited states and, therefore, we obtained the excited states as the second and third solutions. However, for highly excited states, ψ_0 of Eqs. (12)–(14) may not be sufficient: a general method for calculating a series of higher excited states with the FC method was explained in Ref. 22. Actually, to calculate higher excited states, we should employ the following ψ_0 , which is modified from Eqs. (12)–(14),

$$\psi_0 = (1 \pm P_{12}) \left[\left(1 + \sum_i R^i \right) \cdot \exp(-\alpha s) \times \exp(-\beta(R - R_e)^2) \cdot Y_{L,M}^{l_1, l_2} \right] \quad (16)$$

An additional term $\sum_i R^i$ is responsible to the higher vibrational excited states. For more highly excited states, the Morse-type function⁴⁰ given by

$$\psi_0 = (1 \pm P_{12}) \left[\sum_v \exp(-ar_1) \exp(-ar_2) \times \exp\{-\chi \exp(-a(R - R_e))\} \times \exp(-\beta_v(R - R_e)^2) \cdot Y_{L,M}^{l_1, l_2} \right] \quad (17)$$

would be more appropriate to represent efficiently the high anharmonicity, where χ , a , and β_v (v is the vibration level) are additional parameters. Note that in Eqs. (15)–(17) the plus or minus sign of P_{12} is for the singlet or triplet state, respectively, of homonuclear molecules and the term

$(1 \pm P_{12})$ should be removed for heteronuclear molecules.

Before performing calculations, we must fix the nuclear mass to be taken from the experimental data. For H_2^+ , we employed the conventional value of the proton mass as $m_H = 1836.152\,701$ (a.u.) to compare our results with the previous references. However, we also performed the calculations using the newest values listed in CODATA 2006 on the NIST site,⁴¹ where the mass of the proton, deuteron, and triton are given as $m_H = 1836.152\,672\,47$, $m_D = 3670.482\,965\,4$, and $m_T = 5496.921\,526\,9$ (a.u.), respectively. We will note the values we used in both the text and tables in every case. All of the calculations before diagonalization were performed with the computer algebra package MAPLE.⁴² For the diagonalization step, we used our own original eigenvalue solver for arbitrary precision with the GMP (GNU multiple precision arithmetic) library.⁴³ We used MAPLE and GMP with 160-decimal-figure accuracy. Formulations of some integrals for the variational calculation are given in the Appendix.

III. RESULTS

A. Convergence of the FC wave function: Benchmark calculation for the ground state (1^1S) of H_2^+

We first examined the convergent behavior of the FC method for the 1^1S ground state with the g and ψ_0 given in Eqs. (11) and (12). Table I shows the calculated results, where the proton mass was the conventional value of $m_H = 1836.152\,701$ to compare with the previous references. The calculations were stopped at $n=21$ with $M_n=19\,286$ and the calculated energies converged to the exact value from above because of the variational principle. We obtained our best energy of **$-0.597\,139\,063\,123\,405\,074\,834\,134\,096\,025\,974\,142$** a.u., that is, 32 digits of precision. Throughout this paper, the figure that is believed to be correct is shown in bold face.

We compared our results in Table II with the previous non-BO calculations of H_2^+ .^{29–36} Very recently, as described in Sec. I, the most accurate energy was reported by Li *et al.*³³ and this value has almost 30 digits in accuracy. We were successful in slightly improving the accuracy by two digits in spite of using the simple harmonic Gaussian-type function for the R coordinate. Cassar and Drake³² also performed highly accurate calculations but their reported values were lower than ours and Li's results already at the first 21 digits despite using the same nuclear mass. We suspect that some numerical instabilities occurred in their calculations because they performed their calculations in quadruple precision arithmetic (almost 32 digits) but this precision might have been insufficient for obtaining numerical stability.

We also performed the calculations with the proton mass of $m_H = 1836.152\,672\,47$ as the most recent experimental value (CODATA 2006) (Ref. 41) and obtained the energy of **$-0.597\,139\,063\,079\,175\,256\,939\,382\,100\,935\,311\,293$** a.u. at $n=20$ and $M_n=16\,728$. This energy was listed in Table III together with the energies of a few low lying vibronic excited states. The difference between the results with $m_H = 1836.152\,701$ and $m_H = 1836.152\,672\,47$ occurs in the first ten digits of the calculated energy.

TABLE I. Ground-state (1^1S) energy of H_2^+ calculated with the g and ψ_0 given by Eqs. (11) and (12), respectively. The proton mass $m_H=1836.152\ 701$ was used to compare with the previous references. The two nonlinear parameters α and β were roughly optimized about n from 0 to 9.

n^a	M_n^b	α	β	Energy (a.u.)
0	1	0.6695	5.9054	−0.573 217
1	7	0.6136	4.2868	−0.596 661
2	30	0.7362	4.0989	−0.597 133 402
3	83	0.7343	4.1261	−0.597 139 017 109
4	179	0.7519	4.2305	−0.597 139 062 391
5	330	0.7848	4.4119	−0.597 139 063 103 997
6	544	0.8248	4.3588	−0.597 139 063 122 799
7	834	0.8596	4.3279	−0.597 139 063 123 383
8	1 211	0.8984	4.3119	−0.597 139 063 123 404 198
9	1 687	0.9365	4.3183	−0.597 139 063 123 405 038 451
10	2 273	0.9685	4.3826	−0.597 139 063 123 405 073 177
11	2 981	1.0035	4.3200	−0.597 139 063 123 405 074 767
12	3 822	1.0386	4.3200	−0.597 139 063 123 405 074 831 055
13	4 808	1.0736	4.3200	−0.597 139 063 123 405 074 833 976
14	5 950	1.1086	4.3200	−0.597 139 063 123 405 074 834 125 011
15	7 260	1.1437	4.3200	−0.597 139 063 123 405 074 834 133 503
16	8 749	1.1787	4.3200	−0.597 139 063 123 405 074 834 134 052 479
17	10 429	1.2137	4.3200	−0.597 139 063 123 405 074 834 134 092 554
18	12 311	1.2487	4.3200	−0.597 139 063 123 405 074 834 134 095 736
19	14 407	1.2838	4.3200	−0.597 139 063 123 405 074 834 134 096 001 111
20	16 728	1.3188	4.3200	−0.597 139 063 123 405 074 834 134 096 023 914
21	19 286	1.3538	4.3200	−0.597 139 063 123 405 074 834 134 096 025 974 142
Ref. 33				−0.597 139 063 123 405 074 834 134 096 021

