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

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The Schrödinger equations for the hydrogen molecular ion (H₂⁺) and its isotopomers (D₂⁺, T₂⁺, 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 H₂⁺ as -0.597 139 063 123 405 074 142 a.u., which is variationally the best in literature. The difference in the nuclear spin states of 1S (para) and 3P (ortho) of H₂⁺ 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]

I. INTRODUCTION

The Born–Oppenheimer (BO) approximation 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, 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). The method has been applied to various atoms and molecules and gave very accurate results, particularly for H₂⁺, the helium atom, and the hydrogen molecule. The applications were not only limited to the ground state but could also be used for excited states and also for the three-body helium atomic system with the nucleus in motion. 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 H₂⁺ and its isotopomers, the simplest possible molecules, with the FC methodology.

The H₂⁺ ion is important as one of the astronomical interstellar molecules. In optical physics and electron scattering theories, the dissociation of a hydrogen molecule from two-electron resonance excited states produces the H₂⁺ ion, which is a key molecule but unstable and only has a short lifetime. Because the proton is the lightest nucleus, the quantum effect of nuclear motion could be significant for the H₂⁺ ion.

In the BO approximation, the exact form of the wave function of H₂⁺ was proposed by Wind 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. H₂⁺ 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 H₂⁺ with the non-BO Hamiltonian were performed by several authors. In particular, Cassar and Drake reported in 2004 very accurate results with the double exponent basis set expressed as...
\[
\psi = \sum_{p=1}^{2} \sum_{i,j=0} \sum_{k=H_{\text{low}}} c^{(p,i,j,k)} r_{1}^{i} r_{2}^{j} R^{k} \exp(-\alpha^{(p)} r_{1} - \beta^{(p)} r_{2}) - \gamma^{(p)} R \cdot Y_{L,S}^{(i,j,k)}(r_{1}, r_{2}) \pm (1 \leftrightarrow 2),
\]
(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 \(Y_{L,S}^{(i,j,k)}(r_{1}, r_{2})\) are the vector-coupled spherical harmonics with quantum numbers \((L, M, l_{1}, l_{2})\) for the spatial angular momentum derived by Schwartz. The other parameters shown in Eq. (1) were given in their paper. In their basis function, the \(R\) coordinate, \(\exp(-\gamma R)\), and very high powers of \(R^{k}\) were introduced, in which \(\Omega\) (maximum number of \(k\)) was a very large number around 40 and \(\gamma\) was optimized around 20. 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. reported the most accurate calculations of \(H_{2}^{+}\) with a large number of basis functions (8381 functions), which are written as

\[
\psi = \sum_{(i,j,k)} c^{(i,j,k)} r_{1}^{i} r_{2}^{j} R^{k} \exp(-\alpha r_{1}) - \gamma R \cdot Y_{L,S}^{(i,j,k)}(r_{1}, r_{2}) \pm (1 \leftrightarrow 2),
\]
(2)

where \(R^{k}\) also has very high power \((k \approx 35)\), similar to the calculations by Cassar and Drake. They used eight different blocks for the nonlinear parameters of \(\alpha^{(p)}\) and \(\gamma^{(p)}\) to accelerate convergence. 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 \(R \to \infty\) 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-workers 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 \(^1S\) (orth) 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

\[
H = -\sum_{i} \frac{1}{2m_{e}} \frac{\partial^{2}}{\partial s_{i}^{2}} - \sum_{A} \frac{1}{2m_{A}} \frac{\partial^{2}}{\partial s_{A}^{2}} + \sum_{i} \sum_{A} \frac{Z_{A}}{R_{iA}} + \sum_{i < j} \frac{Z_{i}Z_{j}}{R_{ij}} + \sum_{A < B} \frac{Z_{A}Z_{B}}{R_{AB}},
\]
(3)

where \(i\) and \(A\) denote electrons and nuclei, \(m_{e}\) and \(m_{A}\) are their masses, and \(Z_{i}\) and \(Z_{A}\) are their charges, respectively. Recently, Harris 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,

\[
s = r_{1} + r_{2}, \quad t = r_{1} - r_{2}.
\]

