Solving the Schrödinger and Dirac equations of hydrogen molecular ion accurately by the free iterative complement interaction method

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The nonrelativistic Schrödinger equation and the relativistic four-component Dirac equation of H_2^+ were solved accurately in an analytical expansion form by the free iterative complement interaction (ICI) method combined with the variational principle. In the nonrelativistic case, we compared the free ICI wave function with the so-called "exact" wave function as two different expansions converging to the unique exact wave function and found that the free ICI method is much more efficient than the exact method. In the relativistic case, we first used the inverse Hamiltonian to guarantee Ritz-type variational principle and obtained accurate result. We also showed that the ordinary variational calculation also gives a nice convergence when the *g* function is appropriately chosen, since then the free ICI calculation guarantees a correct relationship between the large and small components of each adjacent order, which we call ICI balance. This is the first application of the relativistic free ICI method to molecule. We calculated both ground and excited states in good convergence, and not only the upper bound but also the lower bound of the ground-state energy. The error bound analysis has assured that the present result is highly accurate. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2842068]

I. INTRODUCTION

Schrödinger equation (SE) is the most fundamental equation in the fields of quantum physics and chemistry, but its solution for general system has long been thought to be impossible.[1] However, recently, we have proposed and developed a general methodology for solving the Schrödinger equation in an analytical expansion form. The methodology is based on the study of the structure of the exact wave function.[2–4] The iterative complement interaction (ICI) method was proposed to construct the exact wave function but it included the integrals of higher powers of Hamiltonian, which diverge for atoms and molecules for the existence of singular Coulomb potential. This singularity problem has been overcome by introducing the scaled Schrödinger equation (SSE),[3] which is equivalent to the original SE. The ICI method and the free ICI (Ref. 3) method based on the SSE converge to the exact wave function without encountering the singularity problem. This has enabled us to calculate highly accurate solutions of the SE of various atoms and molecules:[2–5] some were actually the most accurate solutions of the SE so far obtained. Not only the energy but also the nuclear and electron cusp values and the local energy were shown to be highly accurate.[4] Furthermore, due to its simplicity and generality, the ICI and free ICI methods have been extended to solve the relativistic Dirac equation and the Dirac–Coulomb equation, and accurate solutions of the one- and two-electron atoms have been reported[6] but applications to molecules have not yet been done. Here, we describe our ICI formalism for solving the hydrogen molecular ion (H_2^+) at both nonrelativistic and relativistic levels.

H_2^+ is the simplest molecule and recognized important as an interstellar molecule. Quite accurate descriptions of this molecule have been necessary for the assignment of astronomical spectroscopy.[7] Extensive nonrelativistic studies have been done for many years and the exact solutions of H_2^+ and other two-center one-electron systems have been presented[8–10] in analytical expansion form. Relativistic calculations were also made by various methods[11–17] and the major emphasis was the accuracy of the calculated energy: in particular, the finite-element method[11,16] (FEM) and the direct perturbation theory[12] (DPT) gave accurate results. To date, the FEM result has been regarded to be most accurate in energy. However, in these calculations the variational property was not guaranteed. Further, the FEM does not give an analytical expression of the wave function covering all over the coordinate space. Though there exists the calculations using Gaussian-type orbitals[14] and Slater-type orbitals,[17] their results were not as accurate as those of the FEM and DPT.

In this paper, we present variational solutions of the nonrelativistic SE and the relativistic Dirac equation of H_2^+ in analytical expansion forms by applying the free ICI methodology developed in our laboratory. Further, in addition to the upper bound energy, we calculate lower bound energy from the calculated wave function, which guarantees that the present results are highly accurate.

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II. THEORY

A. Definition of the system

The SE for the nonrelativistic H_2^+ is

$$H\psi = E\psi, \tag{1}$$

where the Hamiltonian is given in the Born–Oppenheimer (BO) approximation as

$$H = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}. \tag{2}$$

a and b denote two protons and R is the internuclear distance. Owing to the BO approximation, this three-body problem is converted into a two-center one-particle problem, for which one favorably uses elliptic coordinate.

$$\lambda = \frac{r_a + r_b}{R}, \quad \mu = \frac{r_a - r_b}{R}, \quad \omega. \tag{3}$$

In this coordinate, the kinetic operator is written as

$$-\frac{1}{2}\nabla_e^2 = -\frac{2}{R^2(\lambda^2 - \mu^2)}\left\{ \frac{\partial}{\partial\lambda}(\lambda^2 - 1)\frac{\partial}{\partial\lambda} + \frac{\partial}{\partial\mu}(1 - \mu^2)\frac{\partial}{\partial\mu} \right.$$
$$\left. + \frac{(\lambda^2 - \mu^2)}{(\lambda^2 - 1)(1 - \mu^2)}\frac{\partial^2}{\partial\omega^2} \right\} \tag{4}$$

and the electron-nucleus Coulomb interaction operator by

$$V = V_{en} = -\frac{2\lambda}{R(\lambda^2 - \mu^2)}. \tag{5}$$

The Dirac equation for the relativistic H_2^+ is written similarly to the SE [Eq. (1)] and its Hamiltonian is defined as

$$H = \begin{bmatrix} (V + c^2)I_2 & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & (V - c^2)I_2 \end{bmatrix}, \tag{6}$$

where V represents the electron-nuclei attraction potential given by Eq. (5), $\mathbf{p} = -i\nabla$ is the momentum operator, $\boldsymbol{\sigma}$ the Pauli matrix, and I_2 the 2×2 identity matrix. In all relativistic calculations, we used $c = 1/\alpha = 137.035\,989\,5$.[18]

B. Free ICI method

The SE can be written equivalently in the form of the SSE (Ref. 3) as

$$g(H\psi - E\psi) = 0, \tag{7}$$

where the function $g(r) \geq 0$ scales the singularities of the potential to be finite. The choice of g in the actual calculations will be described in the next section. The simplest ICI (SICI) based on the SSE,

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n \tag{8}$$

is proved to become exact at convergence[3] without encountering the singularity problem for the presence of the scaling function g. When one uses variation principle, the energy becomes lower and lower, is bounded from below, and is guaranteed to become exact at convergence, so that it should converge to the exact solution. The free ICI method is defined by gathering all the independent analytical functions from the right-hand side of Eq. (8) as $\{\phi_k\}^{(n)}$, $k = 1, \ldots, M_n$,

and giving independent coefficient to each function as

$$\psi_{n+1} = \sum_{k=1}^{M_n} c_k \phi_k. \tag{9}$$

Because of the increased freedom, the free ICI method converges faster to the exact wave function than the original SICI. The variables $\{c_k\}^{(n)}$ of the free ICI wave function are calculated by applying the variational principle to Eq. (9).

Since the ICI formalism is guaranteed to reach the exact solution, this free ICI method gives the best possible wave function at each iteration cycle. Note that in the free ICI method, the next iteration cycle does not require the variables $\{c_k\}^{(n)}$ of the former cycles, so that n may be understood as designating the order rather than the iteration cycle. One can get the nth order free ICI functions $\{\phi_k\}^{(n)}$ directly from the initial function ψ_0 by applying the operator part of Eq. (8) n times. The accumulation of errors during iterations does not occur in the free ICI calculations. For the determination of the variables $\{c_k\}^{(n)}$, the secular equation should be solved in high accuracy. For this purpose, we used the GNU multiple precision arithmetic library[19] and the symbolic operation program, MAPLE.[20]

In the free ICI formalism, we have a freedom in the choices of the g function and the initial function ψ_0. The g function should be a functional of the inverse of the Coulomb potential, from its purpose to eliminate the singularity of the Coulomb potential. The initial function should have the symmetry of the state we want to calculate: because the Hamiltonian is totally symmetric, the symmetry of the generated functions is always the same as that of the initial function.

