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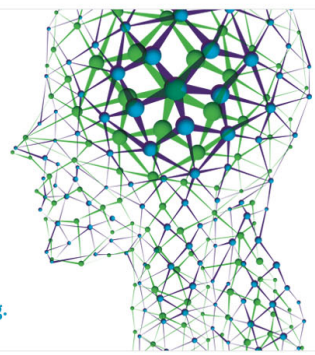

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Solving the Schrödinger equation of molecules by relaxing the antisymmetry rule: Inter-exchange theory

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The Schrödinger equation (SE) and the antisymmetry principle constitute the governing principle of chemistry. A general method of solving the SE was presented before as the free complement (FC) theory, which gave highly accurate solutions for small atoms and molecules. We assume here to use the FC theory starting from the local valence bond wave function. When this theory is applied to larger molecules, antisymmetrizations of electronic wave functions become time-consuming and therefore, an additional breakthrough is necessary concerning the antisymmetry principle. Usually, in molecular calculations, we first construct the wave function to satisfy the *antisymmetry rule, "electronic wave functions must be prescribed to be antisymmetric for all exchanges of electrons, otherwise bosonic interference may disturb the basis of the science."* Starting from determinantal wave functions is typical. Here, we give an antisymmetrization theory, called *inter-exchange (iExg) theory,* by dividing molecular antisymmetrizations to those *within* atoms and *between* atoms. For the electrons belonging to distant atoms in a molecule, only partial antisymmetrizations or even no antisymmetrizations are necessary, depending on the distance between the atoms. So, the above antisymmetry rule is not necessarily followed strictly to get the results of a desired accuracy. For this and other reasons, the necessary parts of the antisymmetrization operations become very small as molecules become larger, leading finally to the operation counts of lower orders of N, the number of electrons. This theory creates a natural antisymmetrization method that is useful for large molecules. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4919843]

I. INTRODUCTION

Chemistry is central to very broad fields of materials science. It deals with complex sciences of matters, their transformations, and even the creations of new matters. Though chemistry is still an empirical science, some chemical theories and concepts are well established. Among them, probably the most important working concepts would be molecular structural formulas and chemical reaction formulas. They are used daily in chemistry and chemical industry as if they are the language to describe the chemistry under study. The essence of these concepts is the local atomic concept that is transferable from chemistry to chemistry.

On the other hand, chemistry is governed by the principles of quantum mechanics, in particular, the Schrödinger equation (SE)[1] and the relativistic Dirac equation (DE)[2] that are written as

$$(H - E)\psi = 0 \tag{1}$$

in a usual notation and the antisymmetry principle that is written as[3]

$$P\psi = (-)^P\psi, \tag{2}$$

where P is an exchange operator of any two electrons in atoms and molecules. In the IUPAC Gold book,[4] the antisymmetry principle is described as "the postulate that electrons must be described by wave functions which are antisymmetric with respect to interchange of the coordinates (including spin) of a pair of electrons. A corollary of the principle is the Pauli exclusion principle." If we can solve the SE under the constraint of the antisymmetry principle in high accuracy at a reasonable speed, we can not only predict chemistry very accurately but also simulate chemical phenomena as precisely as or even more precisely than is possible through experiments. This has long been a dream of many scientists since the birth of the SE in 1926.[1]

In 2000, a breakthrough was initiated[5,6] and in 2004, a general theory of solving the SE was first presented[7] and developed to be useful for solving the SE of general atoms and molecules.[7–15] Our theory was originally called iterative complement interaction (ICI) theory[7] but was renamed later to the free complement (FC) theory[11] because it is not an "iterative" theory. This theory was shown to be useful also for solving the DE.[8] It was applied to very small systems like H_2 molecule[9] and helium atom[10] using the variational principle, and the high accuracy of the FC theory was demonstrated by calculating the energy of the helium atom to more than 40 digits.[10] An integral-free method, called local SE (LSE) method,[12] was introduced for applications to general atoms and molecules. Outlines of the theory and the application examples were summarized in the review articles.[13–15] Recently, using the super-parallel computers, the FC-LSE theory has been applied to solving the SE's of some organic molecules like ethylene and formaldehyde.[15]

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When the theory is applied to larger molecules, the antisymmetrization of the wave function that enforces Eq. (2) becomes a time-consuming step. This is particularly so for the highly accurate theories.[14–25] Therefore, we have published an efficient determinant based method, called Nk method,[26] but this method is not efficient for very complex functions. When many electrons are highly correlated (with many r_{ij} factors, for example), the ordinary determinant-based antisymmetrization theory becomes less-powerful, but a simple $N!$ (N factorial (NF), where N is the number of electrons of the system) algorithm is very time-consuming when N is large. Therefore, only small atoms and molecules were the subjects of the highly accurate calculations of the Schrödinger accuracy with the Hylleraas-CI and related methods,[16–21] exponentially correlated Gaussian methods,[22–25] quantum Monte Carlo methods,[27–29] full CI extrapolation method,[30] and our FC variational[10] and FC-LSE methods.[14,15,31] So, an additional breakthrough concerning the use of the antisymmetry principle is necessary to make these approaches applicable to larger molecules.

Many people have accepted the antisymmetry rule that may be summarized as *electronic wave functions must be prescribed to be antisymmetric for all exchanges of electrons, otherwise bosonic interference may disturb the basis of the science*. For example, many quantum chemistry theories start from Slater determinants, putting all electrons within determinantal wave functions. We will show that the antisymmetry is not necessary for the pair of electrons that are distant even within a single molecule. Actually, we can neglect some (large) parts of the antisymmetrization operations without affecting the accuracy (i.e., chemical accuracy) of the calculations: it would be a big loss if we have to assure antisymmetry for all electron pairs in a molecule.

In this paper, we propose a new antisymmetrization theory for molecules, called *inter*-exchange (*i*Exg) theory, that enables us to relax the antisymmetry rule. We divide antisymmetrization operations for molecules to those *within* atoms and to those *between* atoms in molecules. Then, the antisymmetrizations for the electrons between distant atoms become (partially) negligible and the antisymmetrizations within different atoms are also accelerated. The *i*Exg theory is a natural theory of antisymmetrizations and shows that in very large molecules, even most of the antisymmetry operations are actually unnecessary. For example, we will show that even for small C_2 molecule, only 2.1% of the total antisymmetry operations are necessary for the calculations of the Schrödinger accuracy. Thus, the *i*Exg theory opens a way to relax the antisymmetry "rule" and to realize calculations of very large molecules or systems. It converts $N!$ requirements to the requirements of lower orders of N. We note that the *i*Exg theory is based on the locality of electrons in the electronic structure of molecules. This is supported by the validity of chemical structural formulas and chemical reaction formulas that are used daily in chemistry.

In Sec. II, we will discuss on the locality of electrons in the electronic structure of molecules in relation to the FC theory. Then, we present the *i*Exg theory in some details. After some practical arguments in Sec. IV, we apply the *i*Exg theory to Li_2, C_2, and then to helium fullerene, He_{60}, a 120 electron system in which C of C_{60} (fullerene) is replaced with the helium atom. This calculation would have been *impossible if* we had to perform the antisymmetrizations of 120 electrons, since $120! = \sim 10^{198}$, a huge number, but became easily possible by virtue of the *i*Exg theory.