^aNumber of iteration or order.

^bNumber of basis functions at order n .

B. Vibronic excited states of H_2^+ , HD^+ , and HT^+ for the same symmetry as the ground state

Next, we calculated a few low lying vibronic states of H_2^+ , HD^+ , and HT^+ for the same symmetry as the ground state. We used the functions g and ψ_0 given by Eqs. (11) and (12) (for H_2^+) and (14) (for HD^+ and HT^+) and calculated up to $n=20$ and $M_n=16\ 728$ for H_2^+ and $n=16$ and $M_n=17\ 404$ for HD^+ and HT^+ . The difference in the number of the generated FC functions between homonuclear H_2^+ and heteronuclear HD^+ and HT^+ is due to the difference in the symmetry. Table III shows the calculated results with the masses of H, D, and T as $m_H=1836.152\ 672\ 47$, $m_D=3670.482\ 965\ 4$, and $m_T=5496.921\ 526\ 9$ taken from CO-

DATA 2006.⁴¹ The calculated energies were very accurate for all of the excited states as well as for the ground state. Table III also shows the vibrational frequencies, which are the energy differences between the adjacent states. On the BO approximation, the vibrational frequencies are calculated from the potential curve, but their values are approximate because the coupling of motions of electrons and nuclei are completely neglected. In the non-BO calculations, this coupling effect is included. As shown in Table III, the frequency for H_2^+ between $v=0$ and 1 was $2191.099\ 519\ \text{cm}^{-1}$ and that between $v=1$ and 2 was $2063.889\ 981\ \text{cm}^{-1}$, and these values agree very well with the experimental values.⁴⁴ The latter is slightly smaller than the former by $127.209\ 537\ \text{cm}^{-1}$, re-

TABLE II. Comparison of the energy of the ground 1^1S state of H_2^+ with the recent reference data. $m_H=1836.152\ 701$ was used in all the calculations.

Year	Reference	Energy (a.u.)
1999	Moss ^a	−0.597 139 063 123 4
2000	Hilico <i>et al.</i> ^b	−0.597 139 063 123 40
2002	Frolov <i>et al.</i> ^c	−0.597 139 063 123 405 074 83
2004	Drake <i>et al.</i> ^d	−0.597 139 063 123 405 074 834 331
2007	Li <i>et al.</i> ^c	−0.597 139 063 123 405 074 834 134 096 021
2008	FC	−0.597 139 063 123 405 074 834 134 096 025 974 142

^aReference 29.

^bReference 30.

^cReference 31.

^dReference 32.

^eReference 33.

TABLE III. Energies of the excited states having the same symmetry as the ground state of H_2^+ (at $n=20$ and $M_n=16\,728$), HD^+ (at $n=16$ and $M_n=17\,404$), and HT^+ (at $n=16$ and $M_n=17\,404$) with the mass data of $m_{\text{H}}=1836.152\,672\,47$, $m_{\text{D}}=3670.482\,965\,4$, and $m_{\text{T}}=5496.921\,526\,9$. The g given in Eq. (11) and ψ_0 given in Eq. (12) (for H_2^+) and (14) (for HD^+ and HT^+), respectively, were used. The nonlinear parameters $\alpha=1.3188$ and $\beta=4.32$ were used for all calculations.

	v^a	Energy (a.u.)	Frequency (cm $^{-1}$)	Expt. (Ref. 44)	Hilico (Ref. 30) ^b
H_2^+	0	-0.597 139 063 079 175 256 939 382 100 935 311			-0.597 139 063 123 40
	1	-0.587 155 679 095 614 799 300 630 460 069	2191.099 519	2191	-0.587 155 679 212 75
	2	-0.577 751 904 414 194 306 819 503 068 894	2063.889 981	2064	-0.577 751 904 595 47
HD^+	0	-0.597 897 968 608 954 700 930 919 873 132			-0.597 897 968 644 84
	1	-0.589 181 829 556 745 685 653 388 340	1912.971 405		-0.589 181 829 653 33
	2	-0.580 903 700 218 035 191 975 750	1816.839 385		-0.580 903 700 369 05
HT^+	0	-0.598 176 134 637 481 346 135 342 766 373			
	1	-0.589 932 814 045 479 930 582 963 122	1809.199 748		
	2	-0.582 080 048 852 003 575 371 892	1723.482 746		

^aExcitation level.

^bDifferent mass data were used.

flecting the anharmonicity of the vibrational motions. For HD^+ , these frequencies were 1912.971 405 and 1816.839 385 cm^{-1} , and for HT^+ , they were 1809.199 748 and 1723.482 746 cm^{-1} , respectively. As the nuclear mass becomes heavier, these values become smaller.