This coordinate set is equivalent to the \((s, t, \mu)\) coordinate set for the helium atom used by Hylleraas. The Hamiltonian of the present system is written in atomic units as

\[
H = -\frac{1}{2m_{1}} \left( \frac{\partial^{2}}{\partial s^{2}} + \frac{4}{(s + t)} \frac{\partial}{\partial s} + \frac{4}{(s - t)} \frac{\partial}{\partial t} + \frac{2}{R} \frac{\partial}{\partial R} + 2 \frac{\partial^{2}}{\partial s \partial R} + \frac{2(R^{2} + 2s)}{R(s + t)} \frac{\partial}{\partial s} + \frac{2(R^{2} + 4s)}{R(s + t)} \frac{\partial}{\partial R} \frac{\partial}{\partial s} \right)
\]

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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 \( Y^l_{LM} \) as follows:\(^{38}\)

\[
\hat{L}^+ Y^l_{LM} = \sqrt{\frac{(L-l_2)(L-l_2+1)}{2l_2+3}} Y^{l-1}_{L+1,M},
\]

\[
\hat{L}^- Y^l_{LM} = \sqrt{\frac{(L-l_2)(L-l_2+1)}{2l_2+3}} Y^{l+1}_{L+1,-M}.
\]

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 \( \psi_0 \) as

\[
\psi_{\text{exact}} = f(H)\psi_0
\]

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

\[
\psi_{n+1} = \left[ 1 + C_n g(H - E_n) \right] \psi_n.
\]

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 \( \{\phi_i\}, i = 1, 2, \ldots, M_n \) from the right-hand side of Eq. (9) and give an independent coefficient to each as

\[
\psi_{n+1} = \sum_{i=1}^{M_n} c_i \phi_i.
\]

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 \( \psi_0 \). The \( g \) function we employed is

\[
g = -\frac{1}{V_{Ne}} + \frac{1}{V_{NN}} = \frac{s^2-r^2}{4sZ} + R,
\]

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 \( \psi_0 \) is important because it influences the convergence speed. The initial function \( \psi_0 \) 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 \( \exp(-\gamma(R-R_c)^2) \) 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 \( \psi_0 \) we adopted was

\[
\psi_0 = (1 + P_{12})[\exp(-\alpha r_2)\exp(-\alpha r_1)] 
\times \exp(-\beta(R-R_c)^2) \cdot Y^l_{LM}
\]

\[
= (1 + P_{12})[\exp(-\alpha s)] 
\times \exp(-\beta(R-R_c)^2) \cdot Y^l_{LM},
\]

where \( P_{12} \) represents the permutation operator of two nuclei. \( \alpha \) and \( \beta \) are nonlinear variational parameters and \( R_c \) is also a variational parameter but we fix it at \( R_c=2.0 \) from the equilibrium distance of the nuclei of \( H_2^+ \). (\( L,M,l_1,l_2 \)) of \( Y^l_{LM} \) 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 \( \psi_0 \) given by

\[
\psi_0 = (1 - P_{12})[(1 + t)\exp(-\alpha s)] 
\times \exp(-\beta(R-R_c)^2) \cdot Y^l_{LM}
\]

(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

\[
\psi_0 = \exp(-\alpha s) \cdot \exp(-\beta(R-R_c)^2) \cdot Y^l_{LM}
\]

(14)

for the ground states with \( R_c=2.0 \) and \( Y^l_{LM} \) of (0,0,0,0). The FC wave functions generated from the \( g \) and \( \psi_0 \) of Eqs. (11–14) are expressed as

\[
\begin{align*}
-4\left(\frac{r^2-R^2}{s^2-r^2}\right) \frac{\partial^2}{\partial t^2} + \frac{8t}{s^2-r^2} \frac{\partial}{\partial t} - \frac{2(l_1 + \hat{L}^-)}{m_3(s+t)} \left( \frac{\partial}{\partial s} + \frac{\partial}{\partial t} \right) - \frac{2(l_2 + \hat{L}^-)}{m_3(s-t)} \left( \frac{\partial}{\partial s} - \frac{\partial}{\partial t} \right) + \frac{Z_1 Z_2}{R} \frac{2Z_2 Z_3}{s-t} + \frac{2Z_2 Z_3}{s+t},
\end{align*}
\]
\[ \psi = (1 \pm P_{12}) \sum_{(i,j,k)} s'^i t'^k R^k \exp(- \alpha s) \]
\[ \times \exp(- \beta(R-R_s)^2) \cdot Y_{jL}^{iL} \]  \hspace{1cm} (15)

where both \( i \) and \( k \) run over integers including negative integers and \( j \) 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, however, the negative powers of \( s' \) 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 \( s' \) 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 \( \psi_0 \) 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, \( \psi_0 \) 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 \( \psi_0 \), which is modified from Eqs. (12)–(14),

\[ \psi_0 = (1 \pm P_{12}) \left[ \left( \sum_i R_i^i \right) \cdot \exp(- \alpha s) \right. \]
\[ \left. \times \exp(- \beta(R-R_s)^2) \cdot Y_{jL}^{iL} \right] . \]  \hspace{1cm} (16)