II. LOCALITY AND THE FREE COMPLEMENT THEORY

The FC theory is a general exact theory for solving the SE of atoms and molecules. In this section, we discuss the structure of the FC wave function to clarify the local nature of electrons in molecular electronic structure. The FC theory was explained in some details in the review article,[14] whose Figure 4 gives a flowchart of the FC method. In short, the exact wave function of a molecule is constructed with the system's Hamiltonian[7] using a recurrence formula called the simplest iterative complement (SIC) formula,

$$\psi_n = \left[1 + C_{n-1} g\,(H - E_{n-1})\right]\psi_{n-1}, \tag{3}$$

where n is the order of the FC wave function and C_n and E_n are the coefficient and energy at order n. We start from some initial wave function $\psi_0 = \mathbf{A}\phi_0$, where $\mathbf{A}$ is the N electron antisymmetrizer. If ψ_0 has some overlap with the exact wave function, any ψ_0 is acceptable, though the convergence speed may be different, depending on the quality of ψ_0. The scaling function g was introduced to eliminate the Coulomb singularities[6] and is given by

$$g = \sum_{A,i} r_{A,i} + \sum_{i,j} r_{ij} \tag{4}$$

for general molecules without external fields. At sufficiently large order n of the recurrence formula (3), we can assume ψ_n to become exact ψ. Then, we pick up all the independent analytical functions $\{\phi_I\}$ from the rhs of Eq. (3), give independent coefficient c_I to each function ϕ_I, and rewrite Eq. (3) as

$$\psi = \sum_I c_I \mathbf{A}\phi_I. \tag{5}$$

We refer to the function ϕ_I or $\psi_I = \mathbf{A}\phi_I$ as complement function (cf), since it is an element of the complete functions that describe the exact wave function as expressed by Eq. (5). The coefficients $\{c_I\}$ are determined by the variational method or the LSE method.[11,12] In our formalism, the initial function ψ_0 or its Hartree product ϕ_0 is constructed by the valence bond (VB) or the (localized) molecular orbital (MO) method. In both pictures, each electron is localized within the orbital expressed by the one-centered (VB) or several-centered (MO) Slater or Gauss functions. To obtain the exact wave function, any ψ_0 is acceptable as an initial wave function as far as it has an overlap with the exact wave function. In this paper, we restrict ourselves to choose the local VB function for the simplicity in formulations, more explicitly, the classical Heitler-London-Slater-Pauling (HLSP) type VB function. Then, ϕ_0 is expressed by the Hartree product of (the linear combination, in general, of) the Slater or Gauss orbitals, $\chi_A = \sum c_\kappa r^{a^1_k} x^{a^2_k} y^{a^3_k} z^{a^4_k} \exp(-\alpha_\kappa r_A)$ or $\chi_A = \sum c_\kappa x^{a^1_k} y^{a^2_k} z^{a^3_k} \exp(-\alpha_\kappa {r_A}^2)$, centered on the nucleus A (c_κ denotes coefficient and a^i_k and α_κ show the indices and

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orbital exponent for each Slater or Gauss function) as

$$\phi_0 = \prod_i \chi_A(i) \cdot \sigma, \tag{6}$$

where σ represents the N-electron spin function. Equation (6) may be modified slightly when we use complex initial functions like, for example, the two-equivalent Kekule functions and covalent plus ionic functions. Thus, the general form of the cf is finally written as

$$\phi_I = f_I\left(\{\mathbf{r}_{iA}\},\{r_{ij}\}\right)\phi_0, \tag{7}$$

where $f_I\left(\{\mathbf{r}_{iA}\},\{r_{ij}\}\right)$ denotes the functions composed of the products of x_{iA}, y_{iA}, z_{iA}, r_{iA}, and r_{ij}, where i runs electrons, A denotes nuclei in the molecule, and r_{ij} denotes the inter-electron distance between the electrons i and j.

Now, we have a picture that an electron is captured in an exponential region centered at the nucleus. Since the exponential functions included in ϕ_0 in Eq. (7) decay most rapidly, the prefactor $f_I\left(\{\mathbf{r}_{iA}\},\{r_{ij}\}\right)$ modifies this picture only slightly. Since ϕ_0 is common to all the cfs as seen from Eq. (7), we would be able to have this local picture even for the exact wave function. Thus, the FC theory as expressed by Eqs. (5) and (7) implies that *each electron is captured essentially within the exponential region around the nucleus*, because the exponential function decays most rapidly among many other functions. This is *a theoretical origin of the local concept in chemistry*, which is supported also by the success of molecular structural formulas and chemical reaction formulas used daily in chemistry. We note that the cfs given by Eq. (7) are classified into *atomic* and *inter* ones depending on the nature of the prefactor $f_I\left(\{\mathbf{r}_{iA}\},\{r_{ij}\}\right)$ of Eq. (7): the former consists of the products of the functions belonging only to the same atoms and the latter includes the interatomic functions. However, their decaying behaviors are essentially the same since they are controlled by the ϕ_0 part.

It is necessary to note that when we use the (localized) MO initial function, this picture is modified from one atomic region to several atomic regions, which makes the formulation more complex. For this reason, in the above argument, we have limited our ψ_0 to the simple HLSP-type VB function. In reality, the FC theory corrects the possible shortcoming of the VB or MO picture, since the FC theory is exact.

In our applications of the FC theory, we terminate the expansion given by Eq. (3) or Eq. (5) to some order that is correct at least to chemical accuracy in the absolute energy (i.e., kcal/mol accuracy). For general atoms and molecules, the coefficients $\{c_I\}$ in Eq. (5) are calculated using the LSE method,[11,12] which is an integral-free sampling-type methodology. In the present LSE calculations given in Sec. V, we used the local sampling method[33] in which each sampling coordinate was also localized according to the local picture of the wave function.

III. *i*EXG THEORY

We now propose *i*Exg theory, which is a new antisymmetrization theory for molecules and interacting molecules. It is based on the local nature of the electrons in the electronic structure of molecules and creates a natural efficient way of antisymmetrizations. The theory helps to relax the antisymmetry "rule." It differs completely from the existing theories, mostly determinant-based theories.

