

Chapter 2

Algebraic Molecular Orbital Theory

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2.1 Introduction

Huzinaga described the principle of MO theory from the beginning before the Hartree-Fock-Roothaan theory in his text book (Huzinaga 1980). We can see there a new direction of MO theory. He gave us several hints in his book, for example, effectiveness of nonlinear variational method to obtain better eigenfunctions of atomic and molecular Hamiltonian, an excellent behavior of Slater-type basis functions, and so on. He also mentioned the Hartree-Fock variety which implies a multivariable theory. Inspired by Huzinaga, we shall propose an algebraic MO equation in order to construct a multivariable theory for quantum chemistry.

2.1.1 Multivariable Problem

Quantum chemistry has been developing in the field of physics, chemistry, and biology. Problems of molecular science spread in a wide range of space from nanometer order to meter order, energy from rotational transition energy level to hard x-ray energy level, and time from attosecond order to day order.

In the development of quantum chemistry, molecular orbital calculation has been fairly successful as a practical numerical method. However, there are underlying problems that are not well understood in quantum chemistry. Chemistry is a science that deals with fundamentally multivariable relations existing in atoms and molecules. For example, electronic state and molecular property depend on the molecular parameters, such as atomic position, atomic number, and number of

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constituent nuclei and electrons. However, the traditional molecular orbital theory, such as the Hartree–Fock–Roothaan (HFR) theory (Roothaan 1951) and the Kohn–Sham density functional theory (Hohenberg and Kohn 1964; Kohn and Sham 1964) have been developed without considering multivariable problems in chemistry. In such theories parameters of molecular structure are treated as numerical parameters. For example, MO energy is plotted numerically along the axis of molecular structures. To express the electronic state as a function of molecular parameters is still a basic problem in quantum chemistry. In this chapter multivariable problems that have been overlooked in the development of MO theory are discussed.

2.1.2 Variational Principle

On the basis of analytical basis set expansion method, MO equation is defined by applying the method of Lagrangian multiplier. The analytical basis set expansion method has fundamentally two kinds of parameter, linear combination coefficient and nonlinear orbital exponent. The roll of these parameters is a variational parameter in defining MO equation, and an optimization parameter to obtain approximate solutions of MO equation. However, in the traditional MO theory only linear combination coefficients are adopted, and nonlinear orbital exponents of basis function are fixed at numerical value. This means that the definition of the traditional MO equation is restricted in linear variational space, so that eigenstate cannot reach the exact eigenstate of the Hamiltonian even when the basis set is extended.

In contrast to analytical basis function such as Slater-type function and Gaussian-type function, numerical atomic basis function (Averill and Ellis 1973) is used in the discrete-variational- $X\alpha$ (DV- $X\alpha$) method based on the Hartree-Fock-Slater (HFS) model which is easily applicable from atoms to clusters (Adachi et al. 1978; Adachi 2006; Slater 1974, 1979). Numerical atomic basis function does not have an orbital exponent, but it is numerically generated at every SCF cycle in the MO calculation by solving the Schrödinger equation of atomic radial function for each atomic potential in molecule. In the DV- $X\alpha$ method, the Fock matrix is also defined at every SCF cycle by molecular integrals of numerical atomic basis functions. Although the HFS equation is defined on the linear variational principle, the MO is obtained through a doubly optimization process, i.e., optimization of numerical atomic basis functions and diagonalization of the Fock matrix. Owing to the effect of double optimization, proper MOs can be obtained for atoms and clusters with small basis set in the DV- $X\alpha$ method on the HFS model. However, the traditional MO theories are not applicable to algebraic theory as long as molecular integral is expressed in numerical value. Mukoyama proposed an analytical expression of atomic wave function which is obtained by nonlinear fitting of STFs to a numerical atomic wave function obtained in a similar way to the DV- $X\alpha$ method (Mukoyama and Yasui 1992).