An additional term \( \sum_i R_i^i \) is responsible to the higher vibrational excited states. For more highly excited states, the Morse-type function \( 40 \) given by

\[ \psi_0 = (1 \pm P_{12}) \sum_v \exp(- \alpha r_v) \exp(- \alpha r_v) \]
\[ \times \exp(- \chi \exp(- (a(R-R_v))) \}
\[ \times \exp(- \beta_v(R-R_v)) \cdot Y_{jL}^{iL} \]  \hspace{1cm} (17)

would be more appropriate to represent efficiently the high anharmonicity, where \( \chi \), \( a \), and \( \beta_v \) (\( v \) 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, \( m_D = 370.482 \) 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. \( 32 \) 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 \( \psi_0 \) 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 Drake \( 32 \) 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 S) energy of H + calculated with the ϕ 0 given by Eqs. (11) and (12), respectively. The proton mass m=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.

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<th>M_n</th>
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<th>β</th>
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<td>-0.597 139 063 123 405 074 834 134 096 025 974 142</td>
</tr>
</tbody>
</table>

Ref. 33

1Number of iteration or order.
2Number of basis functions at order n.

B. Vibronic excited states of H₂⁺, HD⁺, and HT⁺ for the same symmetry as the ground state

Next, we calculated a few low lying vibronic states of H₂⁺, HD⁺, and HT⁺ for the same symmetry as the ground state. We used the functions g and ϕ 0 given by Eqs. (11) and (12) for H₂⁺) and (14) for HD⁺ and HT⁺) and calculated up to n=20 and M_m=16 728 for H₂⁺ and n = 16 and M_m = 17 404 for HD⁺ and HT⁺. The difference in the number of the generated FC functions between homonuclear H₂⁺ 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-

TABLE II. Comparison of the energy of the ground 1 S state of H₂⁺ with the recent reference data. m_H =1836.152 701 was used in all the calculations.

<table>
<thead>
<tr>
<th>Year</th>
<th>Reference</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>Moss</td>
<td>-0.597 139 063 123 4</td>
</tr>
<tr>
<td>2000</td>
<td>Hilico et al.</td>
<td>-0.597 139 063 123 40</td>
</tr>
<tr>
<td>2002</td>
<td>Frolov et al.</td>
<td>-0.597 139 063 123 405 074 83</td>
</tr>
<tr>
<td>2004</td>
<td>Drake et al.</td>
<td>-0.597 139 063 123 405 074 834 331</td>
</tr>
<tr>
<td>2007</td>
<td>Li et al.</td>
<td>-0.597 139 063 123 405 074 834 134 096 021</td>
</tr>
<tr>
<td>2008</td>
<td>FC</td>
<td>-0.597 139 063 123 405 074 834 134 096 025 974 142</td>
</tr>
</tbody>
</table>

Ref. 29
9Reference 30.
10Reference 31.
11Reference 32.
12Reference 33.
TABLE III. Energies of the excited states having the same symmetry as the ground state of H\(_2^+\) (at \(n=20\) and \(M_2=16\) 728), HD\(^+\) (at \(n=16\) and \(M_2=17\) 404), and HT\(^+\) (at \(n=16\) and \(M_2=17\) 404) with the mass data of \(m_{H^2}=1836.152\ 672\ 47\), \(m_{D^2}=3670.482\ 965\ 4\), and \(m_{H^2}=5496.921\ 526\ 9\). The \(g\) given in Eq. (11) and \(\psi_0\) 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.