In the *i*Exg theory, the antisymmetrization operations of the electrons in a molecule are divided into those *within* each atom or fragment and those *between* atoms or fragments. For simplicity, we consider a diatomic molecule or a reacting system, AB, where A and B are separated by the distance R_{AB} and have N_A and N_B electrons, respectively, and $N_A + N_B = N$. Then, the antisymmetrizer of AB, $\mathbf{A}_{AB}$ $\equiv \mathbf{A}_{AB}(1,\ldots,N_A,N_A+1,\ldots,N_A+N_B)$, in which the first N_A electrons belong to A and the last N_B electrons to B, is rewritten as

$$\begin{aligned}\mathbf{A}_{AB} &= \mathbf{A}_A\mathbf{A}_B(1 + E_{AB}^{(1)} + E_{AB}^{(2)} + \cdots + E_{AB}^{(k)} + \cdots + E_{AB}^{(K)}) \\ &= \sum_{k=0}^{K} \mathbf{A}_A\mathbf{A}_B E_{AB}^{(k)},\end{aligned} \tag{8}$$

where $\mathbf{A}_A$ and $\mathbf{A}_B$ are the antisymmetrizers for the electrons of A and B, respectively: $\mathbf{A}_A \equiv \mathbf{A}_A(1,\ldots,N_A)$ and $\mathbf{A}_B$ $\equiv \mathbf{A}_B(N_A+1,..,N_A+N_B)$. $E_{AB}^{(k)}$ is the inter-exchange operator of the k pairs of electrons between A and B, $E_{AB}^{(0)} = 1$, and K is the lesser of N_A and N_B: $K = \min(N_A, N_B)$. We specify further the k-electron inter-exchange operator $E_{AB}^{(k)}$ by

$$E_{AB}^{(k)} = \sum\nolimits_{l=1}^{L_k} \varepsilon_{AB}^{(k,l)}, \tag{9}$$

where $\varepsilon_{AB}^{(k,l)}$ is the lth element of the k-electron inter-exchange operators, including parity of the permutation, and L_k is the total number of these operations. When $\varepsilon_{AB}^{(k,l)}$ acts on an $N_A + N_B$ electron function f, k electrons are exchanged between A and B as

$$\begin{aligned}&\varepsilon_{AB}^{(k,l)} f(1,\ldots,N_A,N_A+1,\ldots,N_A+N_B) \\ &\quad = (-)^{\varepsilon} f(a_1^{(k,l)},\ldots,a_{N_A}^{(k,l)},b_1^{(k,l)},\ldots,b_{N_B}^{(k,l)}),\end{aligned} \tag{10}$$

where $(-)^{\varepsilon}$ shows the parity of this exchange.

Thus, the antisymmetrizer for the whole system AB, $\mathbf{A}_{AB}$, is written as a sum of the terms composed of the k-electron exchanges between A and B, E_{AB}^{k}, and then the N_A and N_B electron antisymmetrizations, $\mathbf{A}_A\mathbf{A}_B$. When we apply the antisymmetrizer $\mathbf{A}_{AB}$ to the cf ϕ_I, we do that in two steps: first is the application of the inter-exchange operator, $E_{AB}^{k}\phi_I$, and second is the application of the intra-exchange operator on this result, $\mathbf{A}_A\mathbf{A}_B \cdot E_{AB}^{(k)}\phi_I$. For simplicity, we discuss below the AB system composed of the two atoms A and B, namely, the diatomic molecule AB.

The operation count of each term of Eq. (8) is represented by

$$\begin{aligned}N! &= N_A!N_B!\left(1 + {}_{N_A}C_1\,{}_{N_B}C_1 + {}_{N_A}C_2\,{}_{N_B}C_2\right. \\ &\quad \left. + \cdots + {}_{N_A}C_k\,{}_{N_B}C_k + \cdots + {}_{N_A}C_K\,{}_{N_B}C_K\right) \\ &= N_A!N_B!\sum_{k=0}^{K} {}_{N_A}C_k\,{}_{N_B}C_k,\end{aligned} \tag{11}$$

where ${}_nC_m$ is the binomial coefficient defined by

$${}_nC_m = \binom{n}{m} = \frac{n!}{(n-m)!m!}. \tag{12}$$

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In Eq. (11), $N! = (N_A + N_B)!$ of the left-hand side (lhs) is the total operation counts of the antisymmetrizer $\mathbf{A}_{AB}$ on the left-hand side of Eq. (8) and on the rhs, $N_A!$ is that of $\mathbf{A}_A$, $N_B!$ is that of $\mathbf{A}_B$, and in the parentheses, the term ${}_{N_A}C_k\,{}_{N_B}C_k$ is the operation count of the k-electron inter-exchange operator $E_{AB}^{(k)}$. Therefore, L_k in Eq. (9) is given by $L_k = {}_{N_A}C_k\,{}_{N_B}C_k$.

Equation (8) itself is not new. Similar formula was utilized by McWeeny[32] to study long-range forces. In the present study, we utilize it to build up a new antisymmetrization theory that helps to reduce antisymmetrization operations for large molecules. When we follow strictly the antisymmetry rule, we have to perform all the antisymmetrization operations counted above with Eq. (11). But, is this always necessary? The *i*Exg formula of Eq. (8) gives us a tool to answer this question by examining first the term $E_{AB}^{(k)}\phi_I$ and then the term $\mathbf{A}_A\mathbf{A}_B \cdot E_{AB}^{(k)}\phi_I$, as explained above. Now, we examine first the inter-exchange term $E_{AB}^{(k)}\phi_I$. We notice that this term *decreases exponentially* as the number of the electron exchanges k increases and/or as the distance R_{AB} increases. We explain why.

The cf ϕ_I of a molecule is given by Eq. (7) as a product of the function f_I and the initial function ϕ_0. Now, we refer to ϕ_0 given by Eq. (6). This ϕ_0 always includes the product of the orbital terms $\exp(-\alpha_{i_A} r_{i_A A})\exp(-\alpha_{j_B} r_{j_B B})$, where the electrons i_A and j_B belong to the atoms A and B, respectively. When single electron pair i_A and j_B is exchanged by the operator $E_{AB}^{(k)}$, we obtain $\exp(-\alpha_{i_A} r_{j_B A})\exp(-\alpha_{j_B} r_{i_A B})$, which is *exponentially smaller* than the former, because $r_{j_B A} > r_{i_A A}$ and $r_{i_A B} > r_{j_B B}$ since the atoms A and B are separated by the distance R_{AB}. When such exchange of electrons between A and B is performed k times, the magnitude becomes smaller k-times of the exponential. Therefore, the inter-exchange term $E_{AB}^{(k)}\phi_I$ decreases exponentially as the number of the electron exchanges k increases. Likewise, when the AB distance R_{AB} increases, again the inter-exchange term $E_{AB}^{(k)}\phi_I$ decreases exponentially. When both atoms A and B have many electrons, the higher inter-exchange terms of Eq. (8) become essentially zero and only the first few terms contribute. As the distance R_{AB} increases, the inter-exchange contribution decreases exponentially, and from some distance, it becomes negligible. This is also the case when the atoms A and B are separated by several bonds in a large molecule. The orbital exponent α also affects this exchange contribution: the inter-exchange involving the inner-shell electron contributes much less than that of the valence electrons. As a result of these observations, we understand that in large molecules, many antisymmetrization operations actually give negligibly small results and therefore need not be performed. The above arguments are valid also for the cases where A and/or B are the fragments or the interacting molecules. Thus, one finds that the antisymmetry "rule" defined in the Introduction is actually a too strict rule and therefore can be relaxed to save the computer time: the *i*Exg theory shows such a method.