We next examined the reduced density function to investigate the nature of the present non-BO wave function ψ obtained from this approach. The reduced density function $f(R)$ is defined by

$$f(R) = \int \psi^* \psi d\tau'_R, \quad (18)$$

where $d\tau'_R$ means the integrations are over the coordinates except for the internuclear distance, R . Therefore, the right-hand side of Eq. (18) becomes a function of R and can be expressed as

$$f(R) = \sum_k C_k R^k e^{-2\beta R^2 - (2\alpha - 4\beta R e)R}. \quad (19)$$

Figure 1 shows plots of $f(R)$ for the ground, first, and second excited states of 1^1SH_2^+ . We compare them with the densities calculated from the vibrational wave function of the harmonic oscillator on the BO potential curve. For the ground and second excited states, the number of maximum peaks is

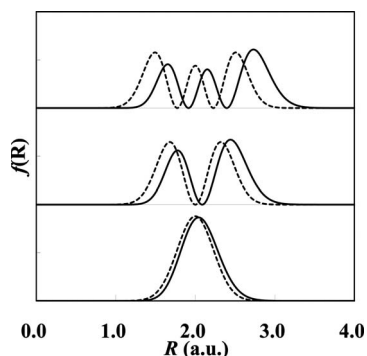


FIG. 1. Plots of the reduced density given by Eq. (18) for the ground and vibronic excited states of H_2^+ of 1^1S symmetry. The solid lines represent the reduced density functions of the ground, first, and second excited states from the bottom. The dotted lines represent the density plots for the harmonic vibrational wave functions.

odd and the plots are roughly symmetric about the central peak position (which should be very close to the equilibrium distance), i.e., the gerade mode of the vibration. In contrast, for the first excited state, the number of maximum peaks is even and the plot is roughly antisymmetric, i.e., the ungerade mode. Obviously, the plots for the harmonic oscillator are completely symmetric about the minimum position of the harmonic potential but the plots from the present non-BO calculations are not completely symmetric and are distorted because of the anharmonicity of the vibrational motion and the non-BO effects, which come from the coupling of electron and nuclei motions. Unsurprisingly, the anharmonicity is automatically included in the non-BO calculations. Moreover, the central peak positions for the excited states move to slightly larger values than those of the ground state. For the ground state, the method locates the central peak position at almost the same position as for the harmonic oscillator. For the excited states, the maximum peak of $f(R)$ at the large R side (outside) is also larger than at the small R side (inside). Because of the anharmonicity, the probability density of $f(R)$ at the large R side becomes larger. It corresponds well with the shape of the BO potential curve including the anharmonicity.

C. The difference between nuclear spin states of 1^1S (para) and 3^1P (ortho) of H_2^+

In this section, we discuss the difference between the 1^1S and 3^1P states. For H_2^+ , because the proton is a fermion and the eigenvalue of its spin angular momentum is a half-integer ($1/2$), the Pauli principle must be satisfied by the wave function with respect to the permutation of the two protons. For two-proton systems, “para H_2^+ ” means a singlet state and “ortho H_2^+ ” means a triplet state. In the BO approximation, both 1^1S and 3^1P have the same electronic structures and, therefore, they are completely degenerate. The non-BO calculations can break this degeneracy from the spin statistics of the nuclei (protons).

The calculations for the 1^1S state have been summarized in Sec. III A. Similar calculations for 3^1P were performed with the same g given by Eq. (11) and ψ_0 given by Eq. (13).

TABLE IV. Energy of the 1^3P state of H_2^+ calculated with g and ψ_0 given by Eqs. (11) and (13), respectively. The proton mass $m_H=1836.152\ 701$ was used to compare with the previous reference data. The two nonlinear parameters α and β were roughly optimized.

n^a	M_n^b	α	β	Energy (a.u.)
0	2	0.5000	3.4011	−0.534 562
1	16	0.6500	4.9283	−0.596 331
2	66	0.7597	4.4688	−0.596 870 838
3	180	0.7844	4.5140	−0.596 873 713 262
4	378	0.8398	4.4946	−0.596 873 738 458
5	690	0.8573	4.4600	−0.596 873 738 824 230
6	1 130	0.8847	4.4186	−0.596 873 738 832 516
7	1 724	0.9221	4.5000	−0.596 873 738 832 756 513
8	2 494	0.9544	4.5000	−0.596 873 738 832 764 408
9	3 464	0.9867	4.5000	−0.596 873 738 832 764 721 013
10	4 656	1.0190	4.5000	−0.596 873 738 832 764 735 144
11	6 094	1.0513	4.5000	−0.596 873 738 832 764 735 875
12	7 800	1.0836	4.5000	−0.596 873 738 832 764 735 917 782
13	9 798	1.1159	4.5000	−0.596 873 738 832 764 735 920 539
14	12 110	1.1482	4.5000	−0.596 873 738 832 764 735 920 730 017
15	14 760	1.1804	4.5000	−0.596 873 738 832 764 735 920 743 846
16	17 770	1.2127	4.5000	−0.596 873 738 832 764 735 920 744 893
Ref. 33				−0.596 873 738 832 764 735 920 744 98

^aNumber of iteration, or order.

^bNumber of basis functions at order n .

Table IV shows the calculated results with every order of the FC, where the proton mass employed was the conventional value of $m_H=1836.152\ 701$ to compare with the previous references. The calculations were stopped at $n=16$ and the calculated energies converged to the exact value with almost the same accuracy as the previous reference.³³ We obtained our best energy of **−0.596 873 738 832 764 735 920 744 893** a.u., that is, 25 digits in accuracy at $n=16$ and $M_n=17\ 770$.