The Dirac equation can also be written in a scaled form as

$$g(H\psi - E\psi) = 0, \tag{10}$$

where the scaling function g, which is scalar, is defined similarly to the nonrelativistic case. The SICI for the Dirac equation is defined similarly to Eq. (8) as

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n \tag{11}$$

and the free ICI by

$$\psi_{n+1} = \sum_{k=1}^{M_n} c_k \phi_k, \tag{12}$$

with C_n and c_k here as four-dimensional diagonal matrices and ϕ_k as four-component spinor functions.

Unlike the nonrelativistic case, we have to take "variational collapse" problem into account for the Dirac equation. Many studies have been explored to overcome this problem[21] and various methods have been developed. Generally, the variational collapse has its origin in an improper limited representation of the wave function: if the description is enough wide and proper, it should not occur.[22] Actually, however, such description is not an easy task as stated below. Hill and Krauthauser[23] proposed an inverse Hamiltonian method to guarante the Ritz-type variational property in a rigorous

sense. Previously, we applied this method to solve the relativistic Dirac–Coulomb equation of one- and two-electron atoms.[6]

In the inverse Hamiltonian method, the Dirac equation is rewritten as

$$H^{-1}\psi = E^{-1}\psi. \qquad (13)$$

Just like in our case of the inverse Schrödinger equation,[24] it is easy to show the equivalence between the original Dirac equation and the inverse one. For the inverse Dirac equation, the lowest positive energy state (corresponding to the electronic ground state) is mapped to the top of the spectrum, i.e., the highest solution against the complete vacuum and, therefore, the following Ritz-like variational principle holds for the inverse Hamiltonian operator

$$\widetilde{E}^{-1} = \frac{\langle \widetilde{\psi}|H^{-1}|\widetilde{\psi}\rangle}{\langle \widetilde{\psi}|\widetilde{\psi}\rangle} \le E_0^{-1}, \qquad (14)$$

where $\widetilde{\psi}$ is a variational trial function for ψ and E_0 is the true energy of the ground electronic state. Here, a difficult problem arise, that is, how we write H^{-1} explicitly in a closed form. A clever trick was introduced by Hill and Krauthauser and enabled us to avoid the explicit use of the inverse Hamiltonian. Namely, we choose our variational function $\widetilde{\psi}$ in the form of

$$\widetilde{\psi} = H\varphi, \qquad (15)$$

in which φ represents a free variation. Then, the variational equation above is written as

$$\widetilde{E}^{-1} = \frac{\langle \varphi|H|\varphi\rangle}{\langle \varphi|H^2|\varphi\rangle} \le E_0^{-1}, \qquad (16)$$

and all the quantities can be calculated without an explicit use of the inverse Hamiltonian. At the diagonalization step of the relativistic free ICI, we utilize the above Ritz-like variational equation to ensure the bound property. However, the choice of the trial function $\widetilde{\psi}$ in the form of Eq. (15) imposes some restriction on φ, since $\widetilde{\psi}$ must be square integrable. The existence of the singular potential in H makes the basis function form of φ to be more limited.

In addition, we calculated the following expectation value

$$\langle E\rangle = \frac{\langle \varphi|H|\varphi\rangle}{\langle \varphi|\varphi\rangle} \qquad (17)$$

using the eigenvector φ calculated by the above inverse method. We call this energy as inverse-regular (IR) energy. Since φ of Eq. (17) was calculated with the use of the inverse Hamiltonian method that avoids the variational collapse, the energy expectation value of this φ would be reliable. To distinguish IR energy from this, we call the energy calculated by the inverse method given by Eq. (16) as inverse-inverse (II) energy. Throughout the paper, we call these inverse Hamiltonian-based methods as "the inverse method."

On the other hand, we may also use the ordinary variational method based on the standard regular Hamiltonian. We call such method "regular method." The energy calculated

from the wave function of the regular method has the form of Eq. (17), so that this energy may be called regular-regular (RR) energy. The IR and RR energies are not bounded from below but have the following interesting features characterized by the ICI method.

It is well known that the Dirac equation connects the large and small components:[22] the exact connection is called "atomic" balance and an approximate one "kinetic" balance. So, when one imposes such balancing condition between the basis sets of the large and small components, one can avoid the variational collapse. Actually, in our free ICI formalism, the correct relationship between the large and small components is imposed between those of the adjacent orders:[6] within each order, the relationship is approximate, so that this balancing does not help much initially at low orders, but as the order increases, it approaches the correct balancing. We call this balancing as "ICI" balance. Thus, within the ICI methodology, even the ordinary variational method based on the regular Hamiltonian may give correct variational solutions as far as the order n is large enough. On the other hand, the II method is always guaranteed to have the bound property as expressed by Eq. (16).

C. Calculation of the lower bound

All types of the energies given in the previous section correspond to the upper bounds of the exact energy. If we can calculate accurate lower bound of the exact energy from the wave function we are at hands, we can estimate correctly the error bars of the calculated energy. From this point of view, the calculation of the lower bound is as important as that of the upper bound and so, many researches for the lower bound have been made (see, for example, Ref. 25). Most of them are related to the variance of the energy given by,

$$\sigma^2 = \frac{\langle \psi|H^2|\psi\rangle}{\langle \psi|\psi\rangle} - \left[\frac{\langle \psi|H|\psi\rangle}{\langle \psi|\psi\rangle}\right]^2. \qquad (18)$$

In spite of its importance, the calculation of the lower bound is not as popular as that of the upper bound, because the calculation of the integral $\langle \psi|H^2|\psi\rangle$ is generally more difficult than that of $\langle \psi|H|\psi\rangle$. Additionally, it is known[26] that one cannot obtain a lower bound as accurately as an upper bound unless we have a quite accurate wave function. Our free ICI wave function gives quite accurate upper bound of the exact energy, so that we can expect that it may also give accurate lower bound to the exact energy. When we use the inverse method, the integral $\langle \psi|H^2|\psi\rangle$ is necessary also for the upper bound calculation. This means that we can calculate the upper and lower bounds at the same time.[26]

Among the various formulas of the lower bound, we utilized the Temple's lower bound[27] given by

$$E_{\mathrm{low}} = \langle \psi|H|\psi\rangle - \frac{\sigma^2}{E_{\mathrm{ex}} - \langle \psi|H|\psi\rangle}, \qquad (19)$$

where E_{ex} is the energy of the first excited state having the same symmetry as the ground state. The calculation of E_{ex} is also easy in the free ICI method because the excited states are obtained as the higher-energy solutions of the diagonal-

TABLE I. Nonrelativistic energy for the ground state ($1\sigma_g$) of H_2^+ ($R=2.0$ a.u.).