We continue further the application of Eq. (8) to ϕ_I. Referring to Eq. (8), the total exchange operator $\mathbf{A}_{AB}$ is rewritten as a sum of the k-electron exchange terms $\mathbf{A}_A\mathbf{A}_B E_{AB}^{(k)}$, which can be further transformed as

$$\begin{aligned}\mathbf{A}_A\mathbf{A}_B E_{AB}^{(k)} &= \sum\nolimits_{l=1}^{L_k} \mathbf{A}_A\mathbf{A}_B\varepsilon_{AB}^{(k,l)} \\ &= \sum\nolimits_{l=1}^{L_k} \mathbf{A}_A^{(k,l)}\mathbf{A}_B^{(k,l)}\varepsilon_{AB}^{(k,l)}.\end{aligned} \tag{13}$$

The first equality was obtained simply by using Eq. (9). In the second equality, $\mathbf{A}_A^{(k,l)}$ and $\mathbf{A}_B^{(k,l)}$ are the antisymmetrizers for the electrons of the systems A and B, respectively, *after* the exchange $\varepsilon_{AB}^{(k,l)}$ is done as in Eq. (10), namely,

$$\begin{aligned}\mathbf{A}_A^{(k,l)} &\equiv \mathbf{A}_A^{(k,l)}(a_1^{(k,l)},\ldots,a_{N_A}^{(k,l)}), \\ \mathbf{A}_B^{(k,l)} &\equiv \mathbf{A}_B^{(k,l)}(b_1^{(k,l)},\ldots,b_{N_B}^{(k,l)}).\end{aligned} \tag{14}$$

The electron coordinates after the exchange $\varepsilon_{AB}^{(k,l)}$ is done are defined in Eq. (10). The second equality of Eq. (13) is valid because the second and third lines generate in different orders the same full list of the electron permutations after all possible k-electron exchanges are done. So, we obtain Eq. (13).

The transformation of the *i*Exg formula given by Eq. (13) is very useful when it is applied to the molecular cf given by Eq. (7). The cf's are classified into *atomic* and *inter* ones depending on the nature of the function $f_I\left(\{\mathbf{r}_{iA}\},\{r_{ij}\}\right)$ whether it includes only the intra-atomic r_{ij} terms or it includes the inter-atomic r_{ij} terms. When we apply the operations given by Eq. (13) to the *atomic* cf's, we obtain

$$\begin{aligned}&\mathbf{A}_A^{(k,l)}\mathbf{A}_B^{(k,l)}\varepsilon_{AB}^{(k,l)}\phi_{IA}(1,..,N_A)\phi_{JB}(N_A+1,..,N_A+N_B) \\ &\quad= (-)^{\varepsilon}\mathbf{A}_A^{(k,l)}\mathbf{A}_B^{(k,l)}\phi_{IA}(a_1^{(k,l)},a_2^{(k,l)},\ldots,a_{N_A}^{(k,l)})\phi_{JB}(b_1^{(k,l)},b_2^{(k,l)},\ldots,b_{N_B}^{(k,l)}) \\ &\quad= (-)^{\varepsilon}\mathbf{A}_A^{(k,l)}\phi_{IA}(a_1^{(k,l)},a_2^{(k,l)},\ldots,a_{N_A}^{(k,l)})\mathbf{A}_B^{(k,l)}\phi_{JB}(b_1^{(k,l)},b_2^{(k,l)},\ldots,b_{N_B}^{(k,l)}),\end{aligned} \tag{15}$$

where the last equality follows because $\mathbf{A}_B^{(k,l)}$ applies only to the b electrons. Thus, for the atomic cf's, the operators $\mathbf{A}_A^{(k,l)}$ and $\mathbf{A}_B^{(k,l)}$ apply *independently* to the electrons of A and B after $\varepsilon_{AB}^{(k,l)}$ is applied, so that the computational labor is reduced from $N_A! \times N_B!$ to $N_A! + N_B!$. This is a big reduction! Actually, the atomic cf's are very important in molecular formations: with the reorganizations of atomic cf's, an important part of the molecular formation is described. Of course, we can use the Nk algorithm for the antisymmetrizers $\mathbf{A}_A$ and $\mathbf{A}_B$.

When the cf ϕ_I includes one inter-electron term like $r_{i_A j_B}$ that connects different atoms or fragments, we have

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$$\mathbf{A}_A^{(k,l)}\mathbf{A}_B^{(k,l)}\varepsilon_{AB}^{(k,l)}r_{i_A j_B}\phi_{IA}(1,..,N_A)\phi_{JB}(N_A+1,..,N_A+N_B)$$
$$=\mathbf{A}_A^{(k,l)}\mathbf{A}_B^{(k,l)}r_{a_i^{(k,l)}b_j^{(k,l)}}\phi_{IA}(a_1^{(k,l)},a_2^{(k,l)},\ldots,a_{N_A}^{(k,l)})\phi_{JB}(b_1^{(k,l)},b_2^{(k,l)},\ldots,b_{N_B}^{(k,l)}). \quad (16)$$

In this case, the operation may be done with the dot-algorithm presented before together with the Nk algorithm[26] and we get the accelerations for the electrons except for $a_i^{(k,l)}$ and $b_j^{(k,l)}$. Then, the operation count becomes $[(N_A-1)!+(N_B-1)!]\,N_AN_B$, which is still much smaller than $N_A!\times N_B!$. As the inter-electron terms bridging A and B increase, the operation count increases. However, if we apply the dot algorithm,[26] further acceleration is possible. Thus, the accelerations in the second stage of the *i*Exg theory are also large, particularly for molecules composed of many atoms and fragments: a systematic formulation will give very large reductions.

We note finally that the sequential application of the intra-atomic antisymmetrizer $\mathbf{A}_A\mathbf{A}_B$ after the inter-exchange operators $E_{AB}^{(k)}$ as given by Eq. (8) may affect the counting of the total number of the necessary exchanges. Namely, though the exchange was substantially small in the first stage, it may increase in the second stage. An example is the 1s electron inter-exchange: though it is almost negligible in the first stage, it becomes non-negligible since the intra-atomic antisymmetrizer may exchange the electrons between the atomic 1s and valence orbitals.

Thus, with the *i*Exg theory, much acceleration seems to be possible by relaxing the antisymmetry rule. Both the first and the second stages above give large reductions of antisymmetry operations compared to those if the antisymmetry rule is strictly followed. This reduction is not restricted to the FC theory, but applies to many different levels of the theories as far as the locality of electrons is assured in the theoretical framework. This situation should actually be almost universal to chemistry since the local atomic concept is guaranteed by the success of the chemical structural formulas and the chemical reaction formulas daily used in chemistry.

For systems consisted of many atoms and/or fragments, like polyatomic molecules and clusters, the *i*Exg formula becomes

$$\mathbf{A}=\mathbf{A}_A\mathbf{A}_B\cdots\mathbf{A}_D(1+E^1+E^2+\cdots+E^{(k)}+\cdots+E^{(K)}), \quad (17)$$

where A, B, . . . , D represent different atoms and/or fragments, $E^{(k)}$ the inter-exchange operator of the k pairs of electrons among the fragments A to D, and K is the maximum of the number of the pairs k. In polyatomic molecules, the atoms may be separated by one, two, three, and so on bonds and therefore, from some m-bonds, the exchange contributions may be safely neglected. In a big molecule, such situations dominate. Therefore, as a molecule becomes large, the number of the unnecessary antisymmetrization operations increases dramatically. Since the antisymmetrization is a time-consuming step for the highly accurate calculations close to the Schrödinger accuracy, the *i*Exg theory naturally reduces the computational costs even to a lower order of N. In this paper, we will show as such an example the calculations of the He_{60} fullerene cluster that has the hypothetical structure similar to the fullerene C_{60}. Though the system has 120 electrons, which are huge for the calculations of the Schrödinger accuracy, the necessary permutations are drastically reduced by the *i*Exg theory, which makes the FC calculations easily possible.