The energy difference between the 1^1S and 1^3P states was $0.000\ 265\ 324$ a.u. ($58.231\ 941\ \text{cm}^{-1}$), which is quite small compared with the energy difference for the frequency ($2191\ \text{cm}^{-1}:v=0$ to $v=1$) of H_2^+ . This energy splitting comes from the difference in the nuclear spin multiplicity. In contrast to H_2^+ , in the helium atom, the energy difference between the 1^1S and 1^3P states is as large as $169\ 088\ \text{cm}^{-1}$,⁴⁵ arising from the difference in the electron spin multiplicity. Because the extensions of the electron and nucleus are quite different, the effects of the Pauli exclusion principle are very different.

We calculated the Boltzmann distribution probability of the 1^1S and 1^3P states of H_2^+ . In addition to the energy difference, the degeneracy of the state, which is unity for the 1^1S state and three for the 1^3P state, also affects the distribution probability. The resultant ratio of populations between the para H_2^+ (1^1S) and ortho H_2^+ (1^3P) states was 1:2.27 at room temperature. The major distribution of H_2^+ was ortho H_2^+ (1^3P) because of its larger spin multiplicity.

D. Vibronic excited states and some expectation values of H_2^+ (1^1S) and H_2^+ (1^3P), and its isotopomers: D_2^+ , T_2^+ , HD^+ , HT^+ , and DT^+

Finally, we applied the present method to the various isotopomers of H_2^+ , i.e., D_2^+ , T_2^+ , HD^+ , HT^+ , and DT^+ and

compared the results with H_2^+ for the 1^1S and 1^3P states. We compared the energy and the expectation values of $\langle r_1 \rangle$, $\langle r_2 \rangle$, and $\langle R \rangle$. Here, for heterosystems, r_1 is defined as the distance between the electron and the lighter nucleus and r_2 as the distance between the electron and the heavier nucleus. Recently, Bubin and co-workers^{34–36} studied these properties accurately for HD^+ and HT^+ with the explicitly correlated Gaussian function method. We performed the FC calculations using the g function given by Eq. (11) and the initial function ψ_0 given by Eq. (12) for H_2^+ of the 1^1S state at $n=14$ and $M_n=5950$. The same g and ψ_0 were used for the ground state of D_2^+ and T_2^+ . Note that D nucleus is a boson that is different from H and T nuclei, which are fermion. The spin eigenstate of D_2^+ is always symmetric and its spatial function should be symmetric because the total wave function of D_2^+ must be symmetric. For D_2^+ , therefore, the same symmetric and spatial initial function can be used as H_2^+ and T_2^+ case. For the heteronuclear systems, we used ψ_0 given by Eq. (14) and $n=11$ and $M_n=5914$. For H_2^+ of the 1^3P state, $n=11$ and $M_n=6094$ were used with ψ_0 given by Eq. (13). Although the order or dimension of the FC is small compared with the results discussed in the above sections, the results have converged to a physically meaningful accuracy. The nuclear mass data used were $m_H=1836.152\ 672\ 47$, $m_D=3670.482\ 965\ 4$, and $m_T=5496.921\ 526\ 9$ for H, D, and T nuclei, respectively, as given in CODATA 2006.⁴¹

The results are summarized in Table V for the lower three states of each system. We obtained the energies with satisfactory accuracy for all of the states of all the systems. The vibrational frequencies between adjacent states are also summarized in the table. As described in Sec. III B, the heavier the nuclear mass, the smaller the frequencies. This observation is easily understandable from the classical picture of a harmonic oscillator where the frequency is propor-

TABLE V. Energies and the expectation values $\langle r_1 \rangle$, $\langle r_2 \rangle$, and $\langle R \rangle$ for the ground and a few excited states of the same symmetry for H_2^+ and its isotopomers. For H_2^+ (1S), D_2^+ , and T_2^+ , the g and ψ_0 in Eqs. (11) and (12) were used at $n=14$ and $M_n=5950$ and, for H_2^+ (3P), Eqs. (11) and (13) were used at $n=11$ and $M_n=6094$, and Eqs. (11) and (14) were used at $n=11$ and $M_n=5914$ for HD^+ , HT^+ , and DT^+ . The nuclear mass data used were $m_{\text{H}}=1836.152\ 672\ 47$, $m_{\text{D}}=3670.482\ 965\ 4$, and $m_{\text{T}}=5496.921\ 526\ 9$. Values of $\alpha=1.1086$ and $\beta=4.32$ were employed for the nonlinear parameters.

