

Free Complement Method for Solving the Schrödinger Equation: How Accurately Can We Solve the Schrödinger Equation

H. Nakatsuji and H. Nakashima

Abstract Free complement (FC) method provides a general and systematic method of solving the Schrödinger equation. In this method, the Hamiltonian of the system modified for the singularity of the potential is used to generate the FC functions that span the exact wave function of the system. Thus, by applying the variation principle to the sum of the complement functions, which we call FC wave function, we can calculate the essentially exact wave function and energy for the ground and excited states of the system. We here show that the Schrödinger equation can be solved to an arbitrary accuracy with the FC method by examining the upper and lower bounds of the energy, local energy, H-square error, cusp condition, and so on, for the helium atom.

Keywords: Solving the Schrödinger equation · Free complement method · Cusp condition · Upper and lower bounds

1 Introduction

This chapter summarizes briefly the lecture of Nakatsuji given on July 10, 2008, at the QSCP-13 workshop at Lansing organized by Prof. Piotr Piecuch of the Michigan State University. Let us first celebrate our exciting memories of this workshop for its high-quality science and good performance, and nice organization, all of which were due to the careful coordination and organization of the workshop by Profs. P. Piecuch and J. Maruani. So, let us first deeply thank Profs. Piotr Piecuch and Jean Maruani for all of this.

The Schrödinger equation has long been believed to be insoluble for over 80 years, since it was discovered by Prof. Erwin Schrödinger in 1926 [1], though it was believed to govern all of chemistry and most of physics [2]. For this reason, all we could have done in quantum science was to formulate “approximate” theories to “understand” or “interpret” the main features of chemical phenomena [2]. Thus,

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quantum chemistry has long been characterized as an approximate science that can never predict phenomena in full accuracy. However, recently, we have found simple, general, and accurate methods of solving the Schrödinger equation [3–13]. We referred to them as iterative complement (configuration) interaction (ICI) method [3, 4] and the free ICI [6] or free complement (FC) method [12], the latter two being the same.

The FC method is completely different from the conventional quantum chemistry. In the state-of-the-art quantum chemistry, one first defines Hartree–Fock orbitals based on the initially chosen basis set and then expands many-electron correlated wave functions by means of the Hartree–Fock orbitals. In this approach, any theory lies between the Hartree–Fock and the full CI and so, the full CI is a goal of this type of the theory. However, the full CI cannot be the exact solution of the Schrödinger equation because of the incompleteness of the basis set first introduced. When we use numerical Hartree–Fock that is free from the basis set, the full CI becomes infinite expansion that cannot be handled in principle.

Explicitly correlated wave function theory [14] is another important approach in quantum chemistry. One introduces inter-electron distances together with the nuclear–electron distances and set up some presumably accurate wave function and applies the variation principle. The Hylleraas wave function reported in 1929 [15] was the first of this theory and gave accurate results for the helium atom. Many important studies have been published since then even when we limit ourselves to the helium atom [16–28]. They clarified the natures and important aspects of very accurate wave functions. However, the explicitly correlated wave function theory has not been very popularly used in the studies of chemical problems in comparison with the Hartree–Fock and electron correlation approach. One reason was that it was generally difficult to formulate very accurate wave functions of general molecules with intuitions alone and another reason was that this approach was rather computationally demanding.

Thus, quantum chemistry has long been a science mainly for understanding and interpretation. It was difficult for quantum chemists to become truly confident on the calculated results. One reason was the approximate nature of the theory and another reason was an incompleteness of the basis set. For example, many people might have experienced the feeling of “maybe, my basis set was not good enough.” In the author’s opinion, quantitative reliability is a key of the theory. Otherwise, one cannot do “confident prediction.” For getting truly quantitative reliability in theoretical quantum science, there is no other way than solving the Schrödinger equation and the Dirac–Coulomb equation accurately.