IV. ESTIMATE OF THE NECESSARY NUMBER OF INTER-EXCHANGES

Now, we estimate the necessary numbers of electron inter-exchanges in the applications of the *i*Exg theory, considering two carbon atoms in the hydrocarbon molecule, all-*trans*-polyacetylene, as an example. As expected from the discussions given in the paragraph below Eq. (12), the possible occurrence of the electron exchange can be estimated by using the square of the overlap between the orbitals to which the exchanging electrons belong. This is a rough estimate because in the cf's of the FC wave function, other factors like $r_{iA}{}^n$ and $r_{ij}{}^m$ also exist in the function f_I as seen in Eq. (7), but their distance dependences are much milder than the exponential dependence of the orbitals. In Table I, we showed the square of the overlap integral for the pair of the carbon orbitals to which the exchanging electrons belong. The Slater orbitals of the exponents α = 5.67(1s) and 1.59(2sp) were used. For the valence 2sp electrons, we used the geometric average of the $p\sigma$ and $p\pi$ overlaps. The C–C bond distance used was 2.75 a.u. (1.45 A), an average of the single and double bonds. The non-bonded C–C distances were estimated from the structure of the all-*trans*-polyacetylene.

Based on the data shown in Table I, we estimated the possible numbers of electron inter-exchanges for the carbon pairs in the polyacetylene and the results are summarized in Table II. Based on our numerical experiences, we estimated that the electron exchange can occur when the square of the overlap integral is larger than 10^{-6}. Table II implied that for the 1s electrons, only one 1s electron inter-exchange with the valence electrons of the nearest neighbor carbon atom needs to be considered. For the valence electrons, one inter-exchange must be considered up to the four bonds, two and three inter-exchanges must be considered up to the two bonds, and four inter-exchanges must be considered for the directly bonded carbons. More than five inter-exchanges need not be considered for one carbon pair. Also, the exchange of electrons between the carbons separated by five or more bonds is safely neglected. We note that for different carbon-carbon pairs, up to six valence electron exchanges can occur, though four exchanges are maximum between the directly bonded carbon pair.

Thus, the *i*Exg theory implies that in a given accuracy, like the chemical or spectroscopic accuracy, only a limited number of electron exchanges need to be considered between the atoms or the fragments separated by some distance R in a molecule or a system. The number of the electron

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TABLE I. Square of the overlap between the orbitals of two different carbon atoms as a measure of the occurrence of the electron inter-exchange between them.[a,b]

Number of exchange	Exchange orbitals	One bond	Two bonds	Three bonds	Four bonds	Five bonds
1	$1s_A$-$1s_B$	0.41×10^{-9}	0.53×10^{-18}	0.17×10^{-29}	~0	~0
1	$1s_A$-$2sp_B$	0.67×10^{-6}	0.41×10^{-8}	0.38×10^{-11}	0.58×10^{-14}	0.42×10^{-17}
1	$2sp_A$-$2sp_B$	0.80×10^{-1}	0.47×10^{-2}	0.26×10^{-4}	0.13×10^{-6}	0.26×10^{-9}
2	$1s_A$-$1s_B$, $1s_A$-$1s_B$	0.17×10^{-18}	0.28×10^{-36}	~0	~0	~0
2	$2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$	0.65×10^{-2}	0.22×10^{-4}	0.69×10^{-9}	0.17×10^{-13}	0.68×10^{-19}
3	$2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$	0.52×10^{-3}	0.10×10^{-6}	0.18×10^{-13}	0.22×10^{-20}	~0
4	$2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$	0.42×10^{-4}	0.48×10^{-9}	0.48×10^{-18}	~0	~0
5	$2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$, $2sp_A$-$2sp_B$, $1s_A$-$2sp_B$	0.28×10^{-10}	0.20×10^{-17}	~0	~0	~0

[a] All-*trans*-polyacetylene structure with all bond lengths of 2.75 a.u. (average of the single and double bonds) was assumed.
[b] ~0 means negligibly small.

exchanges reduces exponentially as the distance R increases. As the size of the molecule or the system becomes larger and larger, the number of the electron pairs for which we need not antisymmetrize increases dramatically. This helps to reduce the computational cost. For very large molecules, the dependence on the system size would be a lower order of N, though at the beginning, the scaling would not be good because as seen above, up to six valence electron exchanges can occur among different carbon-carbon pairs. Applications of the *i*Exg theory to many different levels of theories and to many different types of molecular systems would be necessary to examine its efficiency in chemistry. Below, we give some examples of applications of the *i*Exg theory to the FC-LSE calculations in order to see its implications and its efficiency in molecular calculations.

V. APPLICATIONS OF THE *i*EXG THEORY

A. Chemical bond formation of Li_2

We first show the role of the *i*Exg theory in the FC-LSE calculations of the chemical bond formation process of the Li_2 molecule. We described the wave function of this system by

$$\begin{aligned}\psi &= c_{AB}\mathbf{A}\left[\tilde{\Psi}_A\Psi_B\right] + c_{AB}\mathbf{A}\left[\Psi_A\tilde{\Psi}_B\right] + \sum_I c_I\mathbf{A}\phi_I \\ &= \sum_I c_I^{(A)}\mathbf{A}\left[\phi_I^{(A)}\Psi_B\right] + \sum_I c_I^{(B)}\mathbf{A}\left[\Psi_A\phi_I^{(B)}\right] \\ &\quad + \sum_I c_I\mathbf{A}\phi_I. \end{aligned} \tag{18}$$

TABLE II. Estimate of the possible number of inter-exchanges between the orbitals belonging to different carbons in all-*trans*-polyacetylene.

Number of exchange	Nature of exchange[a]	Number of bonds[b]
1	1s-1s	0
1	1s-val	1
1	val-val	1, 2, 3, 4
2	$(\text{val-val})^2$	1, 2
3	$(\text{val-val})^3$	1, 2
4	$(\text{val-val})^4$	1
5	$(\text{val-val})^5$	0

[a] Val means valence.
[b] 0 means that such exchange does not occur in chemical accuracy even between the nearest neighbor carbons.