	ν^a	Energy (a.u.)	Frequency (cm^{-1})	$\langle r_1 \rangle$	$\langle r_2 \rangle$	$\langle R \rangle$
H_2^+ (1S)	0	-0.597 139 063 079 175 256 939 373 016		1.692 966 208	1.692 966 208	2.063 913 867
	1	-0.587 155 679 095 614 799 279	2191.099 519	1.764 752 230	1.764 752 230	2.199 125 136
	2	-0.577 751 904 414 194 283	2063.889 981	1.839 368 775	1.839 368 775	2.339 751 003
H_2^+ (3P)	0	-0.596 873 738 784 476 119 983		1.694 397 351	1.694 397 351	2.066 619 898
	1	-0.586 904 320 918 598 361	2188.034 311	1.766 243 642	1.766 243 642	2.201 944 950
	2	-0.577 514 034 056 498	2060.929 747	1.840 928 825	1.840 928 825	2.342 700 915
D_2^+	0	-0.598 788 784 304 562 857 674 903 269		1.682 346 538	1.682 346 538	2.044 070 029
	1	-0.591 603 121 831 520 710 239	1577.070 622	1.732 573 538	1.732 573 538	2.138 662 460
	2	-0.584 712 206 896 550 366	1512.381 015	1.784 134 235	1.784 134 235	2.235 803 372
T_2^+	0	-0.599 506 910 096 112 180 587 249 172		1.677 707 679	1.677 707 679	2.035 386 031
	1	-0.593 589 927 768 924 154 523	1298.627 515	1.718 559 684	1.718 559 684	2.112 318 407
	2	-0.587 871 233 588 277 177	1255.108 297	1.760 279 582	1.760 279 582	2.190 908 363
HD^+	0	-0.597 897 968 608 954 700 621		1.688 442 006	1.687 732 429	2.054 803 238
	1	-0.589 181 829 556 745 679 654	1912.971 405	1.750 355 477	1.749 545 901	2.171 318 411
	2	-0.580 903 700 218 035 070	1816.839 385	1.814 343 968	1.813 414 961	2.291 782 413
HT^+	0	-0.598 176 134 637 481 345 390		1.686 767 475	1.685 825 362	2.051 456 621
	1	-0.589 932 814 045 479 912 796	1809.199 748	1.745 058 766	1.743 992 245	2.161 124 416
	2	-0.582 080 048 852 003 373	1723.482 746	1.805 179 364	1.803 965 860	2.274 267 594
DT^+	0	-0.599 130 662 833 885 811 307		1.680 255 515	1.680 023 340	2.039 939 515
	1	-0.592 545 017 179 965 882 666	1445.382 152	1.726 030 854	1.725 774 951	2.126 123 588
	2	-0.586 206 019 855 001 345	1391.249 101	1.772 906 374	1.772 623 450	2.214 406 291

^aExcitation level.

tional to $1/\sqrt{\mu}$, with μ as the reduced mass. Actually, the ratios of $\sqrt{\mu_{\text{H}_2}}/\sqrt{\mu_{AB}}$, where $AB=\text{D}_2, \text{T}_2, \text{HD}, \text{HT}, \text{and DT}$, were 0.707, 0.578, 0.866, 0.817, and 0.646, while the ratios of the frequencies for $\nu=0$ to $\nu=1$ of AB ($=\text{D}_2^+, \text{T}_2^+, \text{HD}^+, \text{HT}^+, \text{and DT}^+$) and H_2^+ (1S) were 0.720, 0.593, 0.873, 0.826, and 0.660. These values are similar and the small differences come from the anharmonicity and the non-BO effects. Comparing the total energy of the ground state for each system, we notice that the energy becomes lower as the nuclear mass becomes larger. The exact ground-state energy of the electronic wave function of H_2^+ in the BO approximation, i.e., for $^{\infty}\text{H}$, is $-0.602\ 634$ a.u. at $R=2.0$ (a.u.).²⁰ The non-BO energies reflect both the zero point energy of the vibrational motion and/or kinetic energy of the nuclei motion and they should be higher than the BO energy. Because the heavier nucleus has a smaller kinetic energy (which is always positive and becomes zero for $^{\infty}\text{H}$), the heavier the nucleus mass is, the lower the energy is.

As described in Sec. III C, the ground-state energy of H_2^+ (3P) was slightly higher than that of H_2^+ (1S) by $58.231\ 941\ \text{cm}^{-1}$. Similarly, the energies of the vibronic excited states of 3P were also higher than those of 1S by $55.166\ 743$ and $52.206\ 509\ \text{cm}^{-1}$ for the first and second excited states, respectively. These energy differences, mainly originating from the nuclear spin states, become smaller as the excitation level increases. This tendency is easily understood because, when electrons are apart from the nuclei, they are not influenced by the nuclear spin states. The vibrational frequency between the ground and first vibrationally excited state of 3P was $2188.034\ 311\ \text{cm}^{-1}$, which was slightly smaller than that of 1S by $3.065\ \text{cm}^{-1}$. That between the first

and second vibrationally excited states was $2060.929\ 747\ \text{cm}^{-1}$, which was smaller than 1S by $2.960\ \text{cm}^{-1}$.

The expectation values $\langle r_1 \rangle$, $\langle r_2 \rangle$, and $\langle R \rangle$ are interesting properties to be compared among the isotopomers. Recently, Bubin and co-workers^{34–36} calculated these properties accurately for HD^+ and HT^+ , and our results were in very good agreement with theirs up to the low lying excited states. Here, we further systematically study these properties for the isotopic species, H_2^+ , D_2^+ , T_2^+ , HD^+ , HT^+ , and DT^+ . For the homonuclear systems, $\langle r_1 \rangle$ and $\langle r_2 \rangle$ are obviously the same because of symmetry. For heteronuclear systems, $\langle r_1 \rangle$ need not be the same as $\langle r_2 \rangle$. Their values were slightly less than 1.7 a.u. for the ground states of all the systems. Although the Coulomb potentials are the same for both homo- and heteronuclear systems, $\langle r_1 \rangle$ (the electron–light nucleus distance) is slightly larger than $\langle r_2 \rangle$ (the electron–heavy nucleus distance) for HD^+ , HT^+ , and DT^+ . Further, the ratio $\langle r_1 \rangle/\langle r_2 \rangle$ becomes slightly smaller as the nuclear mass becomes heavier. These results indicate that the electron tends to be more attracted to the heavier nucleus. The electron near the heavier nucleus is more stable because the heavier nucleus does not easily move or flicker because of its heavy weight, so that the electron can exist nearer the heavier nucleus than near the lighter nucleus.

