Award Accounts

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Deepening and Extending the Quantum Principles in Chemistry

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A brief summary of the author's research projects for deepening and extending the quantum principles in chemistry is given. First, the structure of the exact wave function that is the solution of the Schrödinger equation was clarified and a method of calculating it starting from an approximate wave function is given. The singularity problem intrinsic to atoms and molecules was overcome, and a general method of solving the Schrödinger equation in an analytical form has been established. Quantum chemistry of excited states and ionized states is essential since it is difficult with experiments alone to explore this field due to the short lives of these species. The SAC-CI theory developed in the author's groups offers a powerful method for investigating the chemistry of excited and ionized states. The energy gradient method incorporated into this program is particularly useful for studying geometries and reactions involving these states. The catalysis on a metal surface is a magic process that must be clarified with the help of quantum theory. The author studied it using his dipped adcluster model (DAM) that includes the effects of the free electrons of the bulk metal. The epoxidation reactions of ethylene and propylene were studied with this method. The NMR chemical shifts include much information about the valence electrons of molecular systems. The author clarified that the major electronic mechanisms of the chemical shifts could be attributed to the intrinsic atomic properties that are related to the position of the element in the periodic table. For the chemical shifts induced by heavy ligands, the relativistic effect is sometimes dominant. The spin-orbit effect is most important for light resonant nuclei. For heavier resonant nuclei, other spin-free relativistic effects and the electron correlation effects are also important and they strongly couple with each other, implying an existence of something "unexpected" in the chemistry of heavy elements. Finally, the strategy of the author's study in quantum chemistry is shortly described.

Chemistry is considered to be the results of the realization of several principles, among which the quantum principles are of particular importance since they describe the motions of electrons that govern the structures, reactions, and properties of atoms, molecules, molecular systems, and biological systems.[1] Therefore, one of the most fruitful methodologies would be to deeply understand and cultivate these quantum principles and to realize them in chemistry and biology. Putting this belief into his basic philosophy, the author has pursued his researches in chemistry. Here, on the occasion of the Chemical Society of Japan Award of 2003 being presented to him, some of his achievements are summarized as references for the successors. The topics are mainly collected from the author's studies after 1990, since he was also presented the Physical Chemistry Award of the Chemical Society of Japan for 1990.

The basic trends in theoretical chemistry are threefold: more-and-more-accurate predictions, variety-of-states applicability, and larger-and-larger-system applicability. Since the Schrödinger equation and its relativistic counterpart, which

may be called the Dirac equation for brevity, are the basic principles governing the whole of chemistry,[1] the most straightforward way of achieving the first purpose of theoretical chemistry is to construct a general method of solving these equations as accurately as possible. This has long been a dream of theoretical chemists and physicists, and likewise, that of the author's research life. Recently, this dream has been realized essentially after several years of theoretical considerations on the structure of the exact wave function that started from 1999.[2–8] By the exact wave function, I mean the solution of the Schrödinger equation. The first topic of this account is a method of solving the Schrödinger equation in an analytical form[8] based on the studies reported in this series of articles.[2–8] Two typical examples of applications to helium atom and hydrogen molecule are given from among several applications to atoms and molecules. The results are compared with the best quality wave functions reported in the literature.

The second topic of this account is related to the second and third trends of theoretical chemistry. We have developed a theory called SAC (symmetry adapted cluster)[9,10]/SAC-CI

(configuration interaction)[11–14] theory in 1977–78 as an accurate electronic-structure theory for ground, excited, ionized, and electron-attached states of molecules. The calculations based on the first version of the program applied to the ground and excited states of Be and H_2O were presented in 1978 at Hiroshima in the Symposium on Molecular Science.[15] Since then many developments were done in both theories and programs, mainly in the Nakatsuji laboratory of Kyoto University. The SAC/SAC-CI theory[9–14] and their extensions[16–21] have been applied to the molecular spectroscopy and photochemistry of a variety of molecules of various sizes and have been established as a reliable and useful theory.[22–27] In 1985, the SAC-CI program was released as SAC85 program system[23,28] and in 1991, the SAC-CI general R method was introduced, enabling the calculations of many electron excitation processes.[13] The energy gradient method developed later[29–35] has made it possible to calculate the forces acting on the constituent nuclei of molecules in any electronic states dealt with by the SAC-CI method and has made it possible to study equilibrium geometries and dynamics of molecules in various electronic states. More recently, we have collaborated with Dr. M. Frisch of Gaussian Inc.[34,35] and incorporated our SAC-CI code into the Gaussian03 suit of programs and published it worldwide.[36] It was nice that a method born in our laboratory has grown up to become a tool that is useful to solve chemical problems not only in universities and institutes, but also in chemical and physical industries worldwide.

The SAC-CI method has been applied to various fields of photochemistry. The applications in the initial stage were to examine the accuracy of the new theory[37–40] and to explore some new fields.[41–46] The theory has been shown to be particularly useful to molecular spectroscopies of electronic excitations and ionizations of organic and inorganic molecules and transition metal complexes.[37–39,41,43,46–66] It was also shown to give reliable values of the hyperfine splitting constants of doublet radicals.[44,67,68] It has been applied to the collision induced absorption spectra[69] and the reaction dynamics of excited states.[70,71] A refinement of the program based on the SAC-CI general-R method[13] enabled us to calculate some multielectron processes, like the shake-up states involved in ionization spectra, as quantitatively as can be done for the ordinary single-electron processes. This has opened up a new field, called theoretical fine spectroscopy: the SAC-CI theoretical spectra have become almost as quantitative as the experimental spectra,[72–81] enabling very fine spectroscopic researches in collaboration with the experimentalists.

The perturbation selections adopted in the SAC-CI code[43] have made the calculations of larger systems possible. We have calculated the excitation spectra of many different porphyrin compounds,[82–92] and even performed the geometry optimizations of the ground and excited states of free base porphin.[93] Based on these experiences, we have applied the SAC-CI method to the assignment of the electronic spectra of the whole of the photosynthetic reaction centers of *Rhodopseudomonus viridis*, a bacteria.[94–96] We have further utilized the SAC-CI theory to clarify the origin of the unidirectionality and the effectiveness of the electron transfer in this photosynthetic reaction center.[97–100] The SAC-CI theory has further been applied to surface catalytic reactions of Pd and Pt involving H_2 and acetylene.[101–103] It was then combined with the dipped adcluster model (DAM) for chemisorptions and catalytic reactions on a metal surface[104–108] and applied to the electron transfer and surface photo-luminescent reactions of halogen molecules on alkali metal surfaces.[108,109] It was also applied to the studies of O_2 chemisorptions on an Ag surface[110–112] and of the surface spectroscopy of NO adsorbed on a Pt surface.[113]

The coupled cluster linear response theory (CC-LRT) and the equation of motion coupled cluster (EOM-CC) method are very similar to the SAC-CI theory. In the calculations of the ground-state properties with the coupled-cluster method, Monkhorst[114] described a linear response formulation of the excitation energy from a consideration of the poles of the dynamic polarizability, but this is not a theory for the excited state, because the wave functions of the excited states were not formulated explicitly. Mukherjee[115] gave a more extensive formulation of the coupled cluster linear response theory (CC-LRT). Hirao derived in 1983 the CC-LRT equation starting from the SAC-CI theory.[116] The applications of the CC-LRT were not done before Koch, Jørgensen, and others reformulated it and applied to some molecular systems.[117,118] The equation of motion coupled cluster (EOM-CC) method published in 1989[119,120] was essentially equivalent to the SAC-CI method: the basic theories were identical and the differences were only in the ways of approximations in actual calculations. When the same approximations are done, these three theories give identical results,[26] which constitutes a numerical proof, if necessary, of the equivalence between SAC-CI, CC-LRT, and EOM-CC theories.

The third topic of this account is also related to the second trend of theoretical chemistry. It is related to the chemistry on a metal surface. A metal surface is an infinite system and shows interesting chemistry, like catalysis, when it adsorbs atoms and molecules. Since this is a really huge system, some modeling is necessary to study it theoretically. This is certainly an attractive field to which theory must make some contributions. In 1987, the author proposed the dipped adcluster model (DAM) for catalysis and surface reactions on a metal surface.[104–108] This model has been applied to various chemistries on metal surfaces.[104–112,121–131] As stated above, a combined use of the DAM with the SAC-CI method was very effective to explore the photochemistry on the metal surface.[107–112] We explain here only one example of applications to catalytic reactions, epoxidation reaction of olefins on a silver surface.[121–131]

The last topic of this account is the electronic theory of NMR chemical shifts[132–154] and the importance of the relativistic effect in chemistry.[143–154] The NMR chemical shifts are probably one of the most frequently used properties of molecules in analytical chemistry. We want to note that they involve valuable information about the valence electrons of molecules and molecular systems.[132,133,138] The major electronic mechanisms of the chemical shifts can be attributed to the intrinsic atomic electronic structures that are characterized by the positions of the resonant atoms in the periodic table.[138] Further, when the resonant atom is bonded with heavy elements, the relativistic effects are important and sometimes become the dominant origin of the chemical shift.[143–154] The

heavy element NMR is quite interesting since the spin-dependent and spin-free relativistic effects are both important and they couple strongly with the correlation effects. Though the relativistic effects are important in various aspects of chemistry, we limit ourselves here only to that effect in the NMR chemical shifts.

A brief summary and an overview will then follow and I would like to close this article with acknowledgements to my teachers, colleagues, and students whose supports were essential for realizing these researches.

Method of Solving the Schrödinger Equation

Theory.   The Schrödinger equation (SE) has truly quantitative predictive power in chemistry.[1] Therefore, the theory that enables us to solve the SE has huge scientific and practical merits. For atoms and molecules, the SE is written in time-independent form as

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

where ψ is an exact wave function, E is its energy, and H is the Hamiltonian given by

$$H = -\sum_i \Delta_i/2 - \sum_A \sum_i Z_A/r_{Ai} + \sum_{i>j} 1/r_{ij}$$
$$+ \sum_{A>B} 1/r_{AB} = k_e + V_{ne} + V_{ee} + V_{nn}, \tag{2}$$

where k_e, V_{ne}, and V_{ee} are electron kinetic operator, nuclear-electron attraction operator, and electron–electron repulsion operator, respectively. V_{nn} is the nuclear–nuclear repulsion term which is essentially a constant under the Born–Oppenheimer approximation and so will not be considered hereafter. Up to quite recently, the only practical method of solving the SE was the full-CI method.[155] However, the number of variables involved is astronomical and so its practical merits are quite limited. Furthermore, even if we could get the full-CI solution, it is actually far from the true solution of the SE, because the basis sets used are far from complete. The basis set expansion method most common in modern computational chemistry must be reconsidered.