In the first line, the first term consists of the product of the accurate FC wave function of the two Li atoms A and B in which the atom A is reorganized, as shown by the tilde mark, in the presence of the atom B and the second term represents the reorganized atom B in the presence of atom A. The last term represents the lower-order ordinary FC wave function whose role is to describe mainly the inter-atomic effect. The second line shows more explicit formula. Namely, the wave function of the atom A, Ψ_A is written as $\Psi_A = \sum_I c_I^{(A)}\mathbf{A}_A\phi_I^{(A)}$, where $\left\{\phi_I^{(A)}\right\}$ is the set of the cf's of the Li atom and $\left\{c_I^{(A)}\right\}$ represents their coefficients. In the course of the interaction of the two atoms, we described in the first term the reorganization of the one set of the coefficients $\left\{c_I^{(A)}\right\}$ in the presence of the another atomic wave function $\psi^{(B)}$ and vice versa in the second term. For the reorganized Li atom, we considered the cf's of the order four of the ground-state (M = 190) plus the order three cf's of the 2p-excited state (M = 57) that describe the polarization reorganization. For the fixed Li atom, we used the atomic FC result for the ground-state (n = 4, M = 190) with the given coefficients. The third term was added to describe mainly the inter-atomic term and we used the order two (M = 669) FC wave function of the Li_2 molecule. With the first and second terms, the electron correlations within atoms and their reorganizations in the course of the molecular formation were described and at the same time, the correct dissociation at $R \to \infty$ was ensured. We did not include here the effects of the simultaneous reorganization in both atoms A and B to save the computer time, but this approximation was approved in the results as shown below probably because the equilibrium bond distance, 5.05 a.u. (2.67 Å), of Li_2 is longer than ordinary chemical bonds of organic molecules. The Slater orbitals used for the Li atom were the Clementi-Loetti's Hartree-Fock orbitals.[34] We used 10^6 sampling points generated by the local sampling method.[33]

We showed in Table III the results of the *i*Exg theory applied to the FC-LSE calculations of the Li_2 molecule at the separations of R = 20.0, 10.0, 7.0, 5.05 (equilibrium distance), and 3.0 a.u. The number of the exchanged electrons, Exg, the number of the necessary permutations, the calculated energies, and the H-square errors[5,6] were given. Since Li_2 is a 6-electron system, we examined Exg of 0, 1, 2, and 3 (full). At infinite separations, no exchange of electrons (Exg = 0) was necessary between the two Li atoms. When two Li atoms approach each other to 20 a.u., the results obtained with Exg = 0 were

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TABLE III. Results of the *i*Exg theory for Li_2 molecule calculated with the FC-LSE method at $R = 20.0$, 10.0, 7.0, 5.05 (equilibrium distance), and 3.0 a.u.[a]

R (a.u.)	Method	Number of exchanged electrons	Number of necessary permutations (% to the total)	Energy (a.u.)	ΔE (kcal/mol)[b]	H-square error
∞	FC-LSE			−14.956		
20.0	FC-LSE (*i*Exg)	**0**	**8 (2.78)**	**−14.957**		$\mathbf{1.56\times10^{-3}}$
		1	72 (25)	−14.957		1.56×10^{-3}
		2	136 (47.22)	−14.957		1.56×10^{-3}
		3	144 (50)	−14.957		1.56×10^{-3}
10.0	FC-LSE (*i*Exg)	**0**	**8 (2.78)**	**−14.960**		$\mathbf{9.08\times10^{-3}}$
		1	72 (25)	−14.960		8.80×10^{-3}
		2	136 (47.22)	−14.960		8.79×10^{-3}
		3	144 (50)	−14.960		8.79×10^{-3}
7.0	FC-LSE (*i*Exg)	0	8 (2.78)	(−15.080)[c]		(2.44×10^{0})[c]
		1	**72 (25)**	**−14.977**		$\mathbf{2.65\times10^{-2}}$
		2	136 (47.22)	−14.977		2.71×10^{-2}
		3	144 (50)	−14.977		2.71×10^{-2}
5.05	FC-LSE (*i*Exg)	0	8 (2.78)	(−15.264)[c]	(−168.86)[c]	(2.40×10^{0})[c]
		1	**72 (25)**	**−14.994**	**0.71**	$\mathbf{3.02\times10^{-2}}$
		2	136 (47.22)	−14.994	0.70	3.00×10^{-2}
		3	144 (50)	−14.994	0.70	3.00×10^{-2}
	FC-LSE (Nk or NF)	NF[d]	288 (100)	−14.994	0.70	3.00×10^{-2}
	Exact[e]			−14.9954		
3.0	FC-LSE (*i*Exg)	0	8 (2.78)	(−15.611)[c]		(3.02×10^{0})[c]
		1	72 (25)	(−16.588)[c]		(7.14×10^{-1})[c]
		2	**136 (47.22)**	**−14.920**		$\mathbf{4.38\times10^{-2}}$
		3	144 (50)	−14.920		3.00×10^{-2}

[a]Bold face means physically correct values with the minimum number of permutations.
[b]The energy difference between the FC-LSE and the estimated exact energy at $R = 5.05$ a.u.
[c]Bosonic solution.
[d]Full permutations considering spin ($2^3\times3!\times3!$).
[e]Estimated exact energy.[28]

equal to the results obtained with Exg = 1, Exg = 2, and Exg = 3 in chemical accuracy. Therefore, at this distance, two Li atoms do not exchange electrons. If we knew this fact beforehand, we can save the number of the necessary permutations: the necessary permutations for Exg = 0 are only those within each Li atom, which are only 2.78% of the total number of necessary permutations. This helps to reduce the computational time. At $R = 10.0$ a.u., again the results of Exg = 0, 1, 2, and 3 were all equal to chemical accuracy. So, Exg = 0 at this distance. However, at $R = 7.0$ a.u., the energy obtained with Exg = 0 was too low and the energies obtained with Exg = 1, 2, and 3 were all equal. This shows that at this distance, one electron exchange occurs between the two Li atoms. The result of Exg = 0 was bosonic, symmetric solutions having mixed with the antisymmetric solution and occurred for ignoring the antisymmetry principle. The energy was too low in comparison with the fermion case. At $R = 7.0$ a.u., the number of the necessary permutations was 25% of the total: we can get the 75% saving. At $R = 5.05$ a.u., the equilibrium distance, again the number of the necessary exchange was unity: although the energy for Exg = 0 was bosonic and too low, the energy obtained with Exg = 1 was equal to the ones of Exg = 2 and 3. We confirmed that this energy was equal to the energy calculated by using the NF and Nk algorithms for the antisymmetrizations where all the exchanges were done without any selection. The calculated total energy of Li_2 at the equilibrium distance was −14.994 a.u. which was about 1 mH higher than the known exact energy, −14.9954 a.u. reported by Filippi and Umrigar.[28] When two Li atoms come closer to $R = 3.0$ a.u., the number of the necessary exchange becomes two: the energies for Exg = 2 and 3 were the same, but the energies for Exg = 0 and 1 were bosonic and too low. The repulsive interaction at this distance is just the so-called exchange repulsion.

Figure 1 shows the potential energy curve of the Li_2 molecule calculated with the FC-LSE *i*Exg theory: the lines for Exg = 0, 1, 2, and 3 were shown in purple, green, blue, and red, respectively. As two Li atoms approach from 20 a.u., the interaction potential can be drawn safely with Exg = 0 up to about 9 a.u., but in the shorter region, the curve of Exg = 0 shows a bosonic behavior. The stabilization near 9 a.u. is not due to the exchange, but due to the van der Waals interaction without the electron exchange. To improve this wrong behavior, we have to add one more exchange between two Li atoms and with Exg = 1, we get the improved potential curve up to about 4.6 a.u. The potential minimum was obtained at around $R = 5.05$ a.u. with the curve of Exg = 1, showing that the chemical bond of the Li_2 molecule is formed with the one electron exchange. This Exg = 1 curve shows bosonic behavior at the length shorter than 4.6 a.u., and for shorter regions, we need Exg = 2. We performed the vibrational analysis using the calculated potential energy curve and obtained the equilibrium distance $R_{eq} = 5.049$ a.u. (experiment 5.051 a.u.) and the binding energy $D_0 = 1.032$ eV (experiment 1.069 eV). The Exg = 2 curve showed the bosonic behavior at about $R = 2.05$ a.u. and for shorter regions,

