Scaled Schrödinger Equation and the Exact Wave Function

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We propose the scaled Schrödinger equation and the related principles, and construct a general method of calculating the exact wave functions of atoms and molecules in analytical forms. The nuclear and electron singularity problems no longer occur. Test applications to hydrogen atom, helium atom, and hydrogen molecule are satisfactory, implying a high potentiality of the proposed method.

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To develop a general systematic method of solving the Schrödinger equation (SE) and the corresponding relativistic equation is of central importance in theoretical physics and chemistry. So far, there was no general method of solving the SE in an analytical form. Only full configuration interaction (CI) is a practical method of calculating the "exact" wave function, but the number of the variables involved is astronomical and therefore the application is limited. Furthermore, the full CI solutions are actually far from the solutions of the SE, because the basis sets are usually far from complete. In our series of papers [1–6], we have studied a general method of solving the SE by investigating the structure of the exact wave function. Here, we introduce a variant of the SE and propose a general method of calculating the exact wave functions of atoms and molecules in analytical forms. Test applications are given to some elementary systems.

In the nonrelativistic Born-Oppenheimer approximation, the atomic and molecular system is defined by the Hamiltonian

$$H = \sum_i -\frac{1}{2}\Delta_i - \sum_i \sum_A Z_A/r_{Ai} + \sum_{i>j} 1/r_{ij} \qquad (1)$$

and is described by the exact wave function that is a solution of the SE

$$H\psi = E\psi, \qquad (2)$$

or the inverse Schrödinger equation (ISE) [5]

$$H^{-1}\psi = E^{-1}\psi, \qquad (3)$$

where $H^{-1}H = HH^{-1} = 1$. Note that in the ISE, H is actually the positive Hamiltonian [5].

We summarize briefly the past results [1–6] to introduce our background. A condition for the wave function ψ to have the structure of the exact wave function is expressed as follows. When the unknown variables included in ψ are optimized by the variational principle, and when the resultant ψ satisfies the H-square equation [1–3], then this ψ has the structure of the exact wave function. This is because the variational principle gives the best possible wave function and the H-square equation is valid only for the exact wave function. From this criterion, we have proposed the iterative CI (ICI) method and the simplest extreme (or extended) coupled-cluster (SECC) method as methods of constructing the exact wave function.

Suppose that we divide our H into N_D parts, $H = \sum_{I=1}^{N_D} H_I$, and define the variable operator S by $S = \sum_{I=1}^{N_D} C_I H_I$ with N_D variables $\{C_I\}$. Then, the ICI wave function is defined by the recurrence

$$\psi_{n+1} = (1 + S_n)\psi_n. \qquad (4)$$

The variables are optimized by the variational principle, and, at convergence, ψ_n is proved to be exact. Since each step of the ICI is variational, its energy converges monotonically to the exact value. When $N_D = 1$, it is the simplest ICI (SICI). The ECC wave function is defined by

$$\psi = \exp(S)\psi_0. \qquad (5)$$

The simplest one (SECC) for $N_D = 1$ is proved to be exact, but the optimal C would be minus infinite from a different argument. On the other hand, the general ECC ($N_D \neq 1$) is not guaranteed to be exact [1,3], though it may happen to become exact because of its highly nonlinear nature [3]. This was in contrast to the conjecture given by Nooijen [7] and Piecuch *et al.* [8] (CCGSD is a special case of ECCND for second-quantized Hamiltonian). Descriptions of the excited states with the ICI and ECC methods were given in some details in Refs. [2,4]. The above arguments are also valid for the inverse Hamiltonian case [5].

Singularities.—The atomic and molecular Hamiltonians have nuclear and electron singularities in the second and third terms, respectively, of Eq. (1). In the SE of Eq. (2), the right hand side has no singularities, and, therefore, these singularities caused by the Hamiltonian must be canceled out within the left hand side of the SE. (For example, in a hydrogen atom, the attractive Coulomb force is canceled by the centrifugal force.) This consideration leads easily to the nuclear and electron cusp conditions first derived by Kato [9]. The exact wave functions

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satisfy these conditions, and, therefore, no singularities exist in the SE. However, for *approximate* wave functions, this complete cancellation of the singularities in $H\psi$ does not occur and some problems are caused. For example, in Table I, the integrals of the nth power of the Hamiltonian of the hydrogen atom give correct values for the exact wave function, but diverge for the approximate wave functions for n larger than 3.