Order	Dimension	α	Energy (a.u.)
0	1	1.3	−**1.0**79 384 965 831 435 079 726 6
1	4	1.1	−**1.10**1 421 270 731 672 255 605 4
2	13	0.8	−**1.102 6**27 432 357 876 891 750 1
3	26	1.2	−**1.102 634 2**08 423 548 446 172 2
4	43	1.1	−**1.102 634 214 49**3 685 465 420 5
5	64	1.1	−**1.102 634 214 494 94**5 584 228 3
6	89	1.3	−**1.102 634 214 494 946 461** 243 5
7	118	1.2	−**1.102 634 214 494 946 461 508** 8
Our best result (Order=15, Dim.=494)		1.3	−1.102 634 214 494 946 461 508 968 945
Exact wave function[a]			−1.102 634 214 494 9
Correlated wave function[b]			−1.102 623 7
$23s/9p/4d/4f/2g$:GTO[c]			−1.102 634 0
Finite element method[d]			−1.102 632 7
Finite difference method[e]			−1.102 634 214 497

[a]Reference 31.
[b]Reference 32.
[c]Reference 33.
[d]Reference 34.
[e]Reference 35.

ization for the ground state. Since the lower bound nature is ensured for the inverse method, the same nature is also ensured to the calculated energy of the excited state. So, the inequality $E < E_{ex}$ is assured. Thus, we can safely apply Temple's method even to the relativistic case.[28]

III. RESULTS AND DISCUSSIONS

A. Nonrelativistic case

Here, we performed the free ICI calculations for solving the SE of H_2^+. The g function was chosen as the inverse of the electron-nuclear Coulomb potential written in the elliptic coordinate as

$$g = -\frac{1}{V} = \frac{R(\lambda^2 - \mu^2)}{4\lambda}. \tag{20}$$

For the $1\sigma_g$ ground state, the initial function was the Slater-type function

$$\psi_0 = \exp\left[-\frac{\alpha'}{R}(r_a + r_b)\right] = \exp(-\alpha\lambda), \tag{21}$$

where α and α' are nonlinear parameters with $\alpha' = R\alpha$. In this choice, the free ICI wave function is generated in the analytical expansion form of

$$\Psi = \sum_i c_i \lambda^{m_i} \mu^{n_i} \exp(-\alpha\lambda), \tag{22}$$

where c_i is the variational parameter and m_i is positive or negative integer. Since the $1\sigma_g$ ground state has a gerade symmetry, n_i should be zero or a positive even integer. A simple function, given by James[29]

$$\psi = \exp(-\alpha\lambda)(\mu^2 + \gamma), \tag{23}$$

where γ is a variable coefficient, is regarded as a special example of our form of the exact wave function. We summarize in Table I the calculated energies for the ground state

$1\sigma_g$ at different orders. Alpha values were optimized at each order. The convergence of the free ICI energy was quite good. Our best energy is the known best of the exact energy.

The first excited state $1\sigma_u$ (ungerade) was also calculated, starting from the initial function of the ungerade symmetry

$$\psi_0 = \mu \exp(-\alpha\lambda). \tag{24}$$

The free ICI wave function of the $1\sigma_u$ state is also expressed in the analytical expansion form given by Eq. (22), where n_i should be positive odd integers. The g function was the same as for the $1\sigma_g$ state given by Eq. (21). The results are given in Table II. Just as for the gerade states, the convergence of the free ICI was very good and quite accurate energy was calculated.

For H_2^+, the exact wave function for the nonrelativistic SE is known and given by[8]

$$\psi(\lambda, \mu, \phi) = \Lambda(\lambda)M(\mu)\exp(im\phi), \tag{25}$$

where

$$\Lambda(\lambda) = (1 + \lambda)^\sigma (\lambda^2 - 1)^{|m/2|} \exp(-\alpha\lambda) \sum_{k=0}^{\infty} g_k \left(\frac{1 - \lambda}{1 + \lambda}\right)^k,$$

$$\sigma = \frac{R}{\alpha} - |m| - 1, \tag{26}$$

$$M(\mu) = \sum_{l=0}^{\infty} f_l P_l(\mu),$$

m corresponds to the magnetic quantum number, and $P_l(\mu)$ is associated Legendre function. g_k and f_l are the coefficients determined by the differential equations obtained from the SE by separating the variables. Note that the exact wave function is given also in the analytical expansion form as our free ICI wave function given by Eq. (22). They are two dif-

TABLE II. Nonrelativistic energy for the ungerade excited state ($1\sigma_u$) of H_2^+ ($R=2.0$ a.u.).

Order	Dimension	α	Energy (a.u.)
0	1	0.9	**−0.66**2 993 039 443 155 452 436 195
1	4	0.8	**−0.667** 236 686 962 501 148 195 507
2	13	1.1	**−0.667 534** 068 275 070 663 143 593
3	26	1.0	**−0.667 534 392** 107 704 479 296 447
4	43	1.0	**−0.667 534 392 202** 280 580 231 750
5	64	1.1	**−0.667 534 392 202 382** 893 318 000
6	89	1.1	**−0.667 534 392 202 382 930 3**43 919
7	118	1.1	**−0.667 534 392 202 382 930 361 96**8
Our best result (Order=14, Dim.=433)		1.2	−0.667 534 392 202 382 930 361 970 211 49
Exact wave function[a]			−0.667 534 392 202 4
Correlated wave function[b]			−0.667 507 8
Finite element method[c]			−0.667 533 1
Finite difference method[d]			−0.667 534 392 205

[a]Reference 31.
[b]Reference 32.
[c]Reference 34.
[d]Reference 35.

ferent expressions of the analytical expansion of the one unique exact wave function.

We now want to compare the present free ICI wave function with the exact wave function. However, the exact wave function is defined in the infinite expansion form and, practically, we have to truncate this expansion, which was first introduced by Wind[9] and more elaborate and general cases were studied by Hunter et al.[10] We followed the method of Ref. 10 and determined the coefficients g_k and f_l of Eq. (26). Then, we compare this "truncated exact" wave function with the free ICI wave function. For this purpose, we introduce

$$\sigma^2 = \int (\psi_{t.\text{exact}} - \psi_{f\text{ICI}})^2 d\tau, \tag{27}$$

which shows the deviation of the ICI wave function from the truncated exact one. This quantity is zero, when $\psi_{f\text{ICI}}$ and $\psi_{t.\text{exact}}$ are identical everywhere in the coordinate space.

Here, the exact series of Eq. (26) were truncated at the orders of λ and μ to be less than 23 and 14, respectively, which assures $E=-1.102\,634\,214\,494\,9$ a.u. The criteria for the energy accuracy and the truncation level are essentially the same as those in Ref. 10. We show in Table III the convergence behavior of σ^2. We see that as the order increases, the ICI wave function converges very rapidly to the truncated exact wave function. This is reasonable since the free ICI wave function is also guaranteed to converge to the exact wave function as the order n increases, likewise, the exact

series given by Eq. (26). In other words, now, we have two different series of analytical wave functions that converge to the exact wave function. So, a question is which is more efficient? We examine it below.

First, how many basis functions are necessary for obtaining the similar accuracy? Figure 1 shows a comparison between the truncated exact method and the free ICI method to get the similar energy accuracy. The abscissa corresponds to the energy accuracy in the number of correct figures. Apparently, the convergence of the free ICI wave functions is quite efficient. To calculate the truncated exact wave function, one must iteratively solve the eigenvalue equations and estimate the λ and μ truncation error. They are not an easy task as the dimension grows.[10] Different from the method in Ref. 10, the calculations based on the variational principle are also possible for the truncated exact form. This gives, for example, $-1.102\,634\,214\,494\,946\,461\,508\,97$ a.u. by 110 functions (the order of λ and μ is less than 10 and 18, respectively), to be compared with $-1.102\,634\,214\,494\,946\,461\,508\,80$ a.u. (with 118 functions) of the free ICI results. Both energies are much more accurate than the "nonvariational truncated exact" energy of $-1.102\,634\,214\,494\,9$ a.u. for the 322 functions. Note that the variational energy of the truncated exact

TABLE III. The deviations of ICI wave functions from the exact wave function ($R=2.0$ a.u., α's are same as in Table I).