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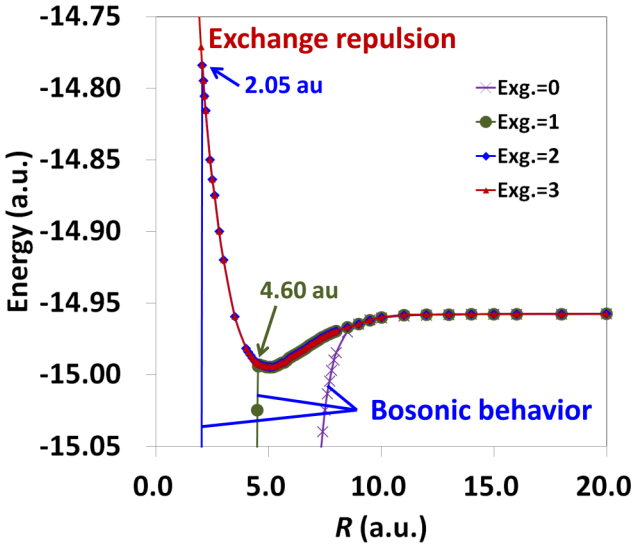

FIG. 1. Potential energy curve of Li_2 with Exg = 0 (purple), 1 (green), 2 (blue), and 3 (red).

all three exchanges (Exg = 3) were necessary to correctly calculate the potential energy curve. Exg = 2 and 3 involve the exchange between the closed-shell 1s electrons that causes repulsions. The so-called "exchange repulsion" is appropriate to describe the nature of the repulsive curve in this region. Thus, the *i*Exg theory not only reduces the computational efforts of the antisymmetrization but also clarifies the nature of the chemical bond and interaction.

B. C_2 molecule

Next, we apply the *i*Exg theory to the FC-LSE calculations of the C_2 molecule (12 electrons, $R = 2.348$ a.u. = 1.243 Å). We generated the order two FC wave functions, both atomic and inter parts, from the VB initial function but we omitted the inter cf's related to the carbon 1s orbitals, which are unimportant. The dimension of the independent atomic cf's was $M = 359$, that of the inter cf's was $M = 340$, and the total cf's was $M = 699$. The Slater orbitals used for the carbon atom were the Clementi-Loetti's Hartree-Fock orbitals.[34] In the LSE calculation, the molecular 10^6 sampling points were synthesized from the atomic local sampling points using the local variance criteria: the set of the sampling points and the corresponding wave function were optimized using the H-square error as a criterion till we get the stationary behavior in the calculated H-square error. In this process, 1200 sampling points (0.12% of the total) were replaced with the new ones. The details of this method will be published elsewhere.[35]

The results of the *i*Exg theory applied to the C_2 molecule were summarized in Table IV. When the number of the electrons exchanged (Exg) between the two carbons was 0–3, the calculated energies were unreliable. When Exg = 4, it was −75.925 99 a.u., and when Exg = 5 and 6, the energy did not change, showing that the additional Exg = 5 and 6 were unnecessary. The present FC energy differs by only 0.51 mH (0.32 kcal/mol) from the exact value −75.9265 a.u. reported by Bytautas and Ruedenberg.[30] These results are parallel to the results shown in Table II. We also used the Nk algorithm[26] instead of the *i*Exg one and compared with the present result. The calculated energy was −75.925 99 a.u., which was completely the same as the *i*Exg result. However, the computational time for the *i*Exg method (9.3 h) was shorter than that for the Nk method (11.8 h). The reason is attributed to the fact that in the *i*Exg calculations, the necessary permutations were only 2.11% of the total, while in the Nk method, all the permutations must be performed following the antisymmetry rule, though the procedure itself is designed to be fast.[26]

C. Helium fullerene, He_{60}

Finally, we apply the FC-LSE *i*Exg theory to solve the SE of helium fullerene He_{60}, a model fullerene composed of helium atoms. The structure is shown in Fig. 2. Without the *i*Exg theory, the calculation of the Schrödinger accuracy is impossible, since He_{60} has 120 electrons whose antisymmetrizations involve $120! = \sim 10^{198}$ or $2^{60} \times 60! \times 60! = \sim 10^{182}$ (considering spin) operations if the NF algorithm is used. However, with the *i*Exg theory, we estimated from the calculations for the He_2 system that only one electron

TABLE IV. C_2 molecule calculated by the FC-LSE method using the *i*Exg method for the antisymmetrization. The results were compared with the exact result and with the result obtained with the Nk method for the antisymmetrization.[a,b]

Number of exchanged electrons, Exg and method	Energy (a.u.)	$\Delta E = E_{FC\text{-}LSE} - E_{exact}$ (kcal/mol)	Number of necessary permutations (% to the total)	Computational time (hour)
0	(−77.871 17)[c]	…	480 (0.001)	0.24
1	(−77.013 48)[c]	…	24 480 (0.07)	0.60
2	(−75.879 98)	…	199 680 (0.60)	3.1
3	(−75.910 28)	…	526 080 (1.59)	7.4
4	**−75.925 99**	**0.32**	**701 280 (2.11)**	**9.3**
5	−75.925 99	0.32	725 280 (2.19)	9.5
6	−75.925 99	0.32	725 760 (2.19)	10.2
Nk method	−75.925 99	0.32	33 177 600 (100)[d]	11.8
Exact[e]	−75.926 5			

[a]Using 1036 cores in parallel with the Fujitsu PRIMERGY CX2550 at the Research Centre for Computational Science, Okazaki.
[b]Bold face means physically correct values with the minimum number of permutations.
[c]Bosonic energy.
[d]Full permutations considering spin ($2^6 \times 6! \times 6!$).
[e]Reference 30.

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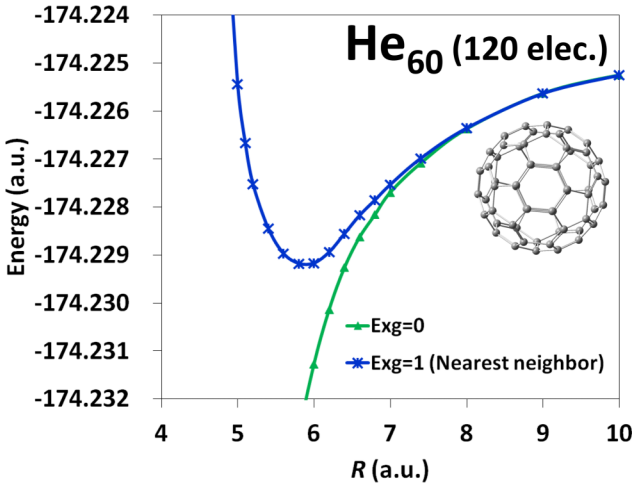

FIG. 2. Potential energy curve of the helium fullerene He_{60} near the equilibrium distance. The blue and green lines show the results for the Exg = 1 and Exg = 0 calculations, respectively, between the nearest-neighbor atoms. The Exg = 0 curve shows the bosonic behavior for the distances shorter than 7.5 a.u.

exchange between the nearest-neighbor atoms was necessary. This led to the simplification that only 21 720 permutations are necessary for this system. This is a huge simplification that turns "impossible" to "easily possible."