In the ICI and ECC formalisms, there appear the integrals over H^n with $n \geq 3$, so that these theories have difficulties for atoms and molecules. This is true for any theories that involve such higher powers of Hamiltonian [10–12]. But, when we use H^{-1} instead of H, such a difficulty does not occur [5]: a problem there was how to write the inverse Hamiltonian in a closed form, though even the expanded form worked well [5]. We show in this Letter an approach that is free from such a difficulty.

Scaled Schrödinger equation.—We introduce the scaled Schrödinger equation (SSE) by

$$g(H - E)\psi = 0, \tag{6}$$

which is equivalent to the SE. The function g, called the scaling function, is a function of electron coordinates. It is a multiplicative operator and generally does not commute with the Hamiltonian. It is always positive (or negative) and nonzero except at the singular points. Even at the singular point r_0,

$$\lim_{r \to r_0} gV \neq 0, \tag{7}$$

where V is the potential operator in the Hamiltonian, in order not to eliminate the information of the Hamiltonian at the singular points: the singularity itself is also important information of the Hamiltonian. In other words, if we introduce $1/g$, its singularity at r_0 is less steep than or equally steep as that of the potential in the Hamiltonian.

The proof of the equivalence between the SE and SSE is almost self-evident. If SE is valid, SSE is valid. Contrarily, if SSE is valid, by multiplying $1/g$ from the left of the SSE, we obtain the SE. This is valid even at the singular points because of Eq. (7).

A choice of g is $g = 1/(-v_{ne} + v_{ee})$, where v_{ne} and v_{ee} are the nuclear-electron attraction operator and electron-electron repulsion operator, respectively. A different choice is $g = -1/v_{ne}v_{ee}$.

Variational principle and square theorem for the SSE.—The variational principle and the square theorem are important for developing the theory of the exact wave function. From Eq. (6), the variational formula for the SSE is written as

$$\langle \delta\psi | g(H - E) | \psi \rangle = 0 \tag{8}$$

for arbitrary $\delta\psi$. This principle may also be used to calculate the best possible wave function within the given functional form of ψ. The energy E may be defined by $E = \langle \psi | gH | \psi \rangle / \langle \psi | g | \psi \rangle$, which is called scaled energy and is different from the Ritz energy, $E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$. The scaled energy does not necessarily have the stationary property, different from the Ritz energy. For the exact wave function, both scaled and Ritz energies become equal to the exact energy.

The square theorem for the SSE is written as

$$\langle \psi | (H - E)g \cdot g(H - E) | \psi \rangle = 0, \tag{9}$$

which is valid only for the exact wave function that satisfies the SSE or SE. The proof is very simple. This equation is rewritten as $\int |g(H - E)\psi|^2 d\tau = 0$, whose integrand is always positive or zero, and, therefore, the integrand must be zero in order that the sum of them is zero, which leads to the SSE. The converse is self-evident. (Q.E.D.)

If ψ is chosen such that its variation put into the variational principle, Eq. (8), leads to the square theorem, Eq. (9), then this ψ has the structure of the exact wave function, since this ψ is guaranteed to become exact after variational calculation.

Simplest ICI and simplest ECC theories based on the SSE.—We can formulate the ICI and ECC theories associated with the SSE. From the above argument, the

TABLE I. Integrals of the higher powers of the Hamiltonian and the scaled Hamiltonian of the hydrogen atom over the Slater-type and Gaussian-type orbitals.

Operator Q in[a,b,c] $\langle \psi \| Q \| \psi \rangle / \langle \psi \| \psi \rangle$	Slater-type Exact ($\alpha = 1.0$)	Slater-type Approximate ($\alpha = 0.8$)	Gaussian-type $\alpha = 0.3$
H	−0.5	−0.48	−0.4240387
H^2	0.25	0.4608	0.4886535
H^3	−0.125	$-\infty$	$-\infty$
vHv	$-\infty$	$-\infty$	$-\infty$
$Hg \cdot (gH)^2$	−0.5625	−0.624	−0.1402396
$HgHgH$	−0.25	−0.2624	−0.0711785
HgH^2	−0.1875	−0.24576	−0.5396678
HgH^3	0.09375	∞	∞

[a] $H = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r}$. [b] $v = -\frac{1}{r}$. [c] $g = r$.

simplest ECC (SECC)

$$\psi = \exp[Cg(H-E)]\psi_0, \tag{10}$$

and the simplest ICI (SICI) defined by the recursion formula

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

are exact when their variables are determined by the variational principle.