As one can clearly see from Eq. 1, the exact wave function ψ is an analytical entity in a mathematical sense. However, there is no general method of solving the SE in an analytical form. Eq. 1 also implies that ψ must be a functional of H. In a series of papers starting from 2000,[2–8] the author has investigated the structure of the exact wave function. He considered two questions. What mathematical structures does the exact wave function have? Is a general theory possible that constructs the exact wave function systematically? As a result, the ICI (iterative configuration or composite interaction) and SECC (simplest extreme coupled cluster) methods have been proposed as general methods of calculating the exact wave function. The details have already been published in the literature and interested readers are recommended to read the original papers.[2–8] The basic ideas may briefly be summarized as follows.

The SE defines the exact wave function and is valid only for the exact wave function. We have some equations that are equivalent to the SE. The variational principle

$$\langle\psi|H - E|\delta\psi\rangle = 0, \tag{3}$$

is used to calculate the best possible ψ in the domain of the function ψ and when this domain is general enough it gives the exact wave function. On the other hand, the H-square equation,

$$\langle\psi|(H - E)^2|\psi\rangle = 0, \tag{4}$$

is valid only when ψ is exact and is strictly identical to the SE.

Comparing Eqs. 3 and 4, we notice that when a ψ including only one variable C satisfies

$$\frac{\partial\psi}{\partial C} = (H - E)\psi, \tag{5}$$

then we can say that this ψ has a structure of the exact wave function, because the variational best of this ψ satisfies the H-square equation. There are two types of ψ's that satisfy Eq. 5. One is the simplest ICI (SICI) given by the recursion formula:

$$\psi_{n+1} = [1 + C_n(H - E_n)]\psi_n, \tag{6}$$

with n being an iteration number. It satisfies Eq. 5 at convergence. The other is the simplest ECC (SECC) given by

$$\psi = \exp[C(H - E)]\psi_0. \tag{7}$$

A different argument shows that C of Eq. 7 may be minus infinity for the exact wave function.[156]

The SICI and SECC can be generalized as follows. We divide the Hamiltonian H into N_D pieces as $H = \sum_{I=1}^{N_D} H_I$. Then, we can generalize the ICI method by introducing the N_D variables $\{C_{I,n}\}$, ICIND:

$$\psi_{n+1} = \left(1 + \sum_{I=1}^{N_D} C_{I,n} H_I\right)\psi_n, \tag{8}$$

which is also guaranteed to be exact at convergence.[3] When we use the second quantized Hamiltonian, $H = \sum_{pr} v_p^r a_r^+ a_p + \sum_{pqrs} w_{pq}^{rs} a_r^+ a_s^+ a_q a_p$, N_D may be taken to be the sum of general singles and doubles (GSD), and so the following ICI-GSD:

$$\psi_{n+1} = \left(1 + \sum_{pr} c_p^r a_r^+ a_p + \sum_{pqrs} c_{pq}^{rs} a_r^+ a_s^+ a_q a_p\right)\psi_n, \tag{9}$$

is also guaranteed to be exact at convergence. Similarly, we can define ECC and ECC-GSD (or CCGSD), but they are not guaranteed to be exact, though some contradictory arguments exist in the literature.[157–160]

Figure 1 shows the convergence process of the minimal basis SICI calculations of some small molecules. Each iteration step of ICI is variational and so the energy monotonically converges from above to the full-CI results. For C_2H_4, for example, the full CI result obtained using 107 952 variables is reproduced by the SICI using only one variable, though the convergence speed is rather slow. Figure 2 shows the ICI-GSD calculations.[161] Here, the convergence is very fast. Actually, ICI-GSD is a special case where the singularity problem described below can be circumvented,[161] and therefore is worth studied for practical utility. However, all these results are anyway of the full-CI accuracy, which is usually quite inaccurate in com-
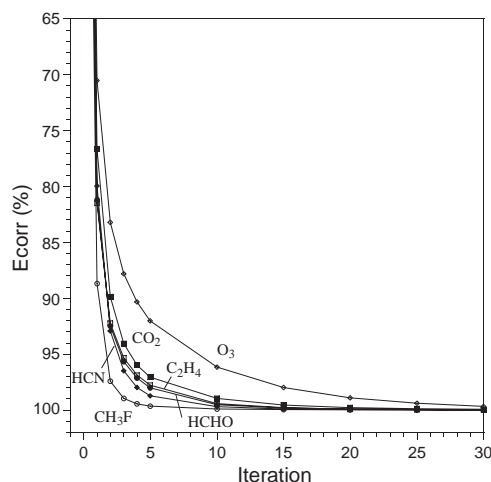
Fig. 1. Convergence of the SICI calculations with the minimal STO-6G basis sets.
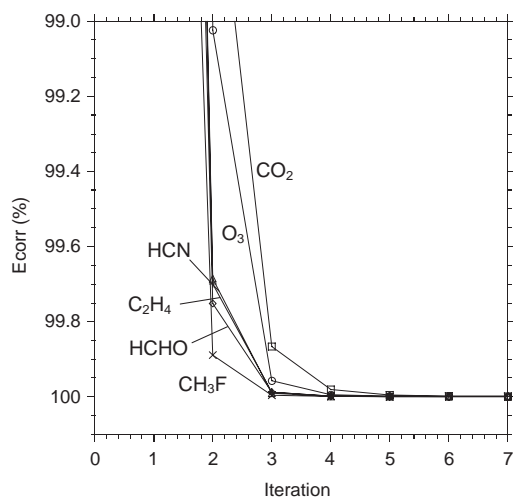

Fig. 2. Convergence of the ICI-GSD calculations with the minimal STO-6G basis sets.

parison with the true solution of the SE.

Now, let us consider a method of solving the SE in an analytical form for atoms and molecules. Then, we immediately encounter a difficulty called the singularity problem. The Hamiltonians for atoms and molecules given by Eq. 2 have singularities in the nuclear attraction and electron–electron repulsion terms. In the SE given by Eq. 1, the rhs, $E\psi$, has no singularity: E is a constant and ψ is a continuous, single-valued, and integrable finite function (this condition is called Q-condition). So, the singularity caused by the potentials in the Hamiltonian must be canceled out within the lhs of the SE (for example, in hydrogen atom, the attractive force must be canceled out, for stability, by the centrifugal force induced by the electronic motion). The cusp condition first derived by Kato[162] is easily derived by this cancellation idea. However, this complete cancellation occurs only for the exact wave function: for approximate wave functions, some singularities remain in $H\psi$ and cause a problem. For example, the integrals $\langle\psi|H^n|\psi\rangle$ do not exist for $n \geq 3$, if ψ is approximate.[8] Then, the theory including higher powers of the Hamiltonian has

difficulties.

The ICI and SECC theories are among the theories that include such higher powers of the Hamiltonian. This is easily seen from the secular equation of the SICI method.[3] In general, as stated in the Introduction, the exact wave function must be a functional of the Hamiltonian applied to some function ψ_0, say $\psi = f(H)\psi_0$ and the function $f(H)$ includes, in general, higher powers of Hamiltonian in the expression of the Maclaurin expansion. So, this is an essential difficulty that must be encountered in any theory describing the true analytical solution of the SE. This difficulty must be solved by going back to the SE itself.

The author has proposed two different ways of solution.[6,8] First, he introduced the inverse Schrödinger equation (ISE),[6]

$$H^{-1}\psi = E^{-1}\psi, \tag{10}$$

which is equivalent to the original SE. At the singular points, H^{-1} is zero and does not have singularity. Some nice features of the theory based on the ISE were demonstrated, but one problem was how to write H^{-1} in a closed form. More recently, he proposed the scaled Schrödinger equation (SSE)[8]

$$g(H - E)\psi = 0, \tag{11}$$

to solve the singularity problem. The scaling function g is a function of electron coordinates and does not commute with the Hamiltonian. It is everywhere positive and non-zero, except at the singular points, and even at the singular points r_0, it must satisfy

$$\lim_{r \to r_0} gV \neq 0, \tag{12}$$

so as not to eliminate the information of the Hamiltonian itself at the singular points: the singularity also contains important information about the system. In Eq. 12, V is the Coulombic potential of Eq. 2. One choice of g would be $g = 1/(-V_{ne} + V_{ee})$. A different choice would be $g = -1/(V_{ne}V_{ee})$. Another choice, $g = r/(r + a)$ for the potential $1/r$ is also a preferable choice where a is a constant.

The SSE has the variational principle and the H-square theorem as the original SE, and therefore we can formulate the ICI and ECC methods based on the SSE; the simplest ICI of the SSE is written, for example, as,

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n. \tag{13}$$

Because of the existence of the scaling function, the integrals involved in this ICI do not diverge.

An analytical nature of the ICI calculation is explained as follows. We start with some guess function ψ_0, which may be determinants including Slater, Gaussian, or mixed functions, but anyway it is an analytical function. The Hamiltonian is just a sum of the differentiation operator (kinetic operator) and the multiplicative operators (potential operator). g is a multiplicative function. Then, ψ_{n+1} is an analytical function with unknown coefficients $\{C_n\}$. We note that the differentiation is always possible and easy.

The role of the ICI method is twofold: one role is to iteratively construct the exact wave function starting from ψ_0 and the other role is to keep the number of the variables small and fixed. A useful extension of the ICI method is obtained by relaxing the second property. Namely, we take all of the M

independent functions $\{\phi_i\}^{(n)}$ included in the ICI wave function given by Eq. 13 and we write the next step as

$$\psi_{n+1} = \sum_i^M c_i \phi_i, \tag{14}$$

by giving an independent coefficient c_i to every ϕ_i. We call this relaxed method the *free ICI* method. In principle, the free ICI method converges faster than the ordinary ICI method. The functions $\{\phi_i\}^{(n)}$ may be called *complement functions* because they are the components of the complete functions that are guaranteed to express the exact wave function at convergence (complete ICI). Thus, ICI here is an abbreviation of *independent complements interaction*.