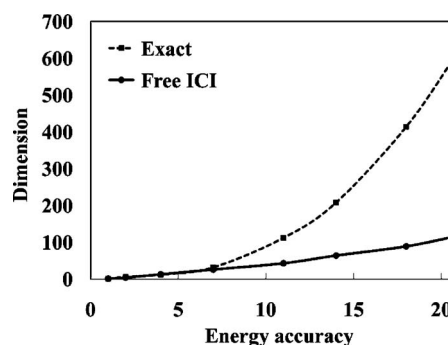| Order	Dimension	σ^2
0	1	1.2635×10^{-2}
1	4	1.0723×10^{-3}
2	13	2.4902×10^{-6}
3	26	7.0255×10^{-10}
4	43	4.8703×10^{-13}

FIG. 1. The efficiency comparison between the free ICI wave function and the exact wave function. The digits in the x axis are defined as the energy eigenvalue that has 10^{-N} (a.u.) accuracy.

TABLE IV. Relativistic energy for the ground state ($1\sigma_g$) of H_2^+ with the g function given by Eq. (21) (R =2.0 a.u., α=2.0: The numbers of the spinor components are shown in the parentheses).

Order	Dimension	II energy (a.u.)
0	4 (1,1,1,1)	−0.659 496 913 372 7
1	11 (1,3,6,1)	−**1.**083 448 433 903 8
2	47 (12,10,16,9)	−**1.10**1 365 364 460 9
3	95 (25,22,29,19)	−**1.102** 433 966 380 5
4	159 (41,37,47,34)	−**1.102** 587 047 480 7
5	239 (62,57,68,52)	−**1.102 6**22 112 824 7
6	335 (86,80,94,75)	−**1.102 6**32 893 567 4
7	447 (115,108,123,101)	−**1.102 6**36 988 619 3
8	575 (147,139,157,132)	−**1.102 6**38 809 768 9
9	719 (184,175,194,166)	−**1.102 6**39 734 980 7
10	879 (224,214,236,205)	−**1.102 64**0 256 624 1
11	1055 (269,258,281,247)	−**1.102 64**0 577 479 9
12	1247 (317,305,331,294)	−**1.102 64**0 789 022 2
13	1455 (370,357,384,344)	−**1.102 64**0 936 651 0
14	1679 (426,412,442,399)	−**1.102 641** 044 331 7
15	1919 (487,472,503,457)	−**1.102 641** 125 455 2
Finite element method[a]		−1.102 641 581 033 8
Direct perturbation theory[b]		−1.102 641 579 453
Finite Difference method[c]		−1.102 641 570 9
Monte Carlo method[d]		−1.102 565
Four-component Gaussian type spinor[e]		−1.102 641 580 1
Minimax theory[f]		−1.102 481

[a]Reference 11.
[b]Reference 12.
[c]Reference 35.
[d]Reference 13.
[e]Reference 14.
[f]Reference 15.

form is lower than that of the free ICI wave function. However, the variational treatment of the truncated exact wave functions is quite difficult because the functions involved in the series are almost linearly dependent on each other and so, the Hamiltonian and overlap matrices must be calculated with very high accuracy. Moreover, the integrations are also difficult because of the existence of the nonlinear terms in Eq. (26). Therefore, it is not practical to perform variational calculations with the "exact" wave function series.

In conclusion, we could say that the free ICI procedure is much more efficient way of solving the nonrelativistic exact wave function of H_2^+ than even the exact treatment of the SE of H_2^+.

B. Relativistic case

Next, we solved the relativistic Dirac equation of H_2^+ by the free ICI method. The initial function we used for the $1\sigma_g$ state was given by[30]

$$\Psi_0 = \begin{bmatrix} \exp(-\alpha\lambda)\exp[i(j_z-1/2)\phi] \\ (\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\exp(-\alpha\lambda)\exp[i(j_z+1/2)\phi] \\ i\exp(-\alpha\lambda)\exp[i(j_z-1/2)\phi] \\ i(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\exp(-\alpha\lambda)\exp[i(j_z+1/2)\phi] \end{bmatrix},$$

(28)

where j_z describes the projection of the total angular momentum on the internuclear axis and is equal to $1/2$ for σ symmetry. We examined two sets of g functions and the first one is the same as that given in Eq. (20). Utilizing this set of

initial and g functions, the free ICI procedure generates the analytical wave function given by

$$\Psi = \sum_i \left\{ \begin{bmatrix} c_i^1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \lambda^{m_i}\mu^{n_i}\exp(-\alpha\lambda) + \begin{bmatrix} 0 \\ c_i^2 \\ 0 \\ 0 \end{bmatrix}(\lambda^2-1)^{1/2} \right.$$

$$\times(1-\mu^2)^{1/2}\lambda^{m_i}\mu^{n_i}\exp(-\alpha\lambda)\exp(i\varphi)$$

$$+ \begin{bmatrix} 0 \\ 0 \\ c_i^3 \\ 0 \end{bmatrix} i\lambda^{m_i}\mu^{n_i}\exp(-\alpha\lambda) + \begin{bmatrix} 0 \\ 0 \\ 0 \\ c_i^4 \end{bmatrix} i(\lambda^2-1)^{1/2}$$

$$\left. \times(1-\mu^2)^{1/2}\lambda^{m_i}\mu^{n_i}\exp(-\alpha\lambda)\exp(i\varphi) \right\}.$$

(29)

Obviously, the first element of the large component has the same form as the nonrelativistic wave function and this means that the wave functions generated by the g function of Eq. (20) have the same structure as the nonrelativistic case. Table IV shows the results of II energy calculations. The II energy converges from above as the order increases and we did not encounter any variational collapse difficulty. However, the speed of the convergence was very slow.

So, we next chose the g function given by

TABLE V. Relativistic energy for the ground state ($1\sigma_g$) of H_2^+ with the g function given by Eq. (31) ($R=2.0$ a.u., $\alpha=2.0$: The numbers of the spinor components are shown in parenthesis and the energy overshooting are noted by bold italic).