Square theorem for the partitioned Hamiltonian and the ICIND method.—The square theorem is generalized with the partitioned Hamiltonian $H = \sum_{I=1}^{N_D} H_I$. Namely, when the partitioned square theorem,

$$\langle\psi|(H-E)g \cdot g(H_I - E_I)|\psi\rangle = 0, \tag{12}$$

holds for all I ($I = 1, \ldots, N_D$), then this ψ is exact. Here, E_I is defined by $\langle\psi|g(H_I - E_I)|\psi\rangle = 0$. The proof is straightforward and so not given here.

Based on the partitioned square theorem, the ICI theory that involves N_D variables (ICIND) is formulated. We introduce the S operator by

$$S_n = \sum_I^{N_D} C_{I,n} g(H_I - E_{I,n}) \tag{13}$$

and define the ICI wave function by using Eq. (4) again (note that the definition of the S operator is different). When this ICIND is calculated with Eq. (8), it gives the exact wave function at convergence.

The secular equation at nth iteration is written as

$$\langle\psi_n|g(H-E_{n+1})|\psi_n\rangle C_{0,n} + \sum_I \langle\psi_n|g(H-E_{n+1}) \cdot g(H_I - E_{I,n})|\psi_n\rangle C_{I,n} = 0 \tag{14}$$

and

$$\langle\psi_n|(H_J - E_{J,n})g \cdot g(H-E_{n+1})|\psi_n\rangle C_{0,n} + \sum_I \langle\psi_n|(H_J - E_{J,n})g \cdot g(H-E_{n+1})g(H_I - E_{I,n})|\psi_n\rangle C_{I,n} = 0 \tag{15}$$

for all J ($J = 1, \ldots, N_D$). When we do not partition the Hamiltonian, it is SICI, and we see from Table I that all the integrals involved exist.

Free ICI Method.—The ICI method for calculating the exact wave function is characterized by two features. (1) It generates the functions that converge iteratively to the exact wave function. (2) The number of the variables is small and fixed to N_D throughout the calculations.

Let us now relax the second property. Namely, we use all the independent functions $\{\phi_k\}^{(n)}$ included in the nth iteration function of the SICI given by Eq. (11) for expanding our wave function, namely,

$$\psi_{n+1} = \sum_{k=1}^{M_n} c_{k,n}\phi_k, \tag{16}$$

where M_n is the number of the independent functions. The coefficient $c_{k,n}$ is calculated by the ordinary Ritz variational principle. Since the functions ϕ_k are generated with the scaled Hamiltonian, we no longer have the singularity problem. We call this method the free ICI method. Since the ICI formulation is guaranteed to reach the exact wave function, this free ICI gives the best possible wave function, in a variational sense, at each iteration. When M_n is not large, we need not keep it to N_D. We further note that in the free ICI, no accumulation of errors occurs, since no variables of the earlier iteration step is used in the later iteration step. We can start nth iteration step without performing the earlier $n-1$ iterations.

We apply the present ICI method based on the SSE to the analytical calculations of the exact wave functions of hydrogen atom, helium atom, and hydrogen molecule.

Hydrogen atom.—The Hamiltonian for the s state of the hydrogen atom is $H = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} - \frac{Z}{r}$. The scaling function is chosen as $g = r$. We performed the free ICI using $\psi_0 = \exp(-\alpha r)$ with $\alpha = 1.5$. $\alpha = 1.0$ is the exact wave function. We see from Table I that the singularity problem does not occur in the present method. Table II gives the results. As the iteration proceeds, the number of the independent functions increases one by one and the Ritz energy converges after seven iterations and the scaled energy by eight iterations to the exact energy up to nine decimal figures.

Helium atom.—The helium atom has both nuclear and electron singularities and therefore is very interesting. There are a lot of calculations in the literature with various types of functions [13–16]. Though these wave functions were cleverly formulated, the physics behind them was not necessarily clear, except for the first few dominant terms. In the present ICI formalism, the wave function is automatically generated in an analytical form, once we choose the initial function ψ_0 and the scaling factor g, and guaranteed to approach the exact wave

TABLE II. Free ICI calculation based on the sSE for the hydrogen atom starting from $\psi_0 = \exp(-1.5r)$.