The free ICI method thus gives an analytical function having the structure of the exact wave function with unknown coefficients [Eq. 14]. It has some merits over the conventional ICI [e.g. Eq. 13]. One is the faster convergence. Second, each iteration is independent, i.e., does not depend on the results of the former iterations. This means no accumulation of errors and further means that you can start from your desired iteration step of a desired accuracy. Third, in the free ICI method, the g function can be chosen more freely. Even if some divergent functions are generated due to some limited choice of g, you just throw out such divergent functions and keep your ψ to satisfy the Q-condition.

Thus, we have established a general method of constructing an analytical function that has the structure of the exact wave function with linear unknown coefficients. When these unknown coefficients are determined by some appropriate method, the free ICI function is guaranteed to become the solution of the SE. You can make it as accurate as you desire by increasing the iteration number.

Now, how do we calculate these unknown coefficients? One is to use the variational principle by calculating the necessary integrals. In the present formalism based on the SSE, the singularity problem does not occur. Though differentiations are always possible, integrations are not always possible. For this reason, the choice of the g-function is not completely free, if one wants to do analytical integration. When analytical integration is difficult, one may use the Monte Carlo integration method. However, it is generally difficult to get highly accurate integrals through the Monte Carlo integration method. Nevertheless, for most problems, chemical accuracy is the accuracy to be required, which is not difficult even with the Monte Carlo integration method.

In the field of quantum Monte Carlo, various methods have already been developed. In particular, in the variational Monte Carlo, the largest problem was the lack of a theory that provides an accurate trial function that is guaranteed to have the structure of the exact wave function.[163] Now, the free ICI method provides one to an arbitrary accuracy: you can jump into large n in the free ICI to get trial functions of high accuracy. For general applications of the present theory to molecules without symmetry, a Monte Carlo type method would be a good choice and such methodologies are under development in our laboratory.

Now a few words about the excited states. As easily understood, the ICI process generates the basis functions not only for the ground state but also for the excited states of the same symmetry. Since we usually start from ψ_0 that approximate the ground state, the ICI process simulates first the ground state, but at the same time, it generates the basis functions appropriate for the excited states. Thus, the second higher-energy solution is an approximation to the first excited state. For getting fast convergence, you may include in ψ_0 the functions that mimic the excited states as well as the ground state.

Calculation of the Analytical Solutions of the SE. The ICI method has been applied to calculate both full CI solutions[7,161] and analytical solutions[8,164–168] of the SE. The former examples were given above in Figs. 1 and 2. Since the analytical solutions are far more accurate than the full CI solutions, our major concern here is how efficiently our ICI method gives the analytical solution of the SE. We have already performed the applications quite successfully to hydrogen atom,[8] helium atom,[8,164] hydrogen molecule,[8,165] Hooke's two-particle atoms,[166] lithium, beryllium, and boron atoms,[167] and HeH$^+$,[168] and others. The results are superior or comparable to the already existing best analytical solutions for these systems, showing the accuracy and the usefulness of the ICI method for the analytical solutions of the SE. Among these, we give here a brief account of the results obtained for the helium atom and the hydrogen molecule.

Table 1 shows the free ICI result for the helium atom. The g factor is $g = 1/\nu_{ne}\nu_{ee}$ and $\psi_0 = \exp(-\alpha s)$ with $s = r_1 + r_2$. The exponent α was optimized at each n. As n increases, the energy decreases. Since ICI is variational at each n, the energy decreases monotonically and approaches the exact value[169] from above. The chemical accuracy, milli-hartree accuracy, is obtained at the second iteration with 26 independent functions. The energy becomes exact up to 9 decimal figures at $n = 7$. The wave function generated automatically by the ICI method is different from the existing one. It is similar to the Hylleraas functions[170] but includes both positive and negative powers of s (in Hylleraas functions, only positive powers of s were included). It is in some sense similar to the Kinoshita function,[171] but different in details. This negative power terms are important for a rapid convergence.

We have examined different choices of the g factor and ψ_0 (the result of Table 1 is due to the simplest choice). Table 2 shows the result of the free ICI calculations with $g = 1 - 1/\nu_{ne} + 1/\nu_{ee}$ and $\psi_0 = (1 + s^{1/2} + u^{1/2})\exp(-\alpha s)$. With this refined choice, the convergence rate is faster and at the 8th iteration the energy agrees to the best Schwartz result[169] up to

Table 1. Free ICI Energy of Helium Atom[a]

Iteration, n	M_n[b]	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
7	738	−2.903 724 377	(2.68)
Best value[b]		−2.903 724 377	

a) $g = \frac{1}{\nu_N}\frac{1}{\nu_e}$ and $\psi_0 = \exp(-\alpha s)$. b) Number of independent functions. c) Ref. 169.

18 decimal figures. You can get as accurate a result as you desire by increasing n. The convergence rate is dependent on the choice of g function and ψ_0, and more detailed examinations will be given elsewhere in the literature.[164]

Table 3 is a summary of the free ICI result for the hydrogen molecule.[165] The ψ_0 is chosen to be $\psi_0 = \exp[-\alpha(\lambda_1 + \lambda_2)](\sum_{i=0}^{\max i} \rho^i)$, where $\lambda_i = (r_{iA} + r_{iB})/R$ and $\rho = r_{12}$. The internuclear distance R is 1.4011 au and $\alpha = 1.1$. The g function

was chosen as $g = 1 - 1/V_1 - 1/V_2 + 1/V_{12}$, where V_i is the nuclear electron attraction potential for electron i and V_{12} is the electron repulsion potential. We see from Table 3 that even from different ψ_0's we will get similar converged energy values by the ICI method. The chemical accuracy is obtained after two or three iterations. The energy shown at the bottom of Table 3 is the best value, in the variational sense, so far obtained in the literature.[172]

Table 4 shows the history of the hydrogen molecule wave function. The present best result shown in Table 3 is given at the bottom of the table. It is comparable with and probably lower than the result obtained by Cencek and Rychlewski using Gaussian functions.[172] Table 4 also shows the historical result of James and Coolidge,[173] the full-CI result with extended basis,[174] and the landmark result[175] of Kolos and Wolniewicz studies.[176] The Hartree–Fock result is also cited for reference.[177] We note again that the wave functions generated by the ICI method were different from those existing in the literature, like those of James and Coolidge[173] and Kolos and Wolniewicz.[175,176] This is an origin of the efficiency of the present free ICI method. More details will be described elsewhere in the literature.[165]

Based on the above results for helium and hydrogen molecule and some results not given here, we can conclude that the method of solving the SE in an analytical form is now

Table 2. Free ICI Energy of Helium Atom[a]

Iteration	Dimension	Energy[b]/au
0	3	−2.890 468 719 627
1	18	−2.903 711 336 015
2	74	−2.903 724 340 354
3	186	−2.903 724 376 978
4	377	−2.903 724 377 033 224
5	668	−2.903 724 377 034 108
6	1080	−2.903 724 377 034 119 316
7	1634	−2.903 724 377 034 119 587 358
8	2351	−2.903 724 377 034 119 597 725

a) $g = 1 - \frac{1}{V_N} + \frac{1}{V_e}$, $\psi_0 = (1 + s^{1/2} + u^{1/2})\exp(-\alpha s)$. b) Best value by Schwartz[169] (dimension, 10257): −2.903 724 377 034 119 598 311.

Table 3. Free ICI Energy of Hydrogen Molecule with Different Initial Functions ($R = 1.4011$ au)

Initial function max i	Number of iteration (n)	Number of functions	Energy/au
0	1	5	−1.164 409 776 802 47
	2	30	−1.172 712 604 472 60
	3	114	−1.174 434 056 534 60
	4	343	−1.174 475 391 331 89
	5	832	−1.174 475 917 716 33
	6	1788	−1.174 475 930 732 94
	Best value		−1.174 475 931 397 74
4	1	33	−1.173 489 787 488 80
	2	260	−1.174 475 797 933 38
	3	951	−1.174 475 931 085 68
	4	2441	−1.174 475 931 391 16
	Best value		−1.174 475 931 397 74
5	1	41	−1.173 497 602 544 99
	2	346	−1.174 475 872 960 00
	3	1276	−1.174 475 931 318 44
	4	3246	−1.174 475 931 397 74
	Best value		−1.174 475 931 397 74

Table 4. History of Hydrogen Molecule Wave Function

Type of wave function	Reference	H–H distance/au	Total energy/au
Hartree–Fock	Sundholm[a]	1.4	−1.133 629 573
Full CI (30s29p12d9f)	Röhse et al.[b]	1.4	−1.174 285
Hylleraas type	James–Coolidge[c]	1.4	−1.173 539[f]
Hylleraas type	Wolniewicz[d]	1.4011	−1.174 475 930 742
Gaussian functions	Cencek–Rychlewski[e]	1.4011	−1.174 475 931 39
Free ICI (extended Hylleraas type)	Present	1.4011	−1.174 475 931 397 74

a) Ref. 177. b) Ref. 174. c) Ref. 173. d) Ref. 175. e) Ref. 172. f) Recalculated by the present author.

established. The free ICI method seems to be remarkably efficient. We have many prospects for works to be done in the future and we are essentially very optimistic about them.

SAC-CI Method Applied to Photochemistry and Photobiology

The SAC/SAC-CI theory itself is exact and yet very simple, so that it compactly describes the physics of the electronic structure of the ground and excited states of molecules. It has the following merits.

1. The ground and excited states calculated by the SAC/SAC-CI theory satisfy the orthogonality and the Hamiltonian-orthogonality to each other, which are the important necessary requirements for any theory dealing with different electronic states at the same time.

2. The theory satisfies size-extensivity and size-intensivity requirements that are important when theories are applied to large molecular systems.

3. The theory satisfies the self-consistency requirement that is important to avoid depending on the choice of the reference functions, which are usually Hartree–Fock.

4. It describes not only one-electron excited states from the ground state, but also multi-electron excited states like those appearing as satellite states in ionization spectra.[13]

5. This theory covers a very wide range of different electronic states, from singlet to septet spin multiplicities, with the same good accuracy. Conceptually, the theory utilizes an approximate transferability of electron correlations between ground and excited states. Figure 3 shows the states that can be studied by the SAC-CI code in Gaussian03 program.[36] It covers ground, excited, ionized, and electron-attached states of valence, Rydberg, inner-valence, and inner-core states.

6. We can directly compare the energies and the properties of different electronic states. This is a very important merit of the SAC/SAC-CI method and is very useful in actual chemical studies.