Order	Dimension	Energy (a.u.)		
		II	IR	RR
0	4 (1,1,1,1)	−0.659 496 913 372 72	**−*1.275*** 910 162 355 89	**−*1.275*** 910 162 224 65
1	20 (8,4,4,4)	**−*1.*** 099 461 794 474 25	**−*1.103 61*** 5 579 600 33	**−*1.104 92*** 4 761 609 26
2	93 (26,19,25,23)	**−1.102 64** 0 840 072 85	**−1.102 641** 023 119 06	**−1.102 642 55** 8 451 92
3	196 (56,45,49,46)	**−1.102 641 5** 77 748 44	**−1.102 641 5** 78 407 21	**−1.102 641 585 96** 6 62
4	336 (90,76,88,82)	**−1.102 641 58** 0 984 89	**−1.102 641 581** 018 02	**−1.102 641 581 034 77**
5	512 (141,122,126,123)	**−1.102 641 581 00** 9 4	**−1.102 641 581 032** 10	**−1.102 641 581 033 70**
6	724 (191,167,186,180)	**−1.102 641 581 01** 5 9	**−1.102 641 581 032** 56	**−1.102 641 581 033** 49
7	975 (262,234,242,237)	**−1.102 641 581 02** 0 0	**−1.102 641 581 033** 11	**−1.102 641 581 033** 58
8	1262 (330,297,321,314)	**−1.102 641 581 02** 2 8	**−1.102 641 581 033** 11	**−1.102 641 581 033** 56
9	1585 (418,383,395,389)	**−1.102 641 581 02** 4 9	**−1.102 641 581 033** 36	**−1.102 641 581 033** 595 2
10	1944 (506,464,491,483)	**−1.102 641 581 02** 6 3	**−1.102 641 581 033** 38	**−1.102 641 581 033** 591 2
11	2341 (611,567,585,578)	**−1.102 641 581 02** 7 5	**−1.102 641 581 033** 44	**−1.102 641 581 033** 598 0
12	2774 (719,668,698,689)	**−1.102 641 581 02** 8 4	**−1.102 641 581 033** 50	**−1.102 641 581 033** 598 1
Finite element method[a]			−1.102 641 581 033 8	
Direct perturbation theory[b]			−1.102 641 579 453	
Finite Difference method[c]			−1.102 641 570 9	
Monte Carlo method[d]			−1.102 565	
Minimax theory[e]			−1.102 481	
Four-component Gaussian type spinor[f]			−1.102 641 580 1	

[a]Reference 11.
[b]Reference 12.
[c]Reference 36.

[d]Reference 13.
[e]Reference 15.
[f]Reference 14.

$$g = 1 - \frac{1}{V} = 1 + \frac{R(\lambda^2 - \mu^2)}{4\lambda}, \tag{30}$$

where we added the factor unity on the right-hand side of Eq. (20). With the use of the same initial wave function as above, the free ICI method generated the analytical wave function written as

$$\Psi = \sum_i \begin{bmatrix} c_i^1 \lambda^{m_i} \mu^{n_i} \exp(-\alpha\lambda)/(\lambda^2 - \mu^2)^{l_i} \\ c_i^2 (\lambda^2 - 1)^{1/2}(1 - \mu^2)^{1/2}\lambda^{m_i}\mu^{n_i}\exp(-\alpha\lambda)\exp(i\varphi)/(\lambda^2 - \mu^2)^{l_i} \\ c_i^3 i\lambda^{m_i}\mu^{n_i}\exp(-\alpha\lambda)/(\lambda^2 - \mu^2)^{l_i} \\ c_i^4 i(\lambda^2 - 1)^{1/2}(1 - \mu^2)^{1/2}\lambda^{m_i}\mu^{n_i}\exp(-\alpha\lambda)/\exp(i\varphi)(\lambda^2 - \mu^2)^{l_i} \end{bmatrix}. \tag{31}$$

The above function includes the function given by Eq. (29) when $l_i=0$, and so it is more general than that of Eq. (29). Note that the g function of Eq. (30) produces also the functions that are not square integrable, so that they have to be eliminated because the wave function must be square integrable. Table V shows the results of the II, IR, and RR energies when we use the g function of Eq. (30). It is remarkable that the energy convergence in Table V is considerably faster than that in Table IV, which shows the importance of the g function given by Eq. (30). The wave function of the form of Eq. (31) was firstly obtained by the present free ICI method. Actually, this type of functions has not been used in the previous studies of H_2^+.

Here, a remark on the numbers of the complement functions between the inverse and regular methods given in Table V. Generally speaking, the inverse and regular methods have different dimensions because the inverse method involves $\langle\phi_i|H^2|\phi_j\rangle$ integration. The functional form of ϕ_i in the inverse method are more limited because there are some functions ϕ_i that $\langle\phi_i|H|\phi_j\rangle$ is finite but $\langle\phi_i|H^2|\phi_j\rangle$ is infinite. However, in the present case, the denominator of Eq. (31) includes only integer indices and, therefore, the dimensions of the inverse and regular methods are the same.

A reason of the accelerated convergence brought about by this new type of functions lies in the balance condition between the large and small components, which is a neces-

sary condition for the exact solution of the Dirac equation. The g function of Eq. (30) is desirable for satisfying this balancing condition between the large and small components. From the large ψ_n^l and small ψ_n^s components of ψ_n, the ICI generates the functions $cg(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_n^l$ into the small component of ψ_{n+1} and the functions $cg(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_n^s$ into the large component of ψ_{n+1}. The factor unity in Eq. (30) assures that ψ_{n+1} contains $c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_n^l$ in its small component and $c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_n^s$ in the large component. They are the kinetic-balancing functions which are of zeroth order of the true balancing. However, with the g function of Eq. (20) that does not contain unity; the ICI cannot generate the zeroth order kinetic-balancing functions in the next order. This is the main reason of the very slow convergence in Table IV. Thus, it is quite significant for the relativistic calculations to contain the factor unity into the g function. The g function of Eq. (30) includes not only unity but also the first order function $(1/V)$ and, therefore, the higher-order exact balancing functions are automatically generated into the wave function of the next order. This is the ICI balance and is very close to the true balancing (atomic balance):[37] a difference is only that it is between neighboring order, not within the same order, which is really necessary. This is one of the most beneficial points of the present free ICI method for solving the relativistic DE.

In Table V, all the energies (II, IR, and RR) show good convergence. The II method is safer than the others since the upper bound nature of the energy is guaranteed. The II energy, however, seems to be less rapidly convergent than the IR and RR energies. The IR and RR energies at $n=12$ and $M=2774$ are $-1.102\,641\,581\,033\,50$ a.u. and $-1.102\,641\,581\,033\,598\,1$ a.u., respectively. In comparison with the best energy of $-1.102\,641\,581\,033\,8$ a.u. in the literature obtained with the finite element method, these energies show very good agreement with each other except for the final digit of 10^{-13} (note we used the same $c=137.035\,989\,5$ for all). The converged value of the RR energy showed the same value to the digit of 10^{-14}, $-1.102\,641\,581\,033\,59$ a.u. from $n=9$ to $n=12$, which indicates that the correct energy of the relativistic H$_2^+$ with $c=137.035\,989\,5$ is $-1.102\,641\,581\,033\,60$ a.u. and the energy from the finite element method might be slightly overshooting at the 10^{-13} digit.

We must note that the IR and RR energies overshoot the true energy (as shown by bold italic) at the earlier stage of free ICI because the balancing between the neighboring order is particularly insufficient in the earlier stages. The overshooting is seen for the IR energies of $n=0$ and 1 and for the RR energies of $n=0$ to 5. As the order n increases, almost variational results are achieved. The IR energy is slightly more stable and safer than the RR energy because the wave function was determined in the constrained variational space by the inverse method. In the RR case, its energy steadily converges to the exact one as the order increases, since the exact balancing is almost attained by the ICI balance at higher orders.

Further, we must note in the table that the convergence becomes slow in the higher-order steps of the calculations. We think that the reason lies in the limited description of the mild singularity with the present g and initial functions. The

exact solution of the DE should have a mild (noninteger close to zero) singularity at the position of the nucleus. Our wave function of Eq. (31) has the denominator $(\lambda^2 - \mu^2)^{l_i}$ ($l_i \geq 0$: integer), which causes a singular behavior of the wave function at the position of the nucleus. However, since l_i is integer, it may be difficult to describe effectively the noninteger mild singularity. Previously, we introduced "mild singular" g function such as $g=r^{99/100}$ in the calculations of the relativistic hydrogen atom, obtaining good convergence.[6] However, a straightforward application of this idea to the present H$_2^+$ molecule would cause difficult integrations. So, we postpone such calculations in the future.