<table>
<thead>
<tr>
<th>(v)</th>
<th>Energy (a.u.)</th>
<th>Frequency (cm(^{-1}))</th>
<th>Expt. (Ref. 44)</th>
<th>Hilico (Ref. 30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(-0.597\ 139\ 063\ 079\ 175\ 256\ 939\ 382\ 100\ 935\ 311)</td>
<td>2191.099 519</td>
<td>2191</td>
<td>(-0.587\ 155\ 679\ 212\ 75)</td>
</tr>
<tr>
<td>1</td>
<td>(-0.587\ 155\ 679\ 212\ 75)</td>
<td>2063.889 981</td>
<td>2064</td>
<td>(-0.577\ 751\ 904\ 595\ 47)</td>
</tr>
<tr>
<td>2</td>
<td>(-0.577\ 751\ 904\ 144\ 194\ 306\ 819\ 503\ 068\ 894)</td>
<td>1912.971 405</td>
<td>1912</td>
<td>(-0.598\ 797\ 968\ 644\ 84)</td>
</tr>
<tr>
<td>1</td>
<td>(-0.589\ 181\ 829\ 556\ 745\ 685\ 653\ 388\ 340)</td>
<td>1816.839 385</td>
<td>1816</td>
<td>(-0.598\ 181\ 829\ 653\ 33)</td>
</tr>
<tr>
<td>2</td>
<td>(-0.580\ 903\ 700\ 218\ 035\ 191\ 975\ 750)</td>
<td>1809.199 748</td>
<td>1809</td>
<td>(-0.580\ 903\ 700\ 369\ 05)</td>
</tr>
</tbody>
</table>

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

\[
f(R) = \int \psi^* \psi d^2r',
\]

(18)

where \(d^2r'\) 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

\[
f(R) = \sum_k C_k R^k e^{-2\beta R^2 - (2\alpha - 4\beta \epsilon) R^2}.
\]

(19)

Figure 1 shows plots of \(f(R)\) for the ground, first, and second excited states of \(^1S\) H\(_2^+\). 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 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 but 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 \(^1S\) (para) and \(^3P\) (ortho) of H\(_2^+\)

In this section, we discuss the difference between the \(^1S\) and \(^3P\) 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 \(^1S\) and \(^3P\) 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 \(^1S\) state have been summarized in Sec. III A. Similar calculations for \(^3P\) were performed with the same \(g\) given by Eq. (11) and \(\psi_0\) given by Eq. (13).
The same accuracy as the previous reference. We obtained calculated energies converged to the exact value with almost

$$\frac{58.231 941 \text{ cm}^{-1}}{H_2}$$

that is, 25 digits in accuracy at

$$-0.596 873 738 832 764 735 920 744 98$$

The energy difference between the 1S and 3P states was 0.000 265 324 a.u. (58.231 941 cm\(^{-1}\)), which is quite small compared with the energy difference for the frequency (2191 cm\(^{-1}\); ν=0 to ν=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 1S and 3P states is as large as 169 088 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 1S and 3P states of H\(^2\)+. In addition to the energy difference, the degeneracy of the state, which is unity for the 1S state and three for the 3P state, also affects the distribution probability. The resultant ratio of populations between the para H\(^2\)+ (1S) and ortho H\(^2\)+ (1P) states was 1:2.27 at room temperature. The major distribution of H\(^2\)+ was ortho H\(^2\)+ (1P) because of its larger spin multiplicity.

Table IV shows the calculated results with every order of the FC, where the proton mass employed was the conventional value of \(m_p=1836.152\) 701 to compare with the previous references.\(^{33}\) We obtained our best energy of

\[-0.596 873 738 832 764 735 920 744 98\] a.u., that is, 25 digits in accuracy at \(n=16\) and \(M_n=17\) 770.

The vibrational frequencies between adjacent states are also compared with the previous reference data. The two nonlinear values of H\(^2\)+ was 0.000 265 324 a.u. and 32 764 735 920 744 98 a.u., that is, 25 digits in accuracy at

\[-0.596 873 738 832 764 735 920 744 98\] a.u.

The energy difference between the 1S and 3P states was 0.000 265 324 a.u. (58.231 941 cm\(^{-1}\)), which is quite small compared with the energy difference for the frequency (2191 cm\(^{-1}\); ν=0 to ν=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 1S and 3P states is as large as 169 088 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 1S and 3P states of H\(^2\)+. In addition to the energy difference, the degeneracy of the state, which is unity for the 1S state and three for the 3P state, also affects the distribution probability. The resultant ratio of populations between the para H\(^2\)+ (1S) and ortho H\(^2\)+ (1P) states was 1:2.27 at room temperature. The major distribution of H\(^2\)+ was ortho H\(^2\)+ (1P) because of its larger spin multiplicity.