7. The energy-gradients, which are the forces acting on the constituent nuclei, can be calculated for any states shown in Fig. 3 for both one- and multi-electron excited states.[29–35] Using these quantities, we can also do geometry optimizations for any of these states.

8. Chemistry and physics are investigated with the same methodology from fine accurate calculations of small molecules to less accurate but reliable calculations of large molecules and molecular systems. The SAC-CI method has been useful for studying fine spectroscopy of molecules, for studying many different electronic states of different natures and qualities at the same time, like those appearing in molecules including transition metals and in the spectra of wide energy range. It has also been useful for studying relatively large molecules like those appearing in the photo-electronic processes in biological systems.

9. In combination with the dipped adcluster model, which is a model for the catalysis and the adsorbate on a metal surface, we can study catalytic reactions of the adsorbates on a metal surface and the surface photochemistry.

Theories of the SAC and SAC-CI methods were explained in some detail in the original papers[9–14] and the earlier review papers.[22–27] Here, I will focus only on some recent applications to the fine spectroscopy and the electronic processes in the photosynthetic reaction center of *Rhodopseudomonus viridis*.

When one studies electronic states in a wide energy range, one finds that they involve not only one-electron excited states but also multi-electron processes like shake-up states in ionization spectroscopy, which are generated by simultaneous ionization–excitation processes. In 1991, the author showed that the SAC-CI theory is able to describe such excitation and ionization processes very accurately when not only singles and doubles (SD) but also higher excitation operators are included in the linked operators of the SAC-CI method.[13] This method was called SAC-CI general-R method in comparison with the SAC-CI SD-R method. This generalization was done actually as a by-product in the generalizations of the SAC-CI method to quasi-degenerate and multi-reference electronic states.[16–21] The SAC-CI general-R method enables us to calculate excitation and ionization spectra over a wide energy region with high accuracy; the method opened a new field called theoretical fine spectroscopy.

Figure 4 shows the photoelectron spectrum of HCl in valence and inner-valence energy region (10–35 eV).[73] The peaks in the outer-valence region are essentially due to the Koopmans one-electron process, but in the inner-valence region the peaks are due to the shake-up processes, i.e., the simultaneous ionization–excitation processes. So, the number of the peaks is larger than the number of the molecular orbitals. In order to describe these photo-electron processes, the theory must be able to describe both one-electron and multi-electron processes with the same good accuracy. The SAC-CI general-R method can do this and gives a theoretical spectrum which is almost indistinguishable from the experimental spectrum[178] as shown in Fig. 4.

Figure 5 shows the inner-valence ionization spectrum of H_2S. The experimental spectrum is due to Brion et al.[179] and the theoretical one is due to Ehara et al.[75] The experimentalists attributed seven peaks in this energy region, while the theorists obtained much more peaks by the SAC-CI method. Actually, due to the SAC-CI general-R calculations, there existed a much larger number of states in the inner-valence energy region than those shown in the spectrum but they did not have intensities that were high enough to be written down. Howev-

SAC/SAC-CI program

Accurate correlation theory for ground and exited states

SAC   singlet closed-shell (ground state)

SAC-CI
— singlet excited states
— triplet ground & excited states
— ionized states (doublet ground & excited states)
— electron-attached states
           (doublet ground & excited states)
— quartet to septet ground & excited states

Energy Gradient (Force acting on nuclei)
Dynamics involving ground and excited states

Subject: Chemistry and Physics involving these states
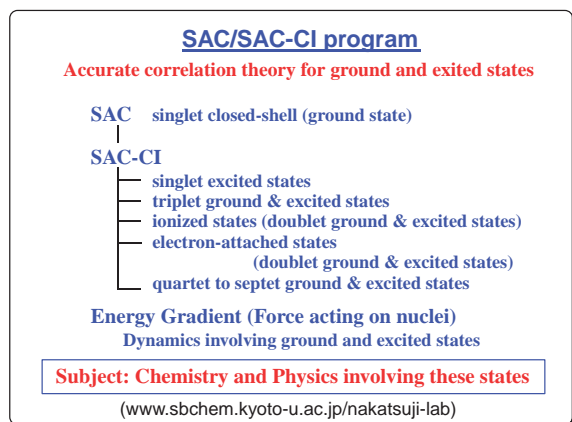
(www.sbchem.kyoto-u.ac.jp/nakatsuji-lab)
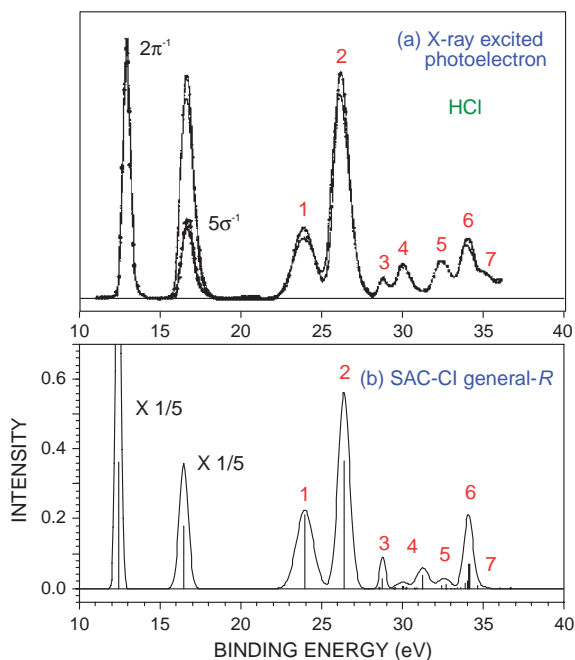
Fig. 3. Chemistry and physics covered by the SAC-CI program on Gaussian03.

Fig. 4. HCl photoelectron spectra (experimental spectrum from Ref. 178 and theoretical SAC-CI spectrum from Ref. 73).

Fig. 5. Inner-valence ionization spectra of H_2S (experimental spectrum from Ref. 179 and SAC-CI theoretical spectrum from Ref. 75).

er, these states are expected to play important roles in the energy-relaxation processes and other dynamic processes in this energy region. Note that the experimental and theoretical spectra are again quite similar showing the reliability and usefulness of the SAC-CI method. If necessary, you can calculate, for example, the equilibrium geometries of these two-electron states by the SAC-CI program.

The accuracy and the reliability of the SAC-CI method illustrated above are examples from theoretical fine spectroscopy. This field is now being developed intensively in our laboratory mainly by Prof. M. Ehara. In collaborations with experimentalists, entirely new dimensions of spectroscopy are being developed that were impossible in the past. Entirely new fields of spectroscopy are being opened with the aids of the very advanced spectroscopic tools and of the simultaneous use of the SAC-CI method for the analyses and understanding of the natures of the spectra.

The energy-gradient method is a useful tool for studying molecular geometries and chemical reactions. The energy gradients are the forces acting on the constituent nuclei of the system. The nuclei of the system move toward these forces and reach the equilibrium geometry or the product of the chemical reaction. This author presented a simple, intuitive force concept for molecular geometries and reactions, called electrostatic (Hellmann–Feynman) force theory (ESF theory).[180–183] This theory is very predictive and works better than the Walsh model[184] and the VSEPR theory.[185] Based on this concept, we understand that the electron-cloud flow is the cause of the chemical reaction, a systematic movement of the nuclear coordinates, which the author called electron-cloud preceding.[182,183] When we can calculate these forces for every state of the ground, excited, ionized, and electron-attached states of singlet to septet spin-multiplicities of one- and many-electron proc-
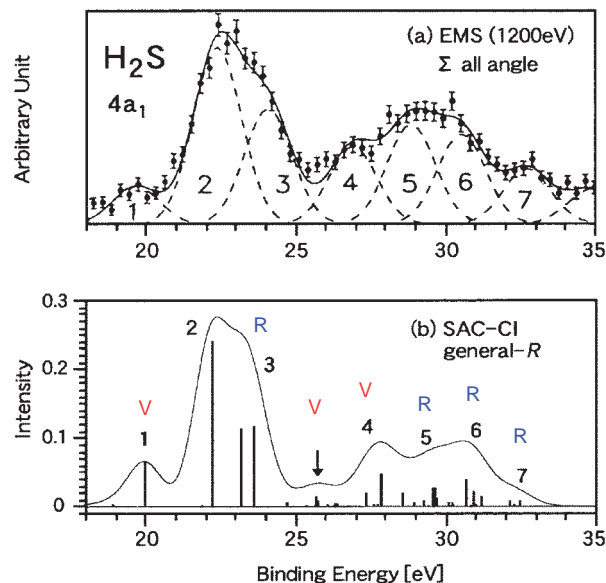
esses, we can certainly do a lot of chemistry. The Gaussian03 SAC-CI program can do this.[36]

Acetylene is a simple molecule whose geometries are observed not only for the one-electron excited state (A state) but also for the two-electron excited state (C state).[186] We have applied the SAC-CI geometry-optimization method to this molecule and obtained the result shown in Table 5.[35] The geometries of the excited states are trans, in contrast to being linear in the ground state. We have applied both SD-R and general-R SAC-CI methods to the excited states. We see from Table 5 that the geometries of all the ground and excited states are rather well reproduced by both SD-R and general-R methods, but the adiabatic excitation energy of the two-electron excited state (C state) is calculated correctly only by the general-R method: the SD-R result differs by as much as 2.3 eV from the experimental value. For the one-electron excited state (A state), both SD-R and general-R methods give reasonable agreement with the experiment.