2 Free Complement Method

In 1999, one of the authors got an inspiration that the Schrödinger equation might be able to be solved. He clarified the structure of the exact wave function and showed a method of obtaining the exact wave function by introducing the ICI method and its variants [3, 4]. However, there still existed a big obstacle, called

singularity problem [6]. Namely, the integrals involved in the formulation diverge to infinity when the Hamiltonian involves Coulomb potential, as it does for atoms and molecules. However, a simple idea came. Instead of solving the original Schrödinger equation,

$$(H - E)\psi = 0, \quad (1)$$

one may solve an equivalent equation, called scaled Schrödinger equation [6].

$$g(H - E)\psi = 0. \quad (2)$$

The factor g is called scaling function. It is always positive but can become zero only at the singular points. Even there, the g function must satisfy

$$\lim_{r \rightarrow 0} gH \neq 0 < \infty, \quad (3)$$

for not to erase the information of the Hamiltonian at the singular regions. Then, we can formulate the simplest ICI (SICI) method based on the scaled Schrödinger equation as

$$\psi_{n+1} = [1 + C_n g(H - E_n)] \psi_n, \quad (4)$$

where E_n is defined by $\langle \psi_n | g(H - E_n) | \psi_n \rangle = 0$. This SICI was also proved to become exact at convergence, and for the existence of the g -function, we do not encounter the singularity problem in the course of the iterative calculations.

When we do the SICI calculations to n -th iteration, the right-hand side of Eq. (4) becomes a sum of the analytical functions multiplied with the coefficients C_i . Now, we reformulate it as follows. We take all the independent analytical functions from there and group them as $\{\phi_i\}$, which we refer to as complement functions, and using them, we expand again our wave function as

$$\psi_{(n+1)} = \sum_i^{M_n} c_i \phi_i. \quad (5)$$

We referred to this wave function as the free ICI wave function. It converges faster to the exact wave function than the original SICI one, because of the increased freedom. In the SICI scheme, the $(n + 1)$ -th result, ψ_{n+1} , depends on all the former results, ψ_m and $C_m (m = 0 \dots n)$, but in the free ICI method, all the coefficients c_i are reoptimized at each n , and therefore, this method is not an iterative method. Then, the naming, the free ICI method may be confusing. So, hereafter we use the new name "free complement (FC)" method instead of the free ICI method. We refer to n of the FC method as an *order*, instead of an iteration number. Thus, the FC method gives a general method of solving the SE in an analytical expansion form.

The FC formalism for the exact wave function may be summarized as follows.

1. The Hamiltonian defines the system.
2. The Hamiltonian paves the way toward its exact wave functions in the analytical expansion form starting from a given initial function ψ_0 : Eq. (4) in the SICI case or Eq. (5) in the FC formalism.
3. This formalism is applicable for any system when its Hamiltonian is defined unambiguously.
4. We have no basis set nightmare: the complement functions, which may correspond to the basis set, are generated by the Hamiltonian of the system and so should be a best possible functions for the system.

A general method for calculating the unknown coefficients in the FC wave function given by Eq. (5) is the variation principle. Applying the variation principle to the FC wave function, we obtain the secular equation

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0, \quad (6)$$

where the Hamiltonian and overlap matrices are defined by

$$\mathbf{H} = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \int \phi_i H \phi_j d\tau & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}, \mathbf{S} = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \int \phi_i \phi_j d\tau & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}. \quad (7)$$

For simple few-electron atoms and molecules, these matrix elements are easily calculated. We apply here our FC formalism only to such systems. Then, starting from the initial wave function ψ_0 and using some appropriate scaling function g , we can calculate the solution of the Schrödinger equation in an analytical expansion form. The accuracy of the calculated results would depend on the choices of ψ_0 , g , and the expansion order n . We show here that, in principle, we can get the solution of the Schrödinger equation to any desired accuracy in this formalism.

3 Super-Accurate FC Calculation of Helium Atom

Helium atom is the simplest case for which the Schrödinger equation cannot be solved in a closed form. There have been many attempts to solve the Schrödinger equation of the helium atom accurately, starting from the famous study by Hylleraas [15–28]. These studies have produced a lot of important insights about the nature of the accurate wave functions of atoms and molecules. We applied the FC method described above to the helium atom immediately after this method was discovered [6]. It gave a strong support that the FC method was correct and useful. We have given more extended accurate calculations [9, 10] and examined the accuracy of the calculated wave functions by studying several properties that are the stringent test of the exactness of the wave functions [12, 13]. We have further studied the effect of nuclear motion [29] and the excited states with and without considering the effect of nuclear motion [30].