The traditional MO equation is defined by using the Lagrangian function which is furnished with a single constraint, the orthonormal condition of MOs. The exact eigenfunction of molecular Hamiltonian satisfies several conditions, such as Kato's cusp condition (Kato 1957; Steiner 1963; Pack and Brown 1966; Chong 1967; Nakatsuji and Izawa 1989; Chapman and Chong 1970; Poling et al. 1971; Rassolov and Chipman 1996; Nagy and Sen 2001; Janosfalvi et al. 2005), the virial theorem, and the Hellmann–Feynman theorem (Feynman 1939; Feinberg et al. 1970; Stanton 1962; Fernández Rico et al. 2007). Although these conditions are necessary conditions being obeyed by the exact solutions of the Schrödinger equation, they are not adopted in the traditional Lagrangian function to define MO equation. However, Reinhardt and Hoggan, Koga and Galek showed that better solutions of the HFR equation can be obtained by using STFs and by adopting the nuclear cusp condition and the virial theorem (Reinhardt and Hoggan 2009; Koga et al. 1999; Galek et al. 2005). These studies suggested that multiple constraint condition is effective in solving the HFR equation. It is interesting that they adopted the nuclear cusp condition and the virial theorem because the former is a local condition and the latter is a global condition.

2.1.3 Trial Functions and Molecular Integrals

Molecular orbital is a model of electronic eigenfunction of the Schrödinger equation of molecule on the mean field approximation. Usually the Hartree–Fock (HF) equation is solved by using basis set expansion method. However, it is practically impossible to obtain the exact solution of the HF equation even when basis set is extended in size; the basis set is not able to expand itself fully in the Hilbert space of the Schrödinger equation as long as it is finite.

The molecular orbital model is used to calculate the electronic structure not only on the HF one-body model but also beyond the HF level. The first group beyond the HF level uses a single determinant for molecular orbitals; density functional theory belongs to this group. In the second group, there are configuration interaction method, perturbation theory, and coupled cluster theory, which use the virtual MOs of the HF model. For this reason, good basis functions are required for better MO calculations beyond the mean field approximation.

Despite of difficulties in evaluating multicenter molecular integrals, Slater-type function (STF) is a superior basis function because it satisfies Kato's nuclear-electron cusp condition and has a good long-range behavior similar to the Schrödinger hydrogen wave function (Kotani et al. 1955; Yasui and Saika 1982). STF has been adopted in advanced MO calculation softwares, such as ADF (Baerends et al. 1973), STOP (Bouferguene et al. 1996), and SMILE (Fernández Rico et al. 2001, 2004), however, it is impossible to address algebraic MO calculation by those software. This is because there is no symbolic information of molecular parameters in molecular integrals expressed by numerical value. STF is a superior basis function but analytical molecular integral over STF is required.

2.1.4 SCF Method

It is crucial to execute MO calculation for any size of atomic system without unnecessary calculations (Dirac 1929). In the traditional MO calculation, SCF iterative technique is used in solving a nonlinear MO equation. This technique is poor at convergence for large molecular system because of quasidegenerate electronic energy structure and huge eigenvalue problem. How to solve the Schrödinger equation without SCF iterative technique is an essential problem for large molecular system.

2.1.5 Nonadiabatic Process

Fundamentally, there is a time dependent discrepancy of motion between electron and nucleus due to a large difference of mass. Electron as a particle with fast velocity and nucleus as a particle with low velocity exchange their momenta via Coulomb interaction in time-dependent process. This cooperative interaction between electrons and nuclei is called nonadiabatic interaction. This is an essential problem in molecular science, such as chemical reaction, slow atomic collision, spectroscopy for electron and nucleus, surface science, solid-state physics, and so on, however, this has been existing as a difficult problem in molecular science since the beginning of quantum mechanics of molecule (Domcke et al. 2004; Baer 2006; Köppel et al. 2009; Nakamura 2012; Longuet-Higgins 1975; Berry 1984; Baer 2002).

The Schrödinger equation consists of fast variables and slow variables in molecule, electron and nucleus. The standard approach for solving the molecular Schrödinger equation is the Born–Oppenheimer (BO) approximation. In this approximation, molecular system has a double-layered energy structure by the large mass difference in which electron motions and nucleus motions are separated as follows. Since the slow variable is a good adiabatic parameter in the BO approximation, the Schrödinger equation for the fast variable can be solved by fixing the slow variable.