Further, we applied the present method to the excited state of σ_u symmetry. We used the g function given by Eq. (30) and, in order to represent the ungerade symmetry, the initial function is

$$\Psi_0 = \begin{bmatrix} \mu \exp(-\alpha\lambda) \\ (\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\mu \exp(-\alpha\lambda) \\ i\mu \exp(-\alpha\lambda) \\ i(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\mu \exp(-\alpha\lambda) \end{bmatrix}. \quad (32)$$

As in the nonrelativistic calculations, just switching the symmetry of the initial function is sufficient to satisfy the symmetry of the wave function. The convergence behaviors of the II and IR energies are shown in Table VI. As in the gerade symmetry case, quite accurate relativistic energy of the $1\sigma_u$ state was calculated. Again, the II energy converges more slowly than the IR energy, though a overshooting of the energy was seen in the IR energy of the initial function. The excited state having the same symmetry as the ground state was calculated at the same time and the result will be shown below.

As stated above, the calculations of the energy lower bounds, in addition to the upper bounds, are important. For using the Temple's method, we also have to calculate the energy upper bound for the first excited state with the σ_g symmetry. For this purpose, it is necessary to include in ψ_0 the functions appropriate to the ground and first excited states. Then, the $2\sigma_g$ state is calculated at the same time as the ground $1\sigma_g$ state as the second lowest state. For this reason, we introduced the double-exponent initial function given by

$$\Psi_0 = \begin{bmatrix} \exp(-\alpha_1\lambda)+\exp(-\alpha_2\lambda) \\ (\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\{\exp(-\alpha_1\lambda)+\exp(-\alpha_2\lambda)\} \\ i\{\exp(-\alpha_1\lambda)+\exp(-\alpha_2\lambda)\} \\ i(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\{\exp(-\alpha_1\lambda)+\exp(-\alpha_2\lambda)\} \end{bmatrix}, \quad (33)$$

where α_1 and α_2 correspond to the exponents of the ground and excited states, respectively. Here, we simply assumed α_2 to be one-half of α_1 from the analogy to the hydrogen atom where an orbital exponent is proportional to the reciprocal of its principal quantum number.

Table VII shows the result of the lower bound calculation at each order. Clearly, the lower bound converged to the exact energy from below as contrasted with the usual variational energy (upper bound) converging from above. As the

TABLE VI. Relativistic energy for the ungerade excited state ($1\sigma_u$) of H_2^+ with the g function given by Eq. (31) ($R=2.0$ a.u., $\alpha=2.0$: The numbers of the spinor components are shown in parentheses and the energy overshooting are noted by bold italic).

Order	Dimension	II energy (a.u.)	IR energy (a.u.)
0	4 (1,1,1,1)	0.985 169 938 972 8	−**1.47**2 694 131 842 6
1	30 (10,7,7,6)	−**0.6**57 454 163 925 1	−**0.66**5 299 061 590 3
2	112 (29,26,33,24)	−**0.667** 361 475 031 9	−**0.667** 380 692 731 2
3	222 (58,55,60,49)	−**0.667 5**46 275 547 9	−**0.667 5**46 629 970 5
4	369 (92,89,102,86)	−**0.667 552** 540 111 1	−**0.667 552** 559 478 0
5	555 (145,138,146,126)	−**0.667 552 7**65 517 6	−**0.667 552 7**66 253 4
6	778 (193,189,211,185)	−**0.667 552 771** 771 0	−**0.667 552 771** 800 0
7	1038 (268,261,269,240)	−**0.667 552 771 9**76 6	−**0.667 552 771 9**88 9
8	1336 (332,326,357,321)	−**0.667 552 771 98**5 7	−**0.667 552 771 99**5 0
9	1672 (428,421,431,392)	−**0.667 552 771 987** 6	−**0.667 552 771 995** 5
Finite element method[a]		−0.667 552 771 996	
Direct perturbation theory[b]		−0.667 552 771 493	
Finite Difference method[c]		−0.667 552 764 0	
Minimax theory[d]		−0.669 175	

[a]Reference 16.
[b]Reference 12.
[c]Reference 36.
[d]Reference 15.

order increases, the width between the lower and upper bounds becomes narrower and narrower. Considering the fact that the lower bound corresponds to the variance of the energy, the present results indicate that a quite accurate wave function is obtained by the free ICI procedure. From the result of Table VII, we can show the absolute error of the calculated energy by the difference between the upper and lower bounds. For the order 8 result in Table VII, this is 1.97×10^{-7} a.u. which is in cm^{-1} unit, 4.3×10^{-2} cm^{-1}: this may be compared to the uncertainty of the recent experimental result, 2×10^{-2} cm^{-1}.[38] Actually, from the theoretical reason, the true value should be much closer to the calculated upper bound energy.

The energy of the $2\sigma_g$ state, an excited state belonging to the same symmetry as the ground state, is shown in Table VIII. It corresponds to E_{ex} of Eq. (19). It was calculated as the second lowest energy of the same eigenvalue problem,

together with the energy of the $1\sigma_g$ state. The present result seems to be better than the DPT result and would be the best one so far obtained.

IV. CONCLUSION

We have already shown in the previous papers[3–6] that the free ICI method provides a general method of solving not only the nonrelativistic SE but also the relativistic Dirac and Dirac–Coulomb equations in analytical expansion forms. In this paper, we have shown that the free ICI method combined with the variational principle gives very accurate analytic wave functions of H_2^+ efficiently in both nonrelativistic and relativistic cases. For the nonrelativistic case, we compared two analytical expansions conversing to the exact wave function: the so-called exact wave function and the present free

TABLE VII. Calculated energy upper and lower bounds (a.u.) for the ground state ($1\sigma_g$) of H_2^+ with the g function given by Eq. (31) and the ψ_0 given by Eq. (36) ($R=2.0$ a.u., $\alpha=2.0$: The numbers of the spinor components are shown in parentheses and the energy overshooting are noted by bold italic).

Order	Dimension	Upper bounds		Lower bounds
		II energy	IR energy	
0	8 (2,2,2,2)	−0.943 164 843 436 9	−**1.172** 887 183 315 5	−4924.519 845 377 3
1	40 (16,8,8,8)	−**1.102** 590 742 249 6	−**1.102** 624 375 451 3	−**1.9**53 823 274 365 0
2	186 (52,38,50,46)	−**1.102 641 5**78 458 7	−**1.102 641 5**78 975 7	−**1.102 6**54 667 381 7
3	392 (112,90,98,92)	−**1.102 641 58**0 989 5	−**1.102 641 581 0**28 1	−**1.102 64**2 557 368 8
4	672 (180,152,176,162)	−**1.102 641 581 0**06 7	−**1.102 641 581 03**1 1	−**1.102 64**2 197 632 7
5	1024 (282,244,252,246)	−**1.102 641 581 01**5 2	−**1.102 641 581 03**2 3	−**1.102 64**2 014 003 6
6	1448 (382,334,372,360)	−**1.102 641 581 02**0 1	−**1.102 641 581 03**2 7	−**1.102 641** 881 501 1
7	1950 (524,468,484,474)	−**1.102 641 581 02**3 4	−**1.102 641 581 033** 1	−**1.102 641** 827 195 2
8	2524 (660,594,642,628)	−**1.102 641 581 02**5 5	−**1.102 641 581 033** 2	−**1.102 641** 777 580 0
Finite element method[a]		−1.102 641 581 033 8		

[a]Reference 11.