The expectation value for the internuclear distance $\langle R \rangle$ is close to 2.0 a.u. for the ground states of all the systems, which is very close to the equilibrium distance obtained from the BO calculations.²⁰ This value of $\langle R \rangle$ becomes slightly

shorter as the nuclear mass becomes heavier for the same reason as those for $\langle r_1 \rangle$ and $\langle r_2 \rangle$, which can never be explained in the BO approximation.

For H_2^+ , the value of $\langle R \rangle$ for 3P was slightly longer than that for 1S . This is explained by the Pauli principle, which prohibits the two protons having the same spin being located at the same spatial position. As a result, the vibrational frequency of 3P is slightly smaller than that of 1S .

When we compared the values of $\langle R \rangle$ between ground and excited states, they are larger for the excited states than for the ground state. This is mainly due to the anharmonicity of the vibrational motion. Similarly, the values of $\langle r_1 \rangle$ and $\langle r_2 \rangle$ of the excited states are larger than those of the ground state.

IV. CONCLUSION

The FC methodology was successfully applied to solve the Schrödinger equation for the hydrogen molecular ion and its isotopomers using the non-BO Hamiltonian. Compared with the previous references, the most accurate energy correct to 32 digits of precision has been obtained for H_2^+ for the 1^1S ground state. Very accurate energies were also obtained for the vibronic ground and excited states of H_2^+ , HD^+ , and HT^+ . The excitation frequencies between the nearest two vibronic states compared well with the experimental values when available. The 1^3P state of H_2^+ has the same electronic structure as the 1^1S state, which corresponds to the 1σ state in the BO approximation, but they have different nuclear spin structures. A very small energy difference of $58.231\,941\text{ cm}^{-1}$ was obtained between the 1^1S and 1^3P states. We have also applied our method to the isotopomers of H_2^+ , i.e., D_2^+ , T_2^+ , HD^+ , HT^+ , and DT^+ . We have calculated not only the energy but also the expectation values of $\langle r_1 \rangle$, $\langle r_2 \rangle$, and $\langle R \rangle$, which showed interesting behaviors between the ground and excited states, between the different nuclear spin states, and among the isotopomers. Because the FC method gives very accurate energies and properties, we could discuss even very fine details of these quantities. Because the FC methodology has also been extended to the relativistic DCE,¹⁶ we can take the relativistic effect into consideration as the next step in the present studies.

In this paper, we established the usage of the Gaussian vibrational functions for the R coordinate and the regular Slater functions for the inter-electron-nucleus coordinate as the basis for the non-BO calculations. This basis is quite simple but has never been applied to the present systems for very accurate level calculations. Bubin and co-workers^{9–11,34–36} introduced the general explicitly correlated Gaussian functional (ECG) form in their non-BO calculations for some years. In their basis, the Gaussian germinal is used for every interparticle coordinates including inter-electron-nucleus coordinate but they do not use the Slater functions, which are suitable for describing electron motions, particularly near the nucleus (cusp). Because the Gaussian vibrational functions are familiar to chemists as vibrational functions, this usage in the initial function of the FC method would be easily extended to more complex molecules, making the non-BO calculations of general atoms and molecules

more feasible. By applying the electron-nuclear Hamiltonian to this initial function, the FC method generates a series of electronuclear complement functions that form a basis for describing an accurate non-BO wave function of the system. When analytical integration over the complement functions becomes difficult, we can apply the local SE (LSE) method,¹⁷ which enables calculation of the FC wave function without doing analytical integrations over the complement functions. The calculation of non-BO states with the FC LSE method is now in progress and will be published in separate papers.

ACKNOWLEDGMENTS

This study has been partially supported financially by a Grant for Creative Scientific Research from the Ministry of Education, Science, Culture, and Sports of Japan.

APPENDIX: ANALYTICAL INTEGRATIONS FOR VARIATIONAL CALCULATION

We here give formulations for analytical integrations over the FC complement functions containing the Gaussian functions for the R coordinate. We want to evaluate analytically the following integral:

$$I = \int_0^\infty \int_0^s \int_{-R}^R \int s^a t^b R^c e^{-\alpha s} e^{-\beta R^2 + 2\beta R e R} \times (Y_{L,M}^{l_1,l_2})^* Y_{L,M}^{\lambda_1,\lambda_2} d\gamma dt dR ds, \quad (\text{A1})$$

where the indices a and b run over nonnegative integers, and c runs over all integers $c < 0$ under the condition $c + b \geq -1$. The nonlinear parameters α and β are positive real numbers. $Y_{L,M}^{\lambda_1,\lambda_2}$ are the solid spherical harmonics, which is an angular momentum eigenfunction of the quantum state $(L, M, \lambda_1, \lambda_2)$. A volume element $d\gamma$ means the integration of $(Y_{L,M}^{l_1,l_2})^* Y_{L,M}^{\lambda_1,\lambda_2}$ over the Euler angles.