After obtaining eigenstates of the fast variables, equation for the slow variables can be defined using the eigenvalues of the first variable and the momentum operator shifted by the gauge potential A defined by

$$A_{mn}(R) = i \int \varphi_m^* \nabla_R \varphi_n dV, \quad (2.1)$$

where i is the imaginary unit, φ stands for the wave function of a fast particle, and R represents the molecular structure. The gauge potential A is designated

the nonadiabatic coupling (NAC) vector. The Schrödinger equation for the slow variable satisfies the hidden local gauge symmetry which keeps the phase of total wave function in time by cancelling global phase of the fast particle, whereas the motion of the slow particle brings about a phase shift to the fast particle during a time interval t in adiabatic process. This phase, designated the Longuet-Higgins/Berry phase, is defined by the path integral of NAC along a motion of the slow particle on the potential energy surface (PES) as

$$\gamma_{mn}(t) = \int_0^t A_{mn}(R(t)) \cdot dR(t). \quad (2.2)$$

In addition of dynamical phase, the time-dependent wave function of the fast particle, electronic wave function, has the Longuet-Higgins/Berry phase.

The nonadiabatic electronic transitions are found in various mechanisms in chemistry, molecular physics and molecular biology. This transition is driven by NAC in the critical region of avoided crossing or conical intersection. This transition has been studied as an electron transition between adiabatic PESs on the BO approximation (Adachi and Yasui 1987).

NAC and the Longuet-Higgins/Berry phase always coexist as a reciprocal relation in the dual-layered molecular energy system. Study of nonadiabatic molecular dynamics is a most difficult but a most interesting problem in chemistry. To disentangle problems in cooperative dynamics between electrons and nuclei is an essential and important problem in molecular science.

2.1.6 Aim of Our Study

As ignored problems which have been existing subconsciously as important problems from the beginning of quantum chemistry, we point out multivariable problems, which is concerned with functional relation between electronic state and molecular structure, introduction of nonlinear variational parameters to define molecular orbital equation, multiple constraint conditions for including electron correlation effect into the Lagrangian function, multivariable expression of molecular integrals over the STFs, cooperative dynamics of electrons and nuclei in molecular systems, method for solving the HFR equation without SCF iterative technique, and so on. Quantum chemistry has been developed without recognizing these multivariable problems.

The aim of our study is to construct a theoretical base to solve these multivariable problems beyond the traditional quantum chemistry constructed on the numerical method. As a first step to construct algebraic quantum chemistry, we shall propose an algebraic MO theory.

2.2 Theory

In this section, we propose a method for defining an algebraic MO equation by the variational principle. Two innovative methods are given, polynomial expression of molecular integrals and the Lagrangian function with extended constraint condition.

2.2.1 Polynomial Expression of Molecular Integrals

In order to retain an atomic picture in a multivariable MO theory, we adopt a linear combination of atomic orbitals approximation (LCAO-MO)

$$\phi_k\left(C, \vec{r}, \zeta, R\right) = \sum_{\alpha}^{atom} \sum_p^{AO(\alpha)} C_{ap}^k \chi_{ap}\left(\vec{r}_{\alpha}, \zeta_{ap}, R_{\alpha}, \{n_{ap}, l_{ap}, m_{ap}\}\right), \quad (2.3)$$

in this study. On the left hand side of Eq. (2.3), ϕ_k denotes for the k -th molecular orbital, and on the right hand side of Eq. (2.3), C the vector of linear combination coefficient of basis function, ζ the set of orbital exponent of the basis function and R the atomic configuration, α the sequence number of constituent atoms, $AO(\alpha)$ the number of basis functions centered at α , p the sequence number of the basis functions at α , χ_{ap} the p -th basis function centered at α , $\{n, l, m\}$ is the set of quantum numbers of the basis function, and r_{α} the polar coordinates of electron with origin at α . In the following the basis function χ is written by omitting the set of quantum numbers $\{n, l, m\}$ in short.

Molecular integral is integration over coordinates of electron which is the fastest particle in molecule. On the assumption that atomic configuration R and nonlinear parameter ζ are constant during integration, molecular integral is defined as a symbolic function with respect to R and ζ . Molecular integral is a minimum symbolic element in the algebraic MO theory on the BO approximation.