D. Vibronic excited states and some expectation values of H\(^2\)+ (1S) and H\(^2\)+ (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 1S and 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 \(\phi_0\) given by Eq. (12) for H\(^2\)+ of the 1S state at \(n=14\) and \(M_n=5950\). The same g and \(\phi_0\) 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 \(\phi_0\) given by Eq. (14) for H\(^2\)+ of the 3P state, \(n=11\) and \(M_n=6094\) were used with \(\phi_0\) given by Eq. (13).

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 IV: Energy of the 1P state of H\(^2\)+ calculated with g and \(\phi_0\) given by Eqs. (11) and (13), respectively.

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

Ref. 33

\(-0.596 873 738 832 764 735 920 744 98\)
TABLE V. Energies and the expectation values \((\langle r_1 \rangle, \langle r_2 \rangle, \text{and} \langle R \rangle)\) for the ground and a few excited states of the same symmetry for \(H_2^+\) and its isotopomers. For \(H_2^+ (1S, D_2^+, T_2^+, H_2^+, H_T^+, \text{and} D_T^+)\), the \(a\) and \(b\) in Eqs. (11) and (12) were used at \(n=14\) and \(M_0=5950\) and, for \(H_2^+ (1P)\), Eqs. (11) and (13) were used at \(n=11\) and \(M_0=5914\) for \(HD^+, HT^+, \text{and} DT^+\). The nuclear mass data used were \(m_1 = 1836.152 672 \text{ cm}^{-1}, m_2 = 3670.482 965 \text{ cm}^{-1}, \text{and} m_{12} = 5496.921 526 \text{ cm}^{-1}.\) Values of \(\alpha = 1.1086\) and \(\beta = 4.32\) were employed for the nonlinear parameters.