Here we overview our applications to the helium atom ground state. In the Hylleraas coordinate defined by

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}, \quad (8)$$

the Hamiltonian in the fixed nucleus approximation is given by

$$H = - \left(\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{\partial^2}{\partial u^2} \right) - 2 \frac{s(u^2 - t^2)}{u(s^2 - t^2)} \frac{\partial^2}{\partial s \partial u} - 2 \frac{t(s^2 - u^2)}{u(s^2 - t^2)} \frac{\partial^2}{\partial u \partial t}, \quad (9)$$

$$- \frac{4s}{s^2 - t^2} \frac{\partial}{\partial s} - \frac{2}{u} \frac{\partial}{\partial u} + \frac{4t}{s^2 - t^2} \frac{\partial}{\partial t} - \frac{4sZ}{s^2 - t^2} + \frac{1}{u},$$

where the last two terms represent the nuclear-electron attraction potential (Z is nuclear charge) and the electron-electron repulsion potential. The other terms originate from the kinetic operator. Using these potentials, we chose the g -function as

$$g = \frac{1}{V_{Ne}} + \frac{1}{V_{ee}}. \quad (10)$$

The initial function ψ_0 was chosen as

$$\psi_0 = [1 + \ln(s + u)] \exp(-\alpha s), \quad (11)$$

where the exponent α was dealt with as a variation parameter. The logarithmic dependence on s and u was introduced to describe well the three-particle coalescence region [16, 18, 20]. Then, the FC calculations are automatic and its wave function is guaranteed to become essentially exact at convergence. The FC wave function in this case is written as

$$\psi = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} [\ln(s + u)]^{j_i} \exp(-\alpha s), \quad (12)$$

where l_i runs both positive and negative [9, 19] integers, $\{m_i, n_i\}$ run non-negative integers (m_i is even integers) and j_i is 0 or 1.

Table 1 shows the convergence of the variational energy [9]. The bold face implies that the figure is confidently reliable. A landmark calculation of the helium atom with the explicitly correlated wave function approach was done by Schwartz [28], who obtained the energy correct to 37 digits by applying the variation principle to his intuitively generated trial wave function. This was a surprising result. In the FC method, all we have to do is to fix ψ_0 and g function. Then, the FC formalism automatically generates a series of analytical functions in the form of Eq. (5). It is generated by the successive applications of the Hamiltonian and the g -function of the system to the starting wave function ψ_0 as expressed by Eq. (4). So, no severe intuition is necessary. Because this FC algorithm is automatic, we could continue the calculations up to the order n of 27 and obtained the energy correct to 41 digits.

Table 1 Ground-state energies of the helium atom calculated with the g function given by Eq. (10) and the initial function ψ_0 given by Eq. (11)^a

n^a	M_n^b	Optimal α	Energy (a.u.) ^c
0	2	1.827	-2.865 370 819 026 71
1	10	1.475	-2.903 536 812 281 53
2	34	1.627	-2.903 724 007 321 45
3	77	1.679	-2.903 724 375 094 16
4	146	1.683	-2.903 724 377 022 34
5	247	1.679	-2.903 724 377 034 05
6	386	1.693	-2.903 724 377 034 119 011 25
7	569	1.704	-2.903 724 377 034 119 592 84
8	802	1.707	-2.903 724 377 034 119 598 24
9	1091	1.713	-2.903 724 377 034 119 598 309 973 48
10	1442	1.724	-2.903 724 377 034 119 598 311 136 32
11	1861	1.738	-2.903 724 377 034 119 598 311 158 76
12	2354	1.757	-2.903 724 377 034 119 598 311 159 23
13	2927	1.779	-2.903 724 377 034 119 598 311 159 244 938 53
14	3586	1.806	-2.903 724 377 034 119 598 311 159 245 187 71
15	4337	1.837	-2.903 724 377 034 119 598 311 159 245 194 18
16	5186	1.866	-2.903 724 377 034 119 598 311 159 245 194 39
17	6139	1.899	-2.903 724 377 034 119 598 311 159 245 194 403 526 60
18	7202	(1.93)	-2.903 724 377 034 119 598 311 159 245 194 404 346 36
19	8381	(1.96)	-2.903 724 377 034 119 598 311 159 245 194 404 433 80
20	9682	(1.99)	-2.903 724 377 034 119 598 311 159 245 194 404 444 83
21	11111	(2.02)	-2.903 724 377 034 119 598 311 159 245 194 404 446 40