In order to construct algebraic MO equation, we prepare polynomial expression of molecular integrals through two steps. In the first step, we execute molecular integral analytically remaining R and ζ in symbol. Even in case when analytical expression of molecular integral is tremendously complicated, analytical molecular integral is a minimum symbolic element that enables to express MO equation in symbol. In the second step, we transfer analytical molecular integral by the Taylor expansion method given by Eq. (2.4) from analytical expression to polynomial expression in order to give an algebraic structure to the MO theory (Yasui 2010, 2011). A method of analytical expression of molecular integrals over STFs is described in detail in the next chapter.

$$f(x) = \sum_{p=0}^{\infty} \frac{1}{p!} \sum_{k=0}^p \binom{p}{k} (-x_0)^{p-k} \left[\left(\frac{d}{dx} \right)^p f(x) \right]_{x=x_0} x^k \cong \sum_{i=0}^N A_i(x_0) x^i, \quad (2.4)$$

where x_0 means the center of the Taylor expansion distributed so as to keep the polynomials in the same order in any region of variables. The last term in Eq. (2.4) is the approximate expression of single variable functions. This method can be easily extended to multivariable functions. Let us show an example for the case of overlap integrals. Overlap integral between basis functions centered at A and B separated by R is given

$$S(\zeta_a, \zeta_b, R)_{AB}^{ab} = \int \chi^* \left(\vec{r}_A, \zeta_a, R_A \right) \chi \left(\vec{r}_B, \zeta_b, R_B \right) dV. \quad (2.5)$$

Applying the Taylor expansion method, overlap integral can be approximately expressed in polynomial with respect to atomic distance R , and orbital exponents ζ_a and ζ_b

$$S(\zeta_a, \zeta_b, R)_{AB}^{ab} \cong \sum_{p_a, p_b, p_R} A(\{n_a, l_a, m_a\}_A, \{n_b, l_b, m_b\}_B)_{p_a, p_b, p_R} \zeta_a^{p_a} \zeta_b^{p_b} R^{p_R}, \quad (2.6)$$

where A stands for coefficient of polynomials expressed by rational number of fields. Coefficients of polynomial molecular integrals can be calculated and stored in advance for R and ζ over full range. Equation (2.6) shows that overlap integral is a polynomial ring with respect to R , ζ_a and ζ_b . The same procedure is applicable for other one-electron molecular integrals and two-electron molecular integrals to change their expressions from analytical to polynomial. By introducing of polynomial expression of molecular integrals into MO equation, we can define MO equation as an algebraic equation. Molecular integral expressed in polynomial works as a polynomial ring in the algebraic MO theory.

2.2.2 Total Electronic Energy

Owing to the polynomial expression of molecular integrals with respect to atomic configuration parameters and nonlinear orbital exponent parameters, we can define total electronic energy as a multivariable function

$$E[N, n, Z, R, C, \zeta] = T[N, n, Z, R, C, \zeta] + V[N, n, Z, R, C, \zeta], \quad (2.7)$$

where N is the number of atoms in molecule, n the number of electrons in molecule, Z the set of nuclear charge for each atom in molecule, R stands for the set of atomic configuration parameters, C is the set of linear combination coefficients, and ζ the set of nonlinear orbital exponents of basis functions, T and V on the right hand side stand for the total kinetic energy of electrons and the total potential energy, respectively.

We write total kinetic energy of electrons in LCAO approximation

$$T[N, n, R, C, \zeta] = \sum_{\alpha, \beta}^N \sum_p^{AO(\alpha)} \sum_q^{AO(\beta)} D_{ap, \beta q}[n, C] t_{ap, \beta q}[R, \zeta], \quad (2.8)$$

where α and β run over all pairs of atoms in molecule, $AO(\alpha)$ stands for the order of basis functions on the α th atom, and a density matrix on the right hand side is defined as

$$D_{ap, \beta q}[n, C] = 2 \sum_k^{occu.MO} C_{ap}^{*k} C_{\beta q}^k, \quad (2.9)$$

where k runs over occupied molecular orbitals, and kinetic molecular integral on the right hand side in Eq. (2.8) is defined in atomic unit as

$$t_{ap, \beta q}[R, \zeta] = \int dV \chi_{ap}^* \left(\vec{r}_\alpha, \zeta_{ap}, R_\alpha \right) \left(-\frac{1}{2} \Delta \right) \chi_{\beta q} \left(\vec{r}_\beta, \zeta_{\beta q}, R_\beta \right). \quad (2.10)$$