TABLE VIII. Relativistic energy for the gerade excited state ($2\sigma_g$) of H_2^+ calculated together with the energies shown in Table VII (R=2.0 a.u., α=2.0: The numbers of the spinor components are shown in parentheses and the energy overshooting are noted by bold italic).

Order	Dimension	II energy (a.u.)	IR energy (a.u.)
0	8 (2,2,2,2)	**−0.**296 724 115 139 101	**−0.*555*** 710 865 686 313
1	40 (16,8,8,8)	**−0.360** 663 614 737 441	**−0.360 8**80 554 712 831
2	186 (52,38,50,46)	**−0.360 871 070** 331 333	**−0.360 871 070 5**82 946
3	392 (112,90,98,92)	**−0.360 871 070 5**72 738	**−0.360 871 070 57**7 867
4	672 (180,152,176,162)	**−0.360 871 070 57**4 860	**−0.360 871 070 578** 133
5	1024 (282,244,252,246)	**−0.360 871 070 57**5 986	**−0.360 871 070 578** 286
6	1448 (382,334,372,360)	**−0.360 871 070 57**6 652	**−0.360 871 070 578** 374
7	1950 (524,468,484,474)	**−0.360 871 070 57**7 086	**−0.360 871 070 578** 394
8	2524 (660,594,642,628)	**−0.360 871 070 57**7 369	**−0.360 871 070 578 415**
Direct perturbation method[a]		−0.360 871 053 244	
Exact (nonrelativistic)[b]		−0.360 864 875 338 3	

[a]Reference 12.
[b]Reference 31.

ICI wave function. It was shown that the free ICI method was even more efficient than solving the exact wave function of H_2^+.

For the relativistic case, this study represents the first application of the free ICI method to molecule. An appropriate choice of the g function was shown important for describing the correct ICI balance between the large and small components of the neighboring ICI wave functions. By using the inverse Hamiltonian method, we could avoid the variational collapse problem and the calculated II energy was an upper bound of the ground state energy. For the ICI balance, even the variational calculations with the regular Hamiltonian were stable giving rapidly converging result. We compared the converging behaviors of the II, IR, and RR energies. The II energy was rather slow in convergence, though it always satisfied upper bound nature. The present relativistic free ICI calculations showed reasonably fast convergences for both the ground and excited states.

We have further calculated the lower bounds of the relativistic energy. The knowledge of both the upper and lower bounds of the relativistic energy showed that the present relativistic wave function and energy are very accurate with the energy error being less than 4.3×10^{-2} cm^{-1}. Actually, the true value should be much closer to the calculated upper bound energy. Generally speaking, the lower bound calculations will become more and more important in future for both the nonrelativistic and relativistic calculations, since we cannot assure the accuracy of the calculated results if the system includes more than five electrons, since there are no highly accurate calculations for the solutions of the SE equation for such systems. For the relativistic case, the calculations of both upper and lower bounds give us further a clear criterion on the occurrence of the variational collapse problem.

Thus, we have shown that the free ICI methodology can give quite accurate solutions for both the Schrödinger equation and the Dirac equation of H_2^+ molecule. In principle, this method can be applicable to any systems if the Hamiltonian is well defined in an analytical form. When analytical integrations over the free ICI complement functions are possible, the wave functions and energies are calculated by the variational method, and if such integrations are impossible, they are calculated by the local Schrödinger equation method developed in our laboratory,[39] both in high accuracy.

APPENDIX: NECESSARY INTEGRALS AND OPERATORS FOR THE HAMILTONIAN AND OVERLAP MATRIX ELEMENTS

In this appendix, we explain some necessary operations and integrals appearing in the nonrelativistic and relativistic cases. Commonly, m stands for integers and n for zero and positive integers.

1. Nonrelativistic case

For the ground state, the overlap and Hamiltonian integrals of H_2^+ molecule are easily done when the wave function is given by Eq. (22), i.e.,

$$\Psi = \sum_i c_i \lambda^{m_i} \mu^{n_i} \exp(-\alpha\lambda). \tag{A1}$$

The index n_i for μ is related to the symmetry of the state: even index for gerade states, odd for ungerade states. The Jacobian and the integration area is $d\lambda d\mu d\phi = R^3(\lambda^2-\mu^2)/8$ and $\lambda:1\sim\infty$, $\mu:-1\sim1$, $\phi:0\sim2\pi$, respectively. The resulting integrals are written generally as

$$I = \int_0^{2\pi} d\phi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \lambda^m \mu^n \exp(-\alpha\lambda). \tag{A2}$$

The integration for μ is readily done. For positive integer m, the integration for λ is done with the incomplete gamma function as

$$\int_1^\infty \lambda^m \exp(-\alpha\lambda)d\lambda = \alpha^{-m-1}\Gamma(m+1,\alpha) \quad (m=0,1,2\ldots) \tag{A3}$$

and for negative m, we use the formula for $m=|m|$

$$\int_1^\infty \frac{\exp(-\alpha\lambda)}{\lambda^m}d\lambda = \begin{cases} \exp(-\alpha)\displaystyle\sum_{k=1}^{m-1}\frac{(k-1)!(-\alpha)^{m-k-1}}{(n-1)!} - \frac{(-\alpha)^{m-1}}{(n-1)!}\exp(\alpha)Ei[-\alpha] & m \geqslant 2 \\ -Ei[-\alpha], & m=1. \end{cases} \tag{A4}$$

2. Relativistic case

In this paper, both the nonrelativistic case and the relativistic case are written by the elliptic coordinate with λ, μ for clarity. However, in the relativistic case, it is convenient to use the transformed elliptic coordinate defined by

$$\lambda = \cosh(s), \quad \mu = \cos(t). \tag{A5}$$

We performed actual calculations in this transformed coordinate. The momentum operators are written as

$$p_x = -i\nabla_x = -i\left[\left\{\frac{2}{R}\frac{\cosh(s)\sin(t)\cos(\varphi)}{\cosh(s)^2-\cos(t)^2}\right\}\frac{\partial}{\partial s} - \left\{\frac{2}{R}\frac{\sinh(s)\cos(t)\sin(\varphi)}{\cosh(s)^2-\cos(t)^2}\right\}\frac{\partial}{\partial t} - \left\{\frac{2}{R}\frac{\sin(\varphi)}{\sinh(s)\sin(t)}\right\}\frac{\partial}{\partial\varphi}\right],$$

$$p_y = -i\nabla_y = -i\left[\left\{\frac{2}{R}\frac{\cosh(s)\sin(t)\sin(\varphi)}{\cosh(s)^2-\cos(t)^2}\right\}\frac{\partial}{\partial s} - \left\{\frac{2}{R}\frac{\sinh(s)\cos(t)\sin(\varphi)}{\cosh(s)^2-\cos(t)^2}\right\}\frac{\partial}{\partial t} + \left\{\frac{2}{R}\frac{\cos(\varphi)}{\sinh(s)\sin(t)}\right\}\frac{\partial}{\partial\varphi}\right],$$

$$p_z = -i\nabla_z = -i\left[\left\{\frac{2}{R}\frac{\sinh(s)\cos(t)}{\cosh(s)^2-\cos(t)^2}\right\}\frac{\partial}{\partial s} - \left\{\frac{2}{R}\frac{\cosh(s)\sin(t)}{\cosh(s)^2-\cos(t)^2}\right\}\frac{\partial}{\partial t}\right], \tag{A6}$$