Free base porphin (FBP) is a key compound in biological chemistry and its excited states appear in many photo-biological processes, like photosynthesis. The SAC-CI method has successfully been applied to the spectroscopy of many porphyrins, hemes, and related compounds, showing its applicability to biologically oriented photochemistry.[82–92] Recently, we have performed the geometry optimization of FBP in its ground and excited states using the SAC-CI method[93] and found that the changes in the geometrical parameters under the excitations are very small. The structural relaxation energies in the excited states were also very small. These properties of porphyrins are merits when the molecules are used as photofunctional compounds in biological systems.[93]

Photo-electronic processes in biology are very attractive field that may be elucidated by the SAC-CI method. Photosynthesis is one of the most attractive phenomena since it constitutes the basis of the existence of life on this globe. After confirming that the SAC-CI theory was able to describe the photo-

Table 5. Spectroscopic Constants of the Ground and Excited States of Acetylene[35]

State	Method	Excitation level	R_{CH} /Å	R_{CC} /Å	θ_{CCH} /degree	T_e /eV
X^1A_g	SAC	—	1.068	1.219	180	—
(linear)	Exptl.[a]		1.063	1.203	180	—
A^1A_u	SD-R	1	1.098	1.377	122.6	5.485
(trans)	General-R	1	1.097	1.385	121.7	5.329
	Exptl.[a]		1.097	1.375	122.5	5.232
C'^1A_g	SD-R	2	1.105	1.634	103.8	10.098
(trans)	General-R	2	1.111	1.643	103.0	7.844
	Exptl.[a]		1.14	1.65	103	7.723

a) Ref. 184.

chemistry of porphyrins,[82–93] we studied the photo-electron processes involved in the photosynthesis in a photosynthetic bacteria, *Rhodopseudomonus viridis*.[94–100] The crystalline structure of the reaction center of this bacteria was already known.[187] The absorption spectra of the reaction center as a whole were observed by Breton[188] but were not assigned by any reliable theory. So, we applied our SAC-CI theory. The photon-energy-assisted long-distance electron transfer couples with the proton transfer in the reaction center and thus the photon energy accumulates as a concentration difference of protons on the two sides of the membrane. The electron transfer pathway in the reaction center was already known to be very efficient and unidirectional, but the reasons were not yet established. We wanted to clarify the reasons of the unidirectionality and effectiveness and the roles of proteins in this photo-electron process.

In the reaction center of *Rhodopseudomonus viridis*, eleven chromophores are involved and the proteins are essentially transparent in the energy region we are interested in. We calculated the absorption spectra of all the chromophores, placing them in the field of proteins and the other chromophores, which were approximated by the electrostatic model putting a point-charge on each atom of protein or chromophore. Figure 6 shows the absorption spectrum and the linear dichroism spectrum of *Rhodopseudomonus viridis* observed experimentally and calculated by the SAC-CI theory. The assignments of the observed peaks were done using both theoretical and experimental information available on that date. This was the first systematic assignment of the spectra with a reliable ab initio theory including electron correlations. The average discrepancy between theory and experiment was 0.13 eV (about 3 kcal/mol). It would constitute a basis for future photochemical studies of the reaction center. For more details, we refer to the original papers and accounts.[94–96]

The rate of electron transfer (ET) is proportional to the square of the transfer integral H_{if} between the initial and the final states of the ET.[189] This factor is called the electronic factor. The nuclear factor involves thermodynamic factors[189] and is therefore more complex to calculate with ab initio theories. We studied the nature of this photon-assisted ET in the reaction center by calculating the electronic factor. Jortner et al.[190] studied the ET using the semi-empirical theory by assuming that the transfer integral was proportional to the overlap between the LU (lowest unoccupied) MO's of the two
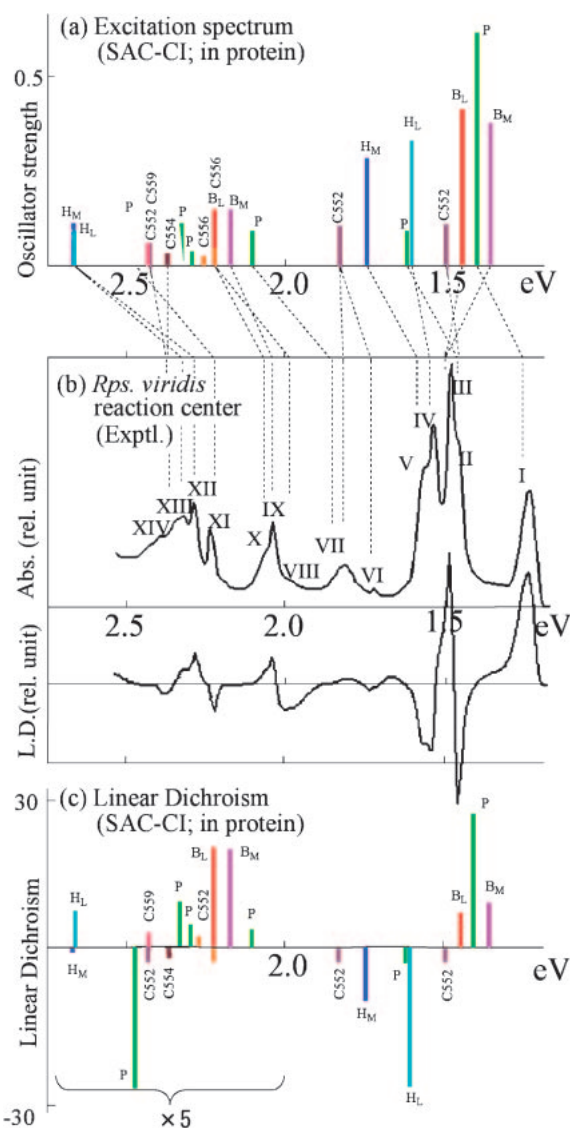

Fig. 6. Absorption and linear dichroism spectra of the photosynthetic reaction center of *Rhodopseudomonus viridis*; (a) SAC-CI theoretical excitation spectrum,[95] (b) experimental absorption and linear dichroism spectra,[188] and (c) SAC-CI theoretical linear dichroism spectrum.[95]
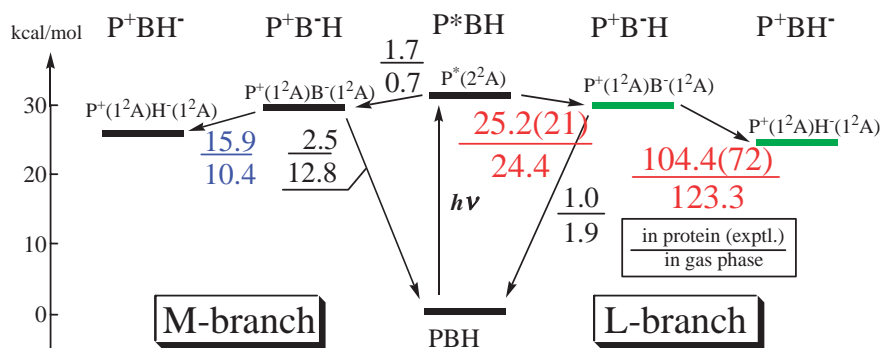
Fig. 7.　Electronic factors for the electron transfers from the special pair (P) to bacteriochlorophyll (B) and to bacteriopheophytin (H) of the photosynthetic reaction center of *Rhodopseudomonus viridis*.

chromophores of the initial and final states. When we calculated the overlap integrals between the LUMO's of the special pair (P) and bacteriochlorophyll (B) with the ab initio methods, the integral was larger for the M-region than for the L-region, in contrast to the actual ET in the L-region. This implies that the ET is not an overlap property: it is a more local property as shown below. We then calculated the transfer integrals of the ET pathways (1) and (2),

$$P^*BH \cdots (1) \dashrightarrow P^+B^-H \cdots (2) \dashrightarrow P^+BH^-, \qquad (A)$$
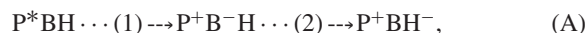
using the SAC-CI wave functions of the excited and ionized states of P, the neutral and anion wave functions of B and the neutral and anion wave functions of bacteriopheophytin (H).[94,97] The results are summarized in Fig. 7.

The rhs of Fig. 7 represents the L-branch and the lhs the M-branch. The first event is the excitation of P giving P*. From P*, the transfer integral to the L-branch B is 25.2 au while to the M-branch B the transfer integral is 1.7 au: the L-branch selectivity is well reproduced. The value in parentheses is the experimentally estimated value[191] and so we see that the theoretical SAC-CI value is in good agreement. The value in the denominator is the SAC-CI value without the protein environment; we can see that the effects of proteins represented by the point-charge model are small. The next step from B to H is again preferable in the L-branch than in the M-branch: no narrow path exists in the next step of the L-branch. Competitive to this path, another pathway is from B to P (from B to P* is up-hill), which is called a charge recombination process. In comparison with the electronic factor from B to H, 104.4 au, the charge recombination process is only 1.0 au, and so is almost forbidden. This is in good agreement with the experimentally known facts. Thus, the SAC-CI method nicely reproduced the experimentally known unidirectionality and the effectiveness of the ET in the reaction center.

Now that the theory has reproduced the experimentally known facts, we can analyze and understand the origin of the phenomena by examining the transfer integrals involved.[94,97] The origin of the L-branch selectivity is attributed to the biological structure of the reaction center. Figure 8 shows the analysis of the transfer integral for the $P^+B^-H \rightarrow P^+BH^-$ process. The center-to-center distance between B and H is almost the same in both the L- and the M-branches. However, the Mulliken bond-order type analysis of the transfer integral showed that the transfer integral between B and H is
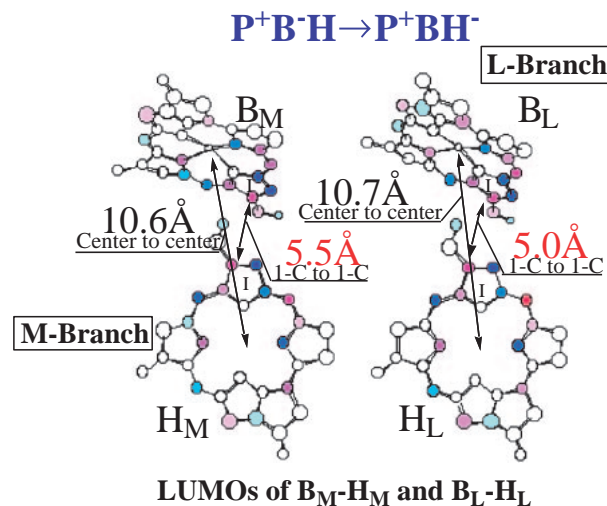

Fig. 8.　LUMO's and the geometries of the B_M–H_M and B_L–H_L that explain the origin of the difference in the electronic factors of the transfer integrals between M and L branches.

mostly due to the single contribution from 1-C of B to 1-C of H and that of the L-branch is much larger than that of the M-branch. The reason is the distance between these atoms: that in the L-branch is 0.5 Å shorter than that of the M-branch. Since the transfer integral depends exponentially on the distance, this 0.5 Å difference causes an order of magnitude difference, as shown in Fig. 8. The ET is a very local phenomenon: it occurs from 1-C of B to 1-C of H and not by face-to-face overlap between the two LUMO's. The same is true for the ET from P*BH to P^+B^-H. Thus, the origin of the L-branch selectivity is attributed to the structural factor.