Iteration	M_n[a]	Ritz energy	Scaled energy
0	1	−0.375	−0.625
1	2	−0.491 025 404	−0.512 259 526
2	3	−0.499 316 143	−0.501 470 244
3	4	−0.499 954 132	−0.500 144 830
4	5	−0.499 997 229	−0.500 011 697
5	6	−0.499 999 844	−0.500 000 825
6	7	−0.499 999 992	−0.500 000 053
7	8	−0.500 000 000	−0.500 000 003
8	9		−0.500 000 000

[a] Number of independent functions.

TABLE III. Free ICI calculation based on the sSE for the helium atom with ψ_0 and g given in the text.

Iteration	M_n[a]	Ritz energy	Optimal α
0	1	−2.847 656 250	1.6875
1	6	−2.901 577 012	1.6728
2	26	−2.903 708 675	1.8803
3	74	−2.903 723 901	2.0330
4	159	−2.903 724 347	2.1998
5	291	−2.903 724 373	2.3307
6	481	−2.903 724 376	2.4862
Best value[b]		−2.903 724 377	

[a]Number of independent functions. [b]Reference [16].

function. We want to test how good this automatic method is. For general atomic and molecular systems, it is difficult to estimate the functional form of the exact wave function only by intuition as cleverly as in the helium atom case.

We introduce the coordinate defined by $s = r_1 + r_2$, $t = -r_1 + r_2$, $u = r_{12}$ with $s \geq u \geq |t|$. We choose the initial function by $\psi_0 = \exp(-\alpha s)$ with α as a variational parameter and the scaling function by $g = u\frac{s^2-t^2}{s}$ to prevent nuclear and electron singularity problem.

Table III summarizes the result of the free ICI based on the SSE. As the iteration proceeds, the Ritz energy approaches the best variational value, −2.903 724 377 a.u., reported in the literature [16]. At the fifth iteration, the free ICI energy was −2.903 724 373 a.u. with 291 independent functions, and at $n = 6$, it was −2.903 724 376 a.u. with 481 functions. These energies were higher by only 4 and 1 nhartrees, respectively, from the best value, which guarantees the validity of the present method. We particularly note that these results were obtained *automatically* by the ICI algorithm as described above. The present ICI wave function included the terms of both positive and negative powers of the variable s. It is different from the Hylleraas expansion that includes only positive powers of s, t, and u, but closer to the Kinoshita one, though different in higher-order terms. The functional form of the ICI wave function depends on the choices of the zero-order wave function ψ_0 and the g factor, and, in this sense, it supports the general Thakkar-Koga expansions [16]. The Hylleraas expansion actually corresponds to choosing $g = u(s^2 - t^2)$ different from the present one. Examinations of the dependence on ψ_0 and g will be given in a forthcoming paper.

Hydrogen molecule.—The free ICI method has also been applied to a hydrogen molecule with $R_{\text{H-H}} = 1.4$ a.u. Using elliptic coordinate [17], the second iteration of the free ICI with the initial function $\psi_0 = \exp[-\alpha(\lambda_1 + \lambda_2)/2](1 + \rho + \rho^2)$ with $\alpha = 2.2$ and $g = \rho(\lambda_1^2 - \mu_1^2)(\lambda_2^2 - \mu_2^2)/\lambda_1\lambda_2$ gave the Ritz variational energy of −1.174 475 703 a.u. with 609 independent functions. This energy is lower than the (nonrelativistic) value of −1.174 475 686 a.u. obtained by Kolos in 1994 [18]. More details will be published in the near future.

Conclusion.—Good performance of the calculations particularly for the helium atom and the hydrogen molecule implies a high potentiality of the proposed method. It is noteworthy that their ICI wave functions are different from the existing ones. Thus, the present ICI formalism based on the SSE provides a general systematic method for calculating the exact wave functions of atoms and molecules in an analytical form. For He and H_2, Hylleraas, James-Coolidge, Kolos, and others were clever enough to imagine the exact wave functions only with intuition. But for general molecules, it is difficult to estimate the analytical form of the exact wave function only by intuition, but the present method generates it automatically, since the differentiations (involved in the Hamiltonian) are always possible, and, furthermore, the integrals in the secular equation step have no singularity problem. It is guaranteed that at convergence we will get the exact wave function. When (analytical) integrations are difficult, the Monte Carlo method [19] may provide a useful tool.

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