The Jacobian is $dsdtd\phi = R^3\sinh(s)\sin(t)(\cosh(s)^2-\cos(t)^2)/8$ and the integration area is $s:0\sim\infty$, $t:-\pi\sim 0$, $\phi:0\sim 2\pi$. Then, the integral has a general form given by

$$I = \int_0^{2\pi}d\varphi\int_0^\infty ds\int_{-\pi}^0 dt\frac{\cosh(s)^m\sinh(s)^{n_1}\cos(t)^{n_2}\sin(t)^{n_3}\exp(-\alpha\cosh(s))}{(\cosh(s)^2-\cos(t)^2)^{n_4}}\exp[i(j_z-1/2)\varphi]. \tag{A7}$$

When $n_4=0$, the above integral is the same as Eq. (A2). In $n_4\geqslant 1$ cases, the denominator causes a singularity at the nuclear position, i.e., $s=0$, $t=-\pi$ or 0. However, some of these integrations are not singular when $\sinh(s)$ and $\sin(t)$ exist in the numerator since they also go to zero at singular points. When $n_4=1$, the integrals of Eq. (A7) are calculated by using the relation

$$\int_{-\pi}^0 \frac{\sin(t)\cos(t)^k}{\cosh(s)^2-\cos(t)^2} = \cosh(s)^{k-1}\left[\sum_{r=0}^{k/2-1}\frac{\cosh(s)^{-k+2r+1}}{k-2r-1}\{1-(-1)^{-k+2r+1}\} + \ln\left(\frac{\cosh(s)-1}{\cosh(s)+1}\right)\right] \tag{A8}$$

and, consequently, the one-dimensional (s coordinate) integrals reduce to

$$\int_0^\infty ds\,\sinh(s)^n\cosh(s)^m\ln(\cosh(s)\pm 1)\exp(-\alpha\cosh(s)). \tag{A9}$$

Most of these integrals were calculated analytically and the others numerically by using the mathematical program MAPLE.[19]
In the case of $n_4\geqslant 2$, we used the following formula for the integration over t

$$\int_{-\pi}^0 dt\frac{\cos(t)^i\sin(t)^j}{(\cosh(s)^2-\cos(t)^2)^k} = -\frac{1}{\cosh(s)^{2k}}B\left(\frac{j+1}{2},\frac{i+1}{2}\right){}_2F_1\left(\frac{i+1}{2},k;\frac{i+j}{2}+1,\frac{1}{\cosh(s)}\right), \tag{A10}$$

where F is the hypergeometric function. After the conversion of F, the resulting s integrants have the form similar to Eq. (A9).

[1] P. A. M. Dirac, Proc. R. Soc. London, Ser. A **123**, 714 (1929).

[2] H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000); H. Nakatsuji and E. R. Davidson, *ibid.* **115**, 2000 (2001); H. Nakatsuji, *ibid.* **115**, 2465 (2001); **116**, 1811 (2002); H. Nakatsuji and M. Ehara, *ibid.* **117**, 9 (2002); **122**, 194108 (2005); H. Nakatsuji, Bull. Chem. Soc. Jpn. **78**, 1705 (2005).

[3] H. Nakatsuji, Phys. Rev. Lett. **93**, 030403 (2004); Phys. Rev. A **72**, 062110 (2005).

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

[5] H. Nakashima and H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007)..

[6] H. Nakatsuji and H. Nakashima, Phys. Rev. Lett. **95**, 050407 (2005).

[7] V. K. Khersonskii, Astrophys. Space Sci. **98**, 255 (1984).

[8] W. G. Baber and H. R. Hasse, Proc. Cambridge Philos. Soc. **31**, 564 (1935).

[9] H. Wind, J. Chem. Phys. **42**, 2371 (1965).

[10] G. Hunter, B. F. Gray, and H. O. Pritchard, J. Chem. Phys. **45**, 3806 (1966); G. Hunter and H. O. Pritchard, *ibid.* **46**, 2146 (1967); **46**, 2153 (1967).

[11] O. Kullie and D. Kolb, Eur. Phys. J. D **17**, 167 (2001).

[12] R. Franke and W. Kutzelnigg, Chem. Phys. Lett. **199**, 561 (1992).

[13] S. A. Alexander and R. L. Coldwell, Phys. Rev. E **60**, 3374 (1999).

[14] F. A. Parpia and A. K. Mohanty, Chem. Phys. Lett. **238**, 209 (1995).

[15] L. La John and J. D. Talman, Chem. Phys. Lett. **189**, 383 (1992).

[16] L. Yang, D. Heinemann, and D. Kolb, Chem. Phys. Lett. **178**, 213 (1991).

[17] P. I. Pavlik and S. M. Blinder, J. Chem. Phys. **46**, 2749 (1967).

[18] W. E. Baylis and G. W. F. Drake, in *Atomic, Molecular, & Optical Physics Handbook*, edited by G. W. F. Drake (AIP, New York, 1996).

[19] About the GMP library (see http://swox.com/gmp/ and http://www.sc.nyu.edu/exact/gore/gmp/).

[20] Computer code MAPLE, Waterloo Maple, Inc., Waterloo, Ontalio, Canada.

[21] W. Kutzelnigg, Chem. Phys. **225**, 203 (1997).

[22] I. P. Grant, in *Atomic, Molecular, & Optical Physics Handbook*, edited by G. W. F. Drake (AIP, New York, 1996); I. P. Grant and H. M. Quiney, Phys. Rev. A **62**, 022508 (2000).

[23] R. N. Hill and C. Krauthauser, Phys. Rev. Lett. **72**, 2151 (1994).

[24] H. Nakatsuji, Phys. Rev. A **65**, 052122 (2002).

[25] F. Weinhold, J. Math. Phys. **11**, 2127 (1970).

[26] A. F. Stevenson and M. F. Crawford, Phys. Rev. **54**, 375 (1938).

[27] G. Temple, Proc. R. Soc. London, Ser. A **119**, (1928).

[28] Z. Chen, G. Fonte, and S. P. Goldman, Phys. Rev. A **50**, 3838 (1994).

[29] H. M. James, J. Chem. Phys. **3**, 9 (1935).

[30] L. Yang, D. Heinemann, and D. Kolb, Phys. Rev. A **48**, 2700 (1993).

[31] J. M. Peek, J. Chem. Phys. **43**, 3004 (1965).

[32] F. Weinhold and A. B. Chinen, J. Chem. Phys. **56**, 3798 (1972).

[33] B. H. Wells and S. Wilson, J. Phys. B **22**, 1285 (1989).

[34] W. Schulze and D. Kolb, Chem. Phys. Lett. **122**, 271 (1985).

[35] L. Laaksonen, P. Pyykko, and D. Sundholm, Int. J. Quantum Chem. **23**, 309 (1983).

[36] L. Laaksonen and I. P. Grant, Chem. Phys. Lett. **109**, 485 (1984).

[37] G. Pestka, Phys. Scr. **69**, 203 (2004).

[38] Y. P. Zhang, C. H. Cheng, J. T. Kim, J. Stanojevic, and E. E. Eyler, Phys. Rev. Lett. **92**, 203003 (2004).

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