The origin of the forbidden charge recombination process is attributed to something like the orbital symmetry control.[94,97] Figure 9 explains the origin. The ET from P to B is essentially from the LUMO of P to the LUMO of B, while the back-transfer is from the LUMO of B to the HOMO of P, since the path from the LUMO of B to the LUMO of P is up-hill. As seen from Fig. 9, the LUMO of P_M is localized in the downward ring in the vicinity of B_L, so that the transfer integral between the edge carbon of this ring of P_M and the edge carbon of the neighboring ring of B_L becomes large (this value is much larg-

H. Nakatsuji

Bull. Chem. Soc. Jpn., **78**, No. 10 (2005)   1715

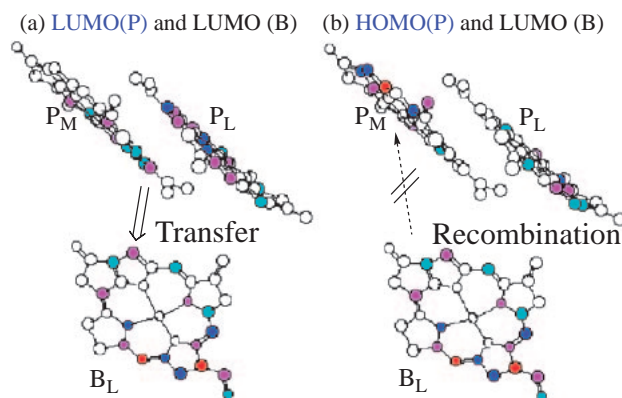(a) LUMO(P) and LUMO (B)   (b) HOMO(P) and LUMO (B)

Fig. 9.   The origin of the forbidden charge recombination process.

er than the corresponding value of the P_L–B_M pair due to the shortness by 0.5 Å, which is the origin of the L-branch selectivity[94,97]). On the other hand, the HOMO of P_M is localized in the region far away from B_L, so that the back-ET from B_L to P_M is difficult. Thus, the charge recombination from B^- to P is ruled out, due to the different localization natures of the HOMO and LUMO of the special pair.

In the ET from P^* to B to H, the protein effect was small, but in the next step of the ETs from H to menaquinone (MQ) and from MQ to ubiquinone (UQ), the protein residues play important roles.[98–100] We sketch here only the important results; for the details you refer to the original papers.[98–100] For the ET from H_L to MQ, the one-bridge mechanism through Trp M250 is important. For the ET from MQ to UQ, the two-bridge mechanism through His M217 and His L190 is by far more important than the other possible pathways.[98]

In *Rhodopseudomonus viridis*, the cytochrome subunit is attached to the reaction center like a cap; an electron is supplied by cytochrome c_2 to this unit and transferred through it to P^+ to neutralize it. The docking site of cytochrome c_2 to this subunit is believed to be close to the top heme c554 and the ET occurs from c554 to P^+. We studied the ET pathway from c554 to P^+.[99] In the cytochrome c unit, four hemes, c554, c556, c552, and c559 are arranged toward P. We calculated the transfer integrals along this pathway, examining the possible roles of the protein residues near the pathway. For the ET from c554 to c559, the ET was shown to be direct and no protein residues were found to play a bridge role. However, for the ET from c559 to P^+, two protein residues were found important. The one-bridge pathway c559–Tyr162–P^+ is most important, but the two-bridge pathway c559–Phe253–Tyr162–P^+ is also important, reducing the transfer integral due to the above one-bridge pathway. The biological implication of such reducing role of the two-bridge pathway c559–Phe253–Tyr162–P^+ is worth studying and the mutation experiment would be interesting.

Figure 10 shows a summary of the ET pathways studied in our laboratory. This study showed a high potentiality of the SAC-CI method in biological photochemistry. There are many important photo-electron processes in biology. Visions due to rhodopsin is another example.[192] This field is now being actively developed in our laboratory, mainly by Dr. Hasegawa.

Before closing this chapter, we note that the SAC-CI world is still expanding vividly in our laboratory. For getting higher efficiency, the direct algorithm currently being developed in our laboratory by Dr. Fukuda is very promising. The SAC-CI applications to truly gigantic systems would soon become possible based on the new framework of the theory now in progress in our laboratory.

Catalytic Reactions on a Metal Surface

Catalysis is one of the most attractive phenomena in chemistry. The reactions that never occur in other conditions smoothly proceed, for example, on metal surfaces. To clarify the origin of this magic is a challenging subject for theoretical chemists. These reactions occur at the interface between finite (adsorbates) and infinite (surface) systems; for the latter, some modeling is necessary for theoretical studies. The model that is most frequently used in theoretical calculations is the cluster model (CM), but this model is not adequate for a metal surface because it does not include the effects of free electrons of the bulk metal that are characteristic to a metal surface. In 1987, the author presented the dipped adcluster model (DAM) for chemisorptions and catalytic reactions on a metal surface.[104] This model is able to include the effects of the free bulk electrons characterizing the metal surface. The admolecule, which is a combined system of the admolecule plus cluster, can easily borrow some electrons from a metal surface and further, the admolecule can be stabilized by the image force exerted from the surface.

Figure 11 explains the concept of the DAM. The adcluster, a combined system of the admolecule and a metal cluster, is dipped onto the electron bath of the free electrons of the metal surface and electron exchange is permitted between the adcluster and the surface. The equilibrium is established when the chemical potential of the admolecule becomes equal to the chemical potential of the metal surface, μ.

$$-\frac{\mathrm{d}E(n)}{\mathrm{d}n} = \mu, \tag{15}$$

where E is the energy of the adcluster and n is the number of electrons and spins transferred into the adcluster. Since the adcluster is an imaginary partial system, the number of the electrons, n need not to be an integer and so we have a quantum chemistry with a non-integer number of electrons. Some interesting physics exists behind the n dependence of the energy E and in the realization of the equilibrium condition. For more details of the DAM, we refer to the original paper and the review article.[104–109]

The DAM has been applied to study O_2 chemisorptions on palladium and silver surfaces,[104,110,111] and to clarify the "harpooning" electron transfer from halogen molecule to alkali-metal surface and the succeeding electron transfer and surface luminescence phenomena.[108,109] It has also been applied to the epoxidation reactions and oxidation reactions of olefins on a silver surface,[121–127] the OH chemisorptions and reactions on an Ag surface,[128] and the hydrogenation reactions of carbon dioxide giving methanol on a Cu/Zn surface,[129–131] where the promoting effect of Zn was studied in some detail. The DAM has also been used, in combination with the SAC-CI method, for studying the spectroscopy of the molecules adsorbed on a metal surface.[107–113] Without the DAM, the large
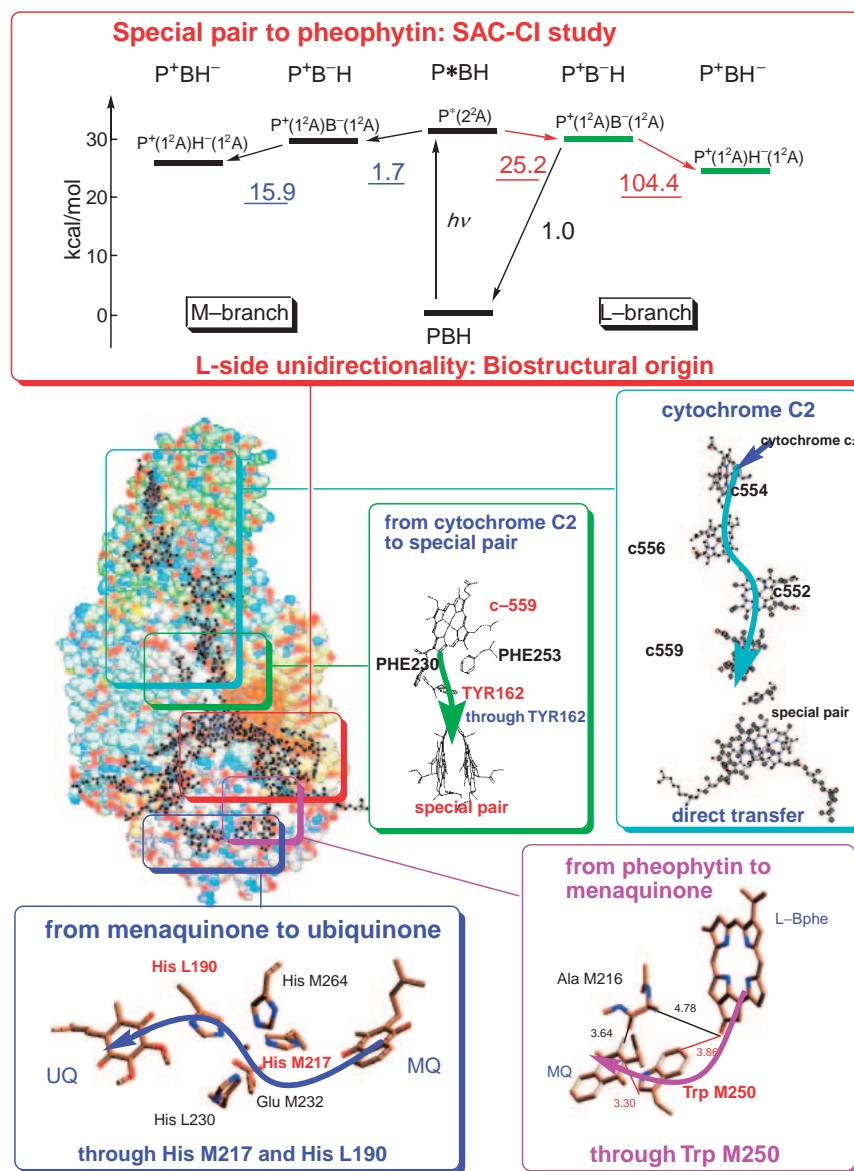
Electron transfer route in the reaction center

Fig. 10.   Summary of the electron-transfer pathway in the photosynthetic reaction center of *Rhodopseudomonus viridis*.
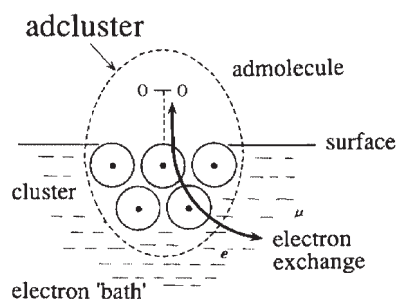
Dipped Adcluster Model (DAM)

Fig. 11.   Concept of the dipped adcluster model (DAM).

lower-energy shifts of the peaks in the UV and photoelectron spectra of the adsorbed molecules from those of the gas-phase were not explained,[113] to be able to explain such shifts may be

considered as an experimental justification of the DAM. An approach that combines the experimental surface spectroscopic measurements and the theoretical DAM/SAC-CI method would become a useful methodology for identifying the species adsorbed on a metal surface: the experimental results alone are insufficient for doing this identification.