Total electronic potential energy is expressed as a sum of nuclear-electron attraction potential energy V^{Ne} , electron-electron repulsion potential energy V^{ee} , and nuclear- nuclear repulsion potential energy V^{NN}

$$V[N, n, Z, R, C, \zeta] = V^{Ne}[N, n, Z, R, C, \zeta] + V^{ee}[N, n, R, C, \zeta] + V^{NN}[N, Z, R]. \quad (2.11)$$

We write nuclear-electron attraction potential energy on the right hand side in Eq. (2.11) in LCAO approximation as

$$V^{Ne}[N, n, Z, R, C, \zeta] = \sum_{\alpha, \beta}^N \sum_p^{AO(\alpha)} \sum_q^{AO(\beta)} D_{ap, \beta q}[n, C] V_{ap, \beta q}^{Ne}[N, Z, R, \zeta], \quad (2.12)$$

where

$$V_{ap, \beta q}^{Ne}[N, R, R, \zeta] = \sum_\gamma^N Z_\gamma v_{ap, \beta q}^\gamma[R, \zeta] \quad (2.13)$$

and nuclear-electron attraction molecular integral on the right hand side in Eq. (2.13) is defined in atomic unit as

$$v_{ap, \beta q}^\gamma[R, \zeta] = \int dV \chi_{ap}^* \left(\vec{r}_\alpha, \zeta_{ap}, R_\alpha \right) \frac{1}{R_\gamma} \chi_{\beta q} \left(\vec{r}_\beta, \zeta_{\beta q}, R_\beta \right), \quad (2.14)$$

where R_γ stands for the distance of γ th atom from the origin of the internal coordinates for molecule. We write total electron repulsion potential in Eq. (2.11) in LCAO approximation as

$$V^{ee}[N, n, R, C, \zeta] = \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta}^N \sum_p^{AO(\alpha)AO(\beta)} \sum_q^{AO(\gamma)AO(\delta)} \sum_r \sum_s \quad (2.15)$$

$$D_{\alpha p, \beta q}[n, C] \left[I_{\alpha p, \beta q, \gamma r, \delta s}[\zeta, R] - \frac{1}{2} I_{\alpha p, \gamma r, \beta q, \delta s}[\zeta, R] \right] D_{\gamma r, \delta s}[n, C],$$

where α, β, γ and δ run over all combinations of four atoms in molecule. We define electron-electron repulsion molecular integral in Eq. (2.15) in atomic unit as

$$I_{\alpha p, \beta q, \gamma r, \delta s}[\zeta, R] = \iint dV_1 dV_2 \chi_{\alpha p}^*(\vec{r}_{1\alpha}, \zeta_{\alpha p}, R_\alpha) \chi_{\beta q}(\vec{r}_{1\beta}, \zeta_{\beta q}, R_\beta) \quad (2.16)$$

$$\frac{1}{r_{12}} \chi_{\gamma r}(\vec{r}_{2\gamma}, \zeta_{\gamma r}, R_\gamma) \chi_{\delta s}(\vec{r}_{2\delta}, \zeta_{\delta s}, R_\delta).$$

Nuclear repulsion potential on the right hand side in Eq. (2.11) is written in atomic unit

$$V^{NN}[N, Z, R] = \sum_{\alpha, \beta}^N Z_\alpha Z_\beta \frac{1}{R_{\alpha\beta}}, \quad (2.17)$$

where $R_{\alpha\beta}$ is a atomic distance between α th atom and β th atom.

The variables in total electronic energy in Eq. (2.7) are separated to two groups. In the first group, number of electrons n and linear variational parameter C belong to the density matrix. In the second group, number of atom N , atomic charge Z , atomic configuration R , and nonlinear orbital exponent ζ belong to the molecular integral. We can prepare molecular integrals in Eqs. (2.5), (2.10), (2.14), and (2.16) in advance for full range of R and ζ , and use them in algebraic MO calculations.

2.2.3 Extension in the Variational Principle

On