The integration of its angular part, given by

$$J_{L,M,l_1,l_2,\lambda_1,\lambda_2} = \int (Y_{L,M}^{l_1,l_2})^* Y_{L,M}^{\lambda_1,\lambda_2} d\gamma, \quad (\text{A2})$$

is estimated by

$$J_{L,M,l_1,l_2,\lambda_1,\lambda_2} = \sqrt{(2l_1+1)(2l_2+1)(2\lambda_1+1)(2\lambda_2+1)} \times r_1^{l_1+\lambda_1} r_2^{l_2+\lambda_2} (-1)^{L+l+\Lambda} \times \sum_{\Lambda} \frac{2\Lambda+1}{2} \begin{pmatrix} l_1 & \lambda_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & \lambda_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \times \left\{ \begin{matrix} \lambda_1 & \lambda_2 & L \\ l_2 & l_1 & \Lambda \end{matrix} \right\} P_{\Lambda} \left(\frac{r_1^2 + r_2^2 - R^2}{2r_1 r_2} \right), \quad (\text{A3})$$

where the parentheses: () and curly braces: {} in the sigma notation represent the Wigner-3j and Wigner-6j symbols, respectively, and P_{Λ} represents the Legendre polynomial. The details are reported in the review of Harris.³⁸ Furthermore, we also converted $J_{L,M,l_1,l_2,\lambda_1,\lambda_2}$ to the expression in the (s, t, R) coordinates, and written as

$$\begin{aligned}
J_{L,M,l_1,l_2,\lambda_1,\lambda_2} &= \sqrt{(2l_1+1)(2l_2+1)(2\lambda_1+1)(2\lambda_2+1)} \\
&\times \left(\frac{s+t}{2}\right)^{l_1+\lambda_1} \left(\frac{s-t}{2}\right)^{l_2+\lambda_2} (-1)^{L+l+\lambda} \\
&\times \sum_{\Lambda} \frac{2\Lambda+1}{2} \begin{pmatrix} l_1 & \lambda_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & \lambda_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \\
&\times \begin{Bmatrix} \lambda_1 & \lambda_2 & L \\ l_2 & l_1 & \Lambda \end{Bmatrix} P_{\Lambda} \left(\frac{s^2+t^2-2R^2}{s^2-t^2} \right). \quad (\text{A4})
\end{aligned}$$

Equation (A4) can be expanded as the sum of products of s , t , and R . Eventually, we only have to evaluate the integral given by

$$K_{l,m,n,\alpha,\beta} = \int_0^{\infty} \int_0^s \int_{-R}^R s^l t^m R^n e^{-\alpha s} e^{-\beta R^2+2\beta Re R} dt dR ds. \quad (\text{A5})$$

First, we change the order of the integration of the three coordinates as follows:

$$K_{l,m,n,\alpha,\beta} = \int_0^{\infty} \int_R^{\infty} \int_{-R}^R s^l t^m R^n e^{-\alpha s} e^{-\beta R^2+2\beta Re R} dt ds dR. \quad (\text{A6})$$

After the integration is performed over t , we get

$$\begin{aligned}
K_{l,m,n,\alpha,\beta} &= \frac{\{1+(-1)^m\}}{(m+1)} \int_0^{\infty} \int_R^{\infty} s^l R^{m+n+1} e^{-\alpha s} e^{-\beta R^2+2\beta Re R} ds dR, \\
&\quad (\text{A7})
\end{aligned}$$

and also over s , we get

$$\begin{aligned}
K_{l,m,n,\alpha,\beta} &= \frac{\{1+(-1)^m\}}{(m+1)\alpha^{l+1}} \int_0^{\infty} \Gamma(l+1, \alpha R) \\
&\times R^{m+n+1} e^{-\alpha R} e^{-\beta R^2+2\beta Re R} dR, \quad (\text{A8})
\end{aligned}$$

where $\Gamma(l+1, \alpha R)$ is the incomplete gamma function. In Eq. (A8), because l runs over nonnegative integers, this incomplete gamma function can be converted to a simple polynomial in R , and we obtain

$$\begin{aligned}
K_{l,m,n,\alpha,\beta} &= \frac{l! \{1+(-1)^m\}}{(m+1)\alpha^{l+1}} \int_0^{\infty} \sum_{k=0}^l \frac{l^k}{k!} R^{m+n+k+1} \\
&\times e^{-\beta R^2-(\alpha-2\beta Re)R} dR. \quad (\text{A9})
\end{aligned}$$

For the reduced density plot of the wave function remaining in the R coordinate, the integrand of Eq. (A9) corresponds to Eqs. (18) or Eq. (19). Finally, it is integrated over R , and we get

$$K_{l,m,n,\alpha,\beta} = \frac{l! \{1+(-1)^m\}}{(m+1)\alpha^{l+1}} \sum_{k=0}^l \frac{l^k \cdot \Gamma(m+n+2+k) \cdot e^{(\alpha-2\beta Re)^2/8\beta} \cdot D_{-(m+n+2+k)}\left(\frac{\alpha-2\beta Re}{\sqrt{2\beta}}\right)}{k! (2\beta)^{(m+n+2+k)/2}}, \quad (\text{A10})$$

where D is the parabolic cylinder function, which can also be converted to the Hermite function as follows,

$$K_{l,m,n,\alpha,\beta} = \frac{l! m! n! \{1+(-1)^m\}_{m+n+1} C_n \sum_{k=0}^l \left(\frac{l}{\sqrt{\beta}}\right)^k}{\alpha^{l+1} \beta^{(m+n+2)/2}} {}_{m+n+k+1} C_k \cdot H_{-(m+n+2+k)}\left(\frac{\alpha-2\beta Re}{2\sqrt{\beta}}\right), \quad (\text{A11})$$

where the factorial part of Eq. (A10) has been converted to a binomial coefficient. Equation (A11) is more reliable than Eq. (A10) for numerical evaluation.

¹M. Born and J. R. Oppenheimer, *Ann. Phys.* **389**, 457 (1927).

²R. G. Woolley and B. T. Sutcliffe, *Chem. Phys. Lett.* **45**, 393 (1977).

³B. T. Sutcliffe, *Adv. Quantum Chem.* **28**, 65 (1997).

⁴B. T. Sutcliffe and R. G. Woolley, *Phys. Chem. Chem. Phys.* **7**, 3664 (2005).