Here, we only briefly review the DAM studies of the partial oxidations of olefins.[121–127] Ethylene is epoxidized on a silver surface to give ethylene oxide with a selectivity of about 85%.[193] We studied two reaction modes, one being an attack of ethylene to molecular superoxide O_2^- on a silver surface and the other being an attack to atomic oxygen O^- on a silver surface. Since the former reaction seemed to be the main reaction course, we explain only this course here. Figure 12 shows the effect of the silver surface, i.e., the energy diagram for the reactions with and without the silver surface. Figure 13 shows
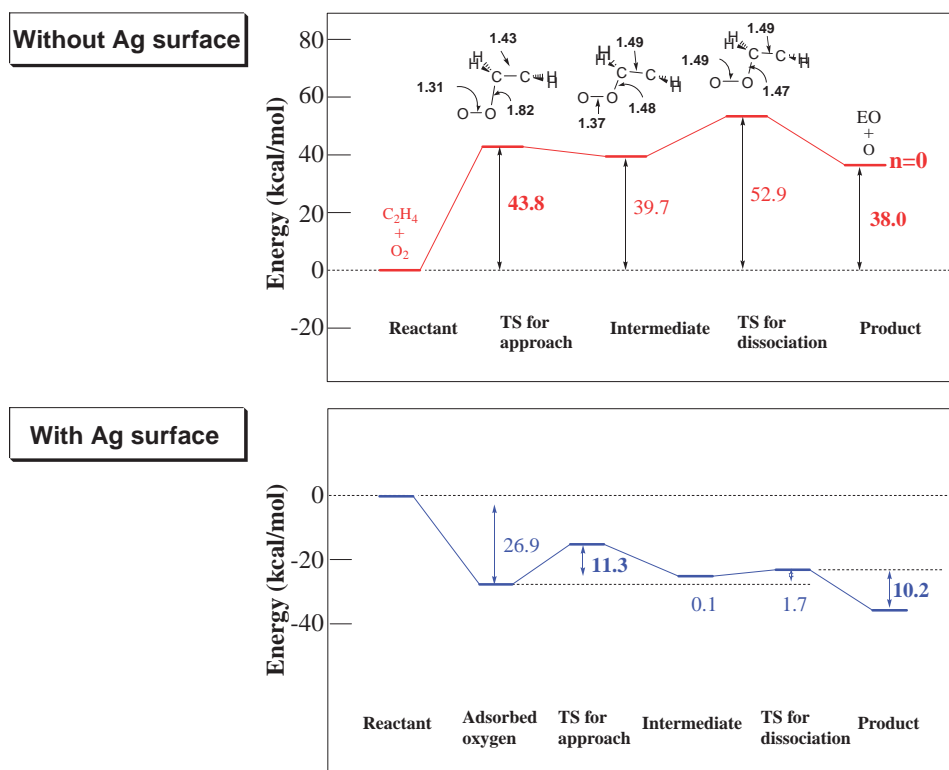
Fig. 12.   Energy diagram showing the effect of the silver surface for the epoxidation of ethylene.
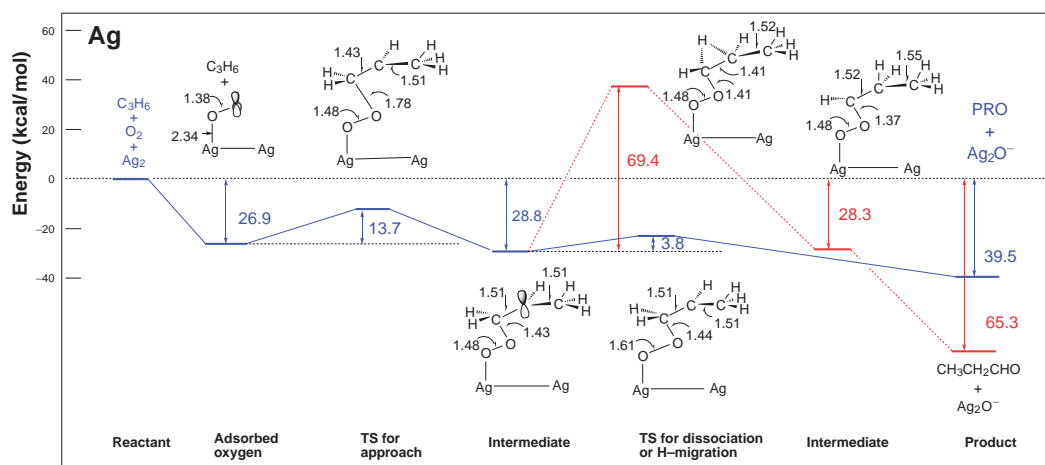

Fig. 13.   Energy diagram, the reaction intermediates, the transition states, and the products along the course of the ethylene epoxidation reaction on a silver surface.

the more detailed energy diagram, the reaction intermediates, the transition states, and the products along the course of the oxidation reaction on a silver surface.

From Fig. 12, you immediately see how large the effect of the silver surface is. Without silver, the barrier of the reaction is too high. Figure 13 shows two reaction courses, one leading to epoxide and the other leading to acetaldehyde, which leads further to a complete oxidization. Two pathways branch from the intermediate adduct. Only the pathway leading to the epoxide is energetically feasible. The barrier to acetaldehyde intermediate is high (71.5 kcal/mol), and therefore this course is forbidden. Thus, the DAM explains the catalytic activity of the silver surface and the selectivity towards the epoxide.

The atomic oxygen on a silver surface was shown to be less selective. The molecular superoxide O_2^- is an active species of epoxidation on a silver surface.

When we replace ethylene with propylene, the selectivity of the epoxidation reaction is much reduced: from 85% to only 2.5%.[194] Most propylene is converted up to complete oxidation. So, the catalysis design leading to propylene oxide is of much practical merit. Figure 14 shows the reaction energy diagram for propylene calculated in a similar way to Fig. 13 for ethylene.[121] You see in Fig. 14 that there are certainly two similar routes leading to propylene oxide and aldehyde, the latter route being energetically forbidden due to its high energy barrier. However, for propylene, there is another route that starts
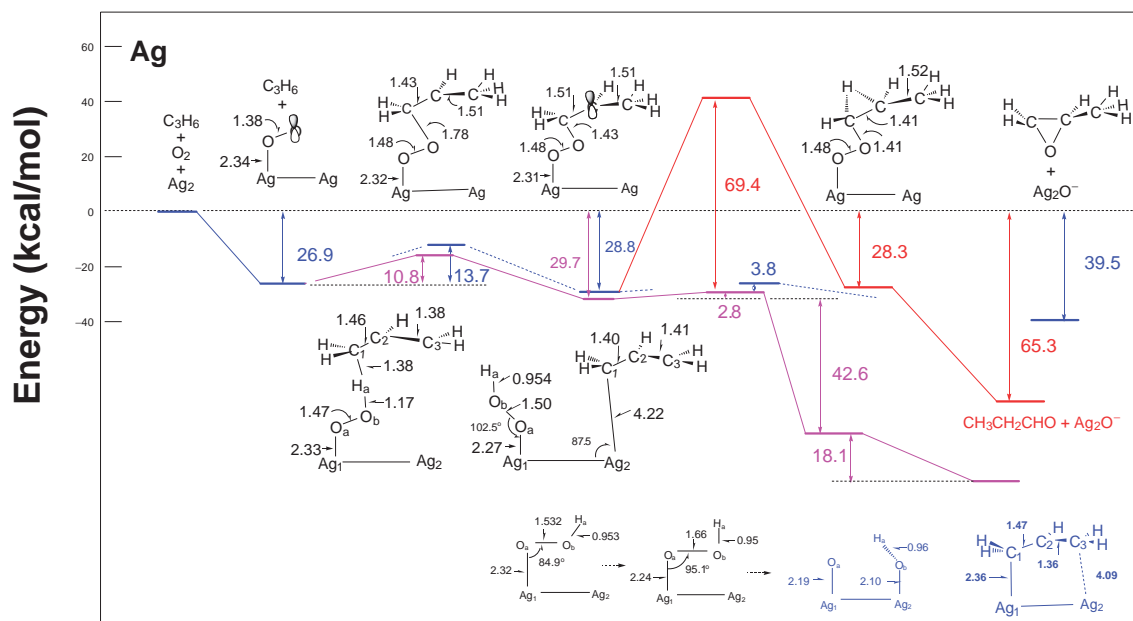
Fig. 14.   Energy diagram, the reaction intermediates, the transition states, and the products along the course of the propylene epoxidation reaction on a silver surface.

from an attack of superoxide to a proton of methyl group that is absent in ethylene. You see that this additional route is also very smooth and lies just below the epoxidation route; in the last stage, this additional route is much more favorable than the other routes and it finally leads to complete oxidation of propylene. Therefore, without any particular artifice, the epoxidation of propylene is difficult with the silver catalysis. However, since we know from Fig. 14 that there is certainly the path on the silver surface leading to propylene oxide, it would be nice if we could invent an artifice to block the route involving the attack of superoxide to the hydrogen of methyl group. Actually, if such hydrogens do not exist, as is the case in styrene, the epoxidation reaction occurs smoothly, like it does for ethylene.

The electronic structures and the reactions of the surface adsorbates are quite interesting subjects that are of importance from both scientific and industrial points of view. However, studies with only experimental means are rather difficult in this field and so the collaborations between theory and experiment would be very desirable for getting deeper understanding of the surface phenomena.