The helium fullerene He_{60} has two different bond distances, $R_1 = 1.0278\ R$ and $R_2 = 0.9721\ R$ and we varied R to calculate the equilibrium structure. The FC wave function was constructed using the theoretical synthetic chemistry method (TSCM) that will be explained in a separate paper.[36] In short, we constructed the FC wave function of He_{60} by the products of the accurate FC wave functions of the constituent He atoms as follows. First, we calculated the order 4 ($M_{He} = 22$) FC wave function of each helium atom. Then, we put this accurate FC wave function of the helium atom at each He position of the helium fullerene and using this initial wave function of He_{60}, we constructed the wave function of the He fullerene with the standard FC method to order 2. This method gave 3587 cf's for He_{60}. For the He atomic orbital, we used Clementi-Loetti's Hartree-Fock orbitals of the Slater basis.[34] The calculations were performed using 2048 cores in parallel with the Fujitsu PRIMERGY RX300 at the Research Centre for Computational Science, Okazaki.

We show in Fig. 2 the calculated potential energy curve of He_{60} near the minimum. In the region $R > \sim 7.5$ a.u., no interatomic exchange was necessary and so the curves of Exg = 0 and 1 overlap. For the region, $\sim 7.5 > R > \sim 5$ a.u., one-exchange between the nearest neighbor atoms was necessary, so that the green line for Exg = 0 showed a bosonic behavior near the minimum. The absolute value of the calculated total energy of He_{60} at the minimum was −174.229 179 a.u. in comparison with the calculated energy of the 60 He atoms at the dissociation, −174.223 168 a.u. (The known exact energy of 60 He atoms is −174.223 463 a.u.[10]) Thus, the binding energy of He_{60} was calculated to be about 3.8 kcal/mol and the equilibrium length at about $R = 5.8$ a.u. (3.1 Å). However, the calculated binding energy may have some error: since He_{60} has 90 He–He interactions, 0.1 kcal/mol accuracy requires the 0.1/90 kcal/mol accuracy per He_2, which is about micro Hartree accuracy and this accuracy is not guaranteed with the present calculational conditions.

TABLE V. He_{60} potential properties calculated by the Hartree-Fock and CCSD methods with the cc-pVDZ and aug-cc-pVDZ basis sets compared with the result of the present FC-LSE *i*Exg theory.

Method	R_{eq} (a.u.)[a]	Absolute energy at R_{eq} (a.u.)[b]	Binding energy (kcal/mol)
Hartree-Fock (cc-pVDZ)	6.0	−171.309 738	0.0689
Hartree-Fock (aug-cc-pVDZ)	6.4	−171.342 501	0.138
CCSD (cc-pVDZ)	5.8	−173.256 258	0.356
CCSD (aug-cc-pVDZ)	5.6	−173.377 465	2.86
FC-LSE (present)	5.8	−174.229 179	3.77

[a]Equilibrium distance.
[b]Exact energy of the 60 He atoms (the dissociation limit of He_{60}) is −174.223 463 a.u.[10]

For comparison, we have performed the Hartree-Fock and coupled-cluster singles and doubles (CCSD) calculations of He_{60} using the Gaussian 09 suite of programs.[37] The full CI and the CCSD parenthesis triples (CCSD(T)) did not work for such a large system. In Table V, the results were summarized and compared with the present FC-LSE *i*Exg result. The Hartree-Fock could scarcely describe the stabilization of this cluster, while the CCSD showed a large basis set dependence: the cc-pVDZ and aug-cc-pVDZ bases gave the binding energies of 0.36 and 2.86 kcal/mol, respectively. Further, the CCSD absolute energies were as higher as by about 1 a.u. than the true value! On the other hand, our result should be correct, being close to the chemical accuracy. The equilibrium distance was calculated similarly with the CCSD and the FC-LSE method.

As seen from this example, the *i*Exg theory would be useful for studies of clusters since generally speaking, the distances between the elements are large, so that the numbers of the necessary electron-exchanges between the elements are small and the *i*Exg theory becomes efficient. The antisymmetrizations within the individual elements may be performed using the efficient Nk method.

VI. CONCLUDING REMARKS AND PROSPECTS

To establish an accurate chemical theory that handles routinely the exact solutions of the SE's of general molecules, we have to find out not only the general efficient theory of solving the SE but also the efficient theory of satisfying the antisymmetry principle for many-electron systems. For the first, the FC LSE methodology[7–15] has opened a way toward accurate calculations of the Schrödinger accuracy. The purpose of the present paper was to pave a way toward an efficient antisymmetry method of essentially order N even for the Schrödinger-accuracy calculations of very large molecules. So far, the antisymmetry "rule" has been postulated, like a "dogma," as if it must[3] be satisfied to any electron pairs in a molecule even if their distances are apart in the molecule. However, the present *i*Exg theory clarified that the antisymmetry "rule" was too restrictive and showed an

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efficient way of reducing vast numbers of antisymmetrization operations in a molecule so that the FC theory becomes more efficiently applied to very large systems: the order-size curve may not be good at the beginning but would become better and better as the size of molecules becomes larger and larger. This is true not only for the highly accurate levels of the theory but also for the lower levels of the approximation, if the locality of electrons is assured in some definite way in the formalism. The standard N^3 algorithm for the determinant would be reduced to a lower order of N for very large molecules. For example, when we handle very large system, it is not clever to put all the electrons of the system into one determinant. It is better to use the *i*Exg theory. Thus, a perspective is opened toward building useful chemical theories that are applicable to much larger systems than before.

In the present formulation of the FC-*i*Exg theory, we assumed the HLSP VB initial function instead of the MO initial function for medium-sized molecules. For calculating the wave function of the Schrödinger accuracy, this is all right since any initial wave function is acceptable in the FC theory, but another reason was that the choice of the MO initial function may cause some complexity in the formulation of the *i*Exg theory. The *i*Exg theory stands on the locality of chemistry but the theoretical framework of the MO theory stands on the delocalized picture which is consistent with the "orbital" picture bearing the orbital energy and the ionization energy as its eigenvalue. When the localized orbital concepts are introduced, the extent of delocalization is reduced to several atoms, which is already small for very large molecules. For the *i*Exg theory, the VB initial is convenient but it is interesting to extend the initial wave function toward the non-orthogonal orbital theory. Further, when we deal with molecular interactions and chemical reactions, we may deal with the fragments by the MO theory and consider their interactions and reactions with the *i*Exg theory. The antisymmetrizations within the fragments and reactants may be dealt with the Nk theory. Since the *i*Exg theory is based on the locality of the molecular electronic structure, it will not work for the systems that have completely delocalized electronic structures. Anyway, many interesting applications are considered and will lead us to a new frontier of theoretical chemistry.

The principle of the *i*Exg theory would be extended even within atoms: in heavy elements, inner-shell orbitals have large exponents, while the valence orbitals have small exponents. Therefore, the electrons of different shells occupy different regions within the atom, which is a similar situation to the atoms in molecules. Therefore, the *i*Exg idea will also apply to the different shells within atoms. This will produce much simplification for the theory of heavy elements.

Further developments of the *i*Exg theory are in progress in our laboratory.

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