<table>
<thead>
<tr>
<th>(v^*)</th>
<th>Energy (a.u.)</th>
<th>Frequency (cm(^{-1}))</th>
<th>(\langle r_1 \rangle)</th>
<th>(\langle r_2 \rangle)</th>
<th>(\langle R \rangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2^+ (1S))</td>
<td>0</td>
<td>0.597 139 063 079 175 256 939 373 016</td>
<td>1.692 966 208</td>
<td>1.692 966 208</td>
<td>2.063 913 867</td>
</tr>
<tr>
<td>1</td>
<td>0.587 155 679 095 614 799 279</td>
<td>2191.099 519</td>
<td>1.764 752 230</td>
<td>1.764 752 230</td>
<td>2.199 125 136</td>
</tr>
<tr>
<td>2</td>
<td>0.577 751 904 414 194 283</td>
<td>2063.889 981</td>
<td>1.839 368 775</td>
<td>1.839 368 775</td>
<td>2.339 751 003</td>
</tr>
<tr>
<td>(H_2^+ (1P))</td>
<td>0</td>
<td>0.596 873 738 784 476 119 983</td>
<td>1.694 397 351</td>
<td>1.694 397 351</td>
<td>2.066 619 898</td>
</tr>
<tr>
<td>1</td>
<td>0.586 904 320 918 598 361</td>
<td>2188.034 311</td>
<td>1.766 243 642</td>
<td>1.766 243 642</td>
<td>2.201 944 950</td>
</tr>
<tr>
<td>2</td>
<td>0.577 514 034 056 498</td>
<td>2060.929 747</td>
<td>1.840 928 825</td>
<td>1.840 928 825</td>
<td>2.342 700 915</td>
</tr>
<tr>
<td>(D_2^+)</td>
<td>0</td>
<td>0.598 788 784 304 562 875 674 903 269</td>
<td>1.682 346 538</td>
<td>1.682 346 538</td>
<td>2.044 070 029</td>
</tr>
<tr>
<td>1</td>
<td>0.591 603 121 831 520 710 239</td>
<td>1577.070 622</td>
<td>1.732 573 538</td>
<td>1.732 573 538</td>
<td>2.138 662 460</td>
</tr>
<tr>
<td>2</td>
<td>0.584 712 206 896 550 366</td>
<td>1512.381 015</td>
<td>1.784 134 235</td>
<td>1.784 134 235</td>
<td>2.235 803 372</td>
</tr>
<tr>
<td>(T_2^+)</td>
<td>0</td>
<td>0.599 506 910 096 112 180 587 249 172</td>
<td>1.677 707 679</td>
<td>1.677 707 679</td>
<td>2.035 386 031</td>
</tr>
<tr>
<td>1</td>
<td>0.593 589 927 768 924 154 523</td>
<td>1298.627 515</td>
<td>1.718 559 684</td>
<td>1.718 559 684</td>
<td>2.112 318 407</td>
</tr>
<tr>
<td>2</td>
<td>0.587 871 233 588 277 177</td>
<td>1255.108 297</td>
<td>1.760 279 582</td>
<td>1.760 279 582</td>
<td>2.190 908 363</td>
</tr>
<tr>
<td>(HD^+)</td>
<td>0</td>
<td>0.597 797 968 608 954 700 621</td>
<td>1.688 442 006</td>
<td>1.687 732 429</td>
<td>2.054 803 238</td>
</tr>
<tr>
<td>1</td>
<td>0.589 181 829 556 745 679 654</td>
<td>1912.971 405</td>
<td>1.750 355 477</td>
<td>1.750 355 477</td>
<td>2.171 318 411</td>
</tr>
<tr>
<td>2</td>
<td>0.580 903 700 218 035 070</td>
<td>1816.839 385</td>
<td>1.814 343 968</td>
<td>1.814 343 968</td>
<td>2.291 782 413</td>
</tr>
<tr>
<td>(HT^+)</td>
<td>0</td>
<td>0.598 176 134 637 481 345 390</td>
<td>1.686 767 475</td>
<td>1.685 825 362</td>
<td>2.051 456 621</td>
</tr>
<tr>
<td>1</td>
<td>0.589 323 814 045 479 912 796</td>
<td>1809.199 748</td>
<td>1.745 058 766</td>
<td>1.745 058 766</td>
<td>2.161 124 416</td>
</tr>
<tr>
<td>2</td>
<td>0.582 080 048 852 003 373</td>
<td>1723.482 746</td>
<td>1.805 179 364</td>
<td>1.805 179 364</td>
<td>2.274 267 594</td>
</tr>
<tr>
<td>(DT^+)</td>
<td>0</td>
<td>0.599 130 662 833 885 811 307</td>
<td>1.680 255 515</td>
<td>1.680 023 340</td>
<td>2.039 939 515</td>
</tr>
<tr>
<td>1</td>
<td>0.592 545 017 179 965 882 666</td>
<td>1445.382 152</td>
<td>1.726 030 854</td>
<td>1.726 030 854</td>
<td>2.126 133 588</td>
</tr>
<tr>
<td>2</td>
<td>0.586 206 019 855 001 345</td>
<td>1391.249 101</td>
<td>1.772 906 374</td>
<td>1.772 906 374</td>
<td>2.214 406 291</td>
</tr>
</tbody>
</table>

\(^*\)Excitation level.

The expectation values \((\langle r_1 \rangle, \langle r_2 \rangle, \text{and} \langle R \rangle)\) 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, \(H_2^+, D_2^+, T_2^+, \text{HD}^+, \text{HT}^+, \text{and} DT^+\). 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

\(\text{higher}\)
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 \( \text{H}_2^+ \), the value of \( R \) 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 correction to 32 digits of precision has been obtained for \( \text{H}_2^+ \) for the \( ^1S \) ground state. Very accurate energies were also obtained for the vibronic ground and excited states of \( \text{H}_2^+ \), HD\(^+\), HD\(^-\), and HT\(^+\). The excitation frequencies between the nearest two vibronic states compared well with the experimental values when available. The \( ^1P \) state of \( \text{H}_2^+ \) has the same electronic structure as the \( ^1S \) state, which corresponds to the \( 1\sigma \) state in the BO approximation, but they have different nuclear spin structures. A very small energy difference of 58.231 \( 941 \) cm\(^{-1} \) was obtained between the \( ^1S \) and \( ^3P \) states. We have also applied our method to the isotopomers of \( \text{H}_2^+ \), i.e., D\(_2^+\), T\(_2^+\), HD\(_+\), HD\(_-\), 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, 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 electron-nuclear 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\(^ {15} \) 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.