Relativistic Quantum Chemistry and the Electronic Theory of NMR Chemical Shifts

Relativity becomes more and more important as the system involves heavier elements. The effects are of particular importance for the molecules in an external magnetic field and so are reflected sensitively in the NMR chemical shifts of molecules when they includes heavy elements in the neighborhood of the resonant nuclei. When molecules do not include heavy elements, the relativistic effects are small and the chemical shifts are expressed by a sum of the diamagnetic term and paramagnetic term. The former is dependent basically only on the molecular geometry and the nuclear species involved. The variety of NMR chemical shifts is mainly caused by the paramagnetic term.

Since 1984, we have studied the electronic mechanisms of the NMR chemical shifts for various resonant nuclei on the periodic table.[132–154] Since chemical shift is a local property of valence electrons near the resonant nuclei,[132] the primary mechanism of the chemical shift is an atomic property that is dependent solely on the position of the element in the periodic table.[138] A detailed account of the electronic mechanism of the chemical shift was given in Refs. 132 and 138. It may be briefly summarized as follows. Since the NMR chemical shift is a measure of the angular momentum of electrons induced around the resonant nuclei by the external magnetic field, the p- and d-electronic structure of the resonant nuclei in the molecule is the central issue. (An s-electron does not have angular momentum.) To rotate, a p-electron has to move from say p_x to p_y (rotation within xy plane) and this rotation is expressed in the paramagnetic term by the excitation of an electron from the p_x-dominant occupied MO i (whose coefficient is C_{xi}) to the p_y-dominant unoccupied MO a (whose coefficient is C_{ya}^*), so that the strength of this rotation is proportional to the density of this transition, say $C_{xi}C_{ya}^*$ and the facility of this rotation is inversely dependent on the excitation energy of this transition $\Delta E_{i \to a}$.

The chemical shifts of the d^n metal complexes, Ti, Nb, Mo, and Mn complexes, are due to the d–d* mechanism. Both the higher-occupied and the lower-unoccupied MO's of these complexes are characterized by the metal d orbitals and the rotation induced by the external magnetic field is expressed by a transition from the occupied d orbital to the unoccupied d orbital. The facility of the rotation (or transition) would be inversely proportional to the excitation energy of the magnetically allowed transitions. We have actually calculated the magnetically allowed d–d* transition energies of several Mo complexes by the SAC-CI method and found a beautiful linearity between the observed chemical shifts and the inverses of the

transition energies.[134,135]

The chemical shifts of the Cu, Ag, Zn, and Cd complexes are due to the d-hole and p-electron mechanisms.[58] These elements have d^{10} s^{1-2} p^0 configurations. The chemical bonds between metal and ligands are mainly due to the s-electrons. However, since an s electron has no angular momentum, the induced angular momentum must come from d- and/or p-electrons. For the Cu complexes, the d–s level spacing is smaller than the s–p one, so that the d-orbital can more easily participate in the chemical bond than the p-orbital. Therefore, as the ligand is electron-withdrawing, the chemical shift increases, because the hole produced in the d-shell gives rise to the angular momentum. We call this d-hole mechanism. For the Cd and Zn complexes, the s–p level spacing is smaller than the d–s one, so that the p-orbital can more easily participate in the bond than the d-orbital. Therefore, the chemical shift increases as the ligand is more electron-donating, since the number of p-electrons near the metal increases. We call this mechanism p-electron mechanism. Note that between the d-hole and p-electron mechanisms, the ligand-electronegativity dependence of the chemical shift is reversed. For Ag complexes, the s–p and d–s spacings are close, so the p-electron and d-hole mechanisms are competitive: the behaviors of the Ag chemical shifts are more complex than those in the other cases.

The Ga and In complexes are interesting examples where the chemical shifts are mainly governed by the diamagnetic term: the chemical shifts are dependent solely on the molecular structure of the complexes, like the metal–ligand distances and ligand nuclear charges.[139,145] These elements have s^2p^1 configuration. The metal p-electron is usually withdrawn almost completely to the ligand sites, because the ligands are usually more electronegative than the Ga and In metals. Therefore, only the s-electrons are left near the metal atoms but the s-electrons have no angular momentum and therefore the paramagnetic term is small. So, for the Ga and In complexes, the chemical shifts are due to the dia-mechanism.

We have investigated the mechanism of the chemical shifts for a variety of metal complexes and found that the primary mechanism of the chemical shift is an intrinsic property of the central resonant metal atom itself and therefore can be understood from the position of the element on the periodic table.[132–142] However, this is not the case when we examine the chemical shift induced by the halogen ligands. We have two different dependences: normal halogen dependence and inverse halogen dependence. The above (non-relativistic) study could explain the inverse halogen dependence, but not the normal one. There were many examples of the normal dependence, but the origin was not clear until we showed it to be due to the relativistic effect.[143]

Figure 15 shows the proton NMR chemical shifts of the hydrogen halides. It shows a typical normal halogen dependence.[143] When we calculate it by non-relativistic theory, we get a dot result: we get essentially no chemical shift by changing the halogen from a light one to a heavy one. However, when we calculate it with the relativistic method, which we invented by modifying the UHF method,[143] we could very nicely reproduce the observed trends—normal halogen dependence. Thus, the proton chemical shifts in HX series are entirely due to the relativistic effect. This proton NMR experiment
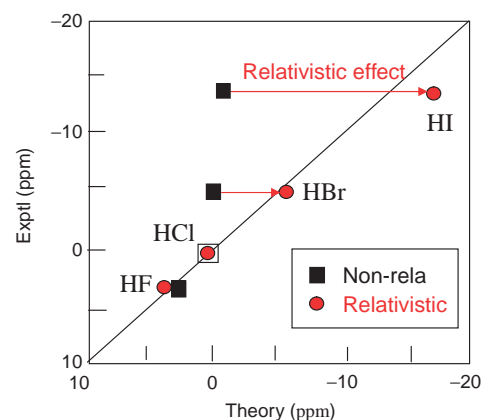

Fig. 15. Importance of the relativistic effect on the proton NMR chemical shifts of the hydrogen halides.

actually observes a relativistic effect! Among the relativistic effects, the spin-orbit effect was most important.

A similar importance of a relativistic effect, spin-orbit effect among others, was observed in many ab-initio theoretical calculations published from our laboratory,[143–154] and now it is generally accepted that the normal halogen dependence is due to the relativistic effect, though the inverse halogen dependence is understood mainly from the electronegativity of the ligand.

Among the relativistic effects, the spin-orbit effect of the directly bonded heavy elements was most important for the chemical shifts of the relatively light nuclei. However, for the chemical shift of heavy resonant nuclei, like mercury and lead, other spin-free relativistic effects were also very important, the correlation effects were also shown to be very important and furthermore, the couplings between these effects were also very important.[148,149,151–154] Therefore, when we calculate the chemical shifts of heavy resonant nuclei, we have to include all the relativistic effects and the correlation effects at the same time. For this purpose, we have developed a straightforward method: first we solve the four-component Dirac–Fock equation and then solve the coupled-cluster equation based on the Dirac–Fock solution.[154] However, at this moment, the computer time and the required memory are too large to perform calculations for heavier resonant nuclei with the use of satisfactorily large basis sets. We then have also developed two-component Douglass–Kroll–Hess transformation for magnetic shielding calculations.[152,153] Then, we may use less computationally demanding electron-correlation method like Møller–Plesset perturbation method. Such a combination is certainly practical at this moment, though the more straightforward method described above will certainly become orthodox in the near future. It is important to open a new field in relativistic quantum chemistry.

Summary

Quantum principles in chemistry give us a basis of imagination for understanding this wonderful world. The author has tried to describe some branches of chemistry in terms of the concepts of the quantum mechanics. When he started quantum chemistry, the excited states were something very difficult to calculate by the quantum chemical method. The SAC-CI theo-

ry he introduced certainly has made it much easier. It has realized the quantum chemistry involving a variety of electronic states, singlet to septet ground and excited states, ionized states and electron-attached states. The energy-gradient technique has made this method even more useful. It has opened new fields like theoretical fine spectroscopy and biological photochemistry. Through the use of the SAC-CI code in the Gaussian suit of programs, this theory would provide a useful method to solve chemical and physical problems in science and industry worldwide.

The magic of catalysis on a metal surface has stimulated the author's imagination and brought about a model, called dipped adcluster model (DAM) of the adsorbate on a metal surface, including the roles of the free electrons characteristic to the metals. The DAM has been useful to describe electronic structures of the adsorbates on a metal surface, so that it was useful for studying catalytic reactions, electron transfers, and photoelectronic processes on a metal surface. It will provide a useful theoretical spectroscopic tool for identifying surface adsorbates on metal surfaces by combining it with the SAC-CI method.

The NMR chemical shifts are probably the most frequently observed properties of molecules in analytical chemistry. The author showed that these quantities include rich chemistry reflecting fine information about the valence electrons of molecules. He clarified the origins of the trends observed in the NMR chemical shifts of various resonant nuclei and showed that the principal mechanism of the chemical shifts is an intrinsic electronic property of the resonant atom itself and therefore can be understood from the position of the element on the periodic table. Further, when the element is connected with heavy elements, the NMR chemical shift is shown to be influenced very sensitively by their relativistic effects. For example, the proton chemical shift of the hydrogen halide series was shown to be due entirely to the relativistic effect, in particular the spin-orbit effect, of the heavier halogens. The normal halogen dependence was attributed to the relativistic effect. For heavy element NMR, both spin-dependent and spin-free relativistic effects are important, the electron correlation effects are also important, and further, they strongly couple with each other, making its chemistry rich, though the calculations are rather complex and time consuming. This suggests the existence of something very interesting in the chemistry of heavy elements.

Doing theoretical chemistry, the author has felt more and more strongly the importance of developing a general theory of solving the Schrödinger equation without approximation. Quantum chemistry must be truly predictive not only qualitatively but also quantitatively. Since 1999, he could have a stream of ideas that allowed him to realize this dream. He first investigated the structure of the exact wave function and developed the method of constructing the exact wave function starting from an approximate one. An obstacle on the way to the exact analytical solutions for atoms and molecules was the singularity problem intrinsic to the Coulombic nuclear and electron potentials, but this was solved by introducing the scaled Schrödinger equation. His method has immediately been applied to several atoms and molecules with success: the free ICI method based on the scaled Schrödinger equation is now safely said to be an established method of solving the Schrödinger equation of atoms and molecules in an analytical form for both ground and excited states. An extension to the relativistic case has been finished[195] and an extension to the time-dependent case is now in progress. We expect many flowers and fruits along this orthodox route of quantum chemistry.

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