⁵N. C. Handy and A. M. Lee, *Chem. Phys. Lett.* **252**, 425 (1996).

⁶M. Tachikawa, K. Mori, H. Nakai, and K. Iguchi, *Chem. Phys. Lett.* **290**, 437 (1998).

⁷H. Nakai, M. Hoshino, and K. Miyamoto, *J. Chem. Phys.* **122**, 164101 (2005).

⁸H. Nakai, *Int. J. Quantum Chem.* **107**, 2849 (2007).

⁹M. Cafiero, S. Bubin, and L. Adamowicz, *Phys. Chem. Chem. Phys.* **5**, 1491 (2003).

¹⁰M. Cafiero and L. Adamowicz, *Chem. Phys. Lett.* **387**, 136 (2004).

¹¹S. Bubin, M. Cafiero, and L. Adamowicz, *Adv. Chem. Phys.* **131**, 377 (2005).

¹²H. Nakatsuji, *J. Chem. Phys.* **113**, 2949 (2000); H. Nakatsuji and E. R.

Davidson, *ibid.* **115**, 2000 (2001); H. Nakatsuji, *ibid.* **115**, 2465 (2001); H. Nakatsuji, *ibid.* **116**, 1811 (2002); H. Nakatsuji and M. Ehara, *ibid.* **117**, 9 (2002).

¹³H. Nakatsuji, *Phys. Rev. Lett.* **93**, 030403 (2004).

¹⁴H. Nakatsuji, *Phys. Rev. A* **72**, 062110 (2005).

¹⁵H. Nakatsuji, *Bull. Chem. Soc. Jpn.* **78**, 1705 (2005).

¹⁶H. Nakatsuji and H. Nakashima, *Phys. Rev. Lett.* **95**, 050407 (2005).

¹⁷H. Nakatsuji, H. Nakashima, Y. Kurokawa, and A. Ishikawa, *Phys. Rev. Lett.* **99**, 240402 (2007).

¹⁸Y. Kurokawa, H. Nakashima, and H. Nakatsuji, *Phys. Rev. A* **72**, 062502 (2005).

¹⁹H. Nakashima and H. Nakatsuji, *J. Chem. Phys.* **127**, 224104 (2007).

²⁰A. Ishikawa, H. Nakashima, and H. Nakatsuji, *J. Chem. Phys.* **128**, 124103 (2008).

²¹Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, *Phys. Chem. Chem. Phys.* **10**, 4486 (2008).

²²H. Nakashima, Y. Hijikata, and H. Nakatsuji, *J. Chem. Phys.* **128**, 154108 (2008).

²³H. Nakashima and H. Nakatsuji, *J. Chem. Phys.* **128**, 154107 (2008).

²⁴V. K. Khersonskij, *Astrophys. Space Sci.* **98**, 255 (1984).

²⁵P. L. Jacobson, R. A. Komara, W. G. Sturru, and S. R. Lundeen, *Phys. Rev. A* **62**, 012509 (2000).

- ²⁶P. Blythe, B. Roth, U. Fröhlich, H. Wenz, and S. Schiller, *Phys. Rev. Lett.* **95**, 183002 (2005).
- ²⁷P. L. Jacobson, D. S. Fisher, C. W. Fehrenbach, W. G. Sturuss, and S. R. Lundeen, *Phys. Rev. A* **56**, R4361 (1997); P. L. Jacobson, D. S. Fisher, C. W. Fehrenbach, W. G. Sturuss, and S. R. Lundeen, *ibid.* **57**, 4065 (1998).
- ²⁸H. Wind, *J. Chem. Phys.* **42**, 2371 (1965).
- ²⁹R. E. Moss, *J. Phys. B* **32**, L89 (1999).
- ³⁰L. Hilico, N. Billy, B. Grémaud, and D. Delande, *Eur. Phys. J. D* **12**, 449 (2000).
- ³¹D. H. Bailey and A. M. Frolov, *J. Phys. B* **35**, 4287 (2002).
- ³²M. M. Cassar and G. M. F. Drake, *J. Phys. B* **37**, 2485 (2004).
- ³³H. Li, J. Wu, B.-L. Zhou, J.-M. Zhu, and Z.-C. Yan, *Phys. Rev. A* **75**, 012504 (2007).
- ³⁴S. Bubin and L. Adamowicz, *Chem. Phys. Lett.* **403**, 185 (2005).
- ³⁵S. Bubin, E. Bednarz, and L. Adamowicz, *J. Chem. Phys.* **122**, 041102 (2005).
- ³⁶E. Bednarz, S. Bubin, and L. Adamowicz, *J. Chem. Phys.* **122**, 164302 (2005).
- ³⁷C. Schwartz, *Phys. Rev.* **123**, 1700 (1961).
- ³⁸F. E. Harris, *Adv. Quantum Chem.* **47**, 129 (2004).
- ³⁹E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929).
- ⁴⁰P. M. Morse and E. C. G. Stueckelberg, *Phys. Rev.* **33**, 932 (1929); P. M. Morse, *ibid.* **34**, 57 (1929).
- ⁴¹<http://physics.nist.gov/cuu/Constants/>.
- ⁴²Computer algebra package MAPLE, Waterloo Maple Inc., Waterloo, Ontario, Canada (see <http://www.maplesoft.com/>).
- ⁴³About the GMP library, see <http://swox.com/gmp/> and <http://www.cs.nyu.edu/exact/core/gmp/>.
- ⁴⁴P. W. Atkins, *Physical Chemistry*, 6th ed. (Oxford University Press, Oxford, 1998).
- ⁴⁵H. Nakashima, Y. Hijikata, and H. Nakatsuji (unpublished).