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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:

\[
I = \int_0^\infty \int_0^R \int_{-\infty}^R s^3 \rho R e^{-\alpha s} e^{-\beta R^2 + \gamma R} \, ds \, dR 
\times (Y_{l_1l_2}^{\alpha x})^* Y_{l_2l_1}^{\lambda x} d\gamma dt \, d\alpha 
\]

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 \( \alpha \) and \( \beta \) are positive real numbers. \( Y_{L,M}^{\lambda x} \) 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 \( (Y_{l_1l_2}^{\alpha x})^* Y_{l_2l_1}^{\lambda x} \) over the Euler angles.

The integration of its angular part, given by

\[
J_{L,M,l_1,l_2,\lambda_1,\lambda_2} = \int (Y_{l_1l_2}^{\alpha x})^* Y_{l_2l_1}^{\lambda x} \, d\gamma , \quad (A2)
\]

is estimated by

\[
J_{L,M,l_1,l_2,\lambda_1,\lambda_2} = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2\lambda_1 + 1)(2\lambda_2 + 1)}{4\pi}} \times \\
\left( \begin{array}{c} \lambda_1 \\ l_1 \end{array} \right) \left( \begin{array}{c} \lambda_2 \\ l_2 \end{array} \right) \left( \begin{array}{c} \lambda \\ L \end{array} \right) P_\lambda \left( \frac{r_1^2 + r_2^2 - R^2}{2r_1r_2} \right) , \quad (A3)
\]

where the parentheses: \( () \) and curly braces: \( \{ \} \) in the sigma notation represent the Wigner-3j and Wigner-6j symbols, respectively, and \( P_\lambda \) 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...
\[ J_{L,M,l_1,l_2,\lambda_1,\lambda_2} = \sqrt{(2l_1 + 1)(2l_2 + 1)(2\lambda_1 + 1)(2\lambda_2 + 1)} \times \left( \frac{s + l}{2} \right)^{l_1 + \lambda_1} \left( \frac{s - l}{2} \right)^{l_2 + \lambda_2} (-1)^{l + \lambda} \times \sum_{\alpha} \frac{2\Lambda + 1}{2} \left( \begin{array}{ccc} l_1 & \lambda_1 & \Lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_2 & \lambda_2 & \Lambda \\ 0 & 0 & 0 \end{array} \right) \times \left( \begin{array}{c} \lambda_1 \lambda_2 \\ l_1 \end{array} \right) P_L \left( \frac{s^2 + r^2 - 2R^2}{s^2 - r^2} \right). \] (A4)

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

\[ K_{l,m,n,a,b} = \int_0^\infty \int_0^R \int_{-R}^R s^l t^m R^n e^{-\alpha s} e^{-\beta R^2} Re R dt \, ds \, dR. \] (A5)

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

\[ K_{l,m,n,a,b} = \int_0^\infty \int_0^R \int_{-R}^R s^l t^m R^n e^{-\alpha s} e^{-\beta R^2} Re R dt \, ds \, dR. \] (A6)

After the integration is performed over \( t \), we get

\[ K_{l,m,n,a,b} = \frac{l! \{1 + (-1)^m\}}{(m + 1) \alpha^{\frac{1}{2}}} \sum_{k=0}^l \frac{\Gamma(m + n + 2 + k) \cdot e^{(\alpha - 2\beta R^2) / 2\beta} \cdot D_{l,\alpha + 2\beta} \left( \frac{\alpha - 2\beta R^2}{2\sqrt{\beta}} \right)}{k! (2\beta)^{l + k + 2}} \cdot H_{l,m,n,a,b}, \] (A10)

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

\[ K_{l,m,n,a,b} = \frac{l! \cdot m! \cdot n! \cdot (1 + (-1)^m)_{m+n+1} \cdot C_n}{\alpha^{\frac{1}{2}} \beta^{m+n+2} / 2} \sum_{k=0}^l \left( \frac{l}{\sqrt{\beta}} \right)^k_{m+n+k+1} \cdot C_k \cdot H_{l,m,n,a,b} \left( \frac{\alpha - 2\beta R^2}{2\sqrt{\beta}} \right), \] (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.
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44 P. M. Morse and E. C. G. Stueckelberg, Phys. Rev. 33, 932 (1929); P. M. Morse, ibid. 34, 57 (1929).
45 http://physics.nist.gov/cuu/Constants/
46 Computer algebra package MAPLE, Waterloo Maple Inc., Waterloo, Ontario, Canada (see http://www.maplesoft.com/).
47 About the GMP library, see http://savannah.nongnu.org/ and http://www.swox.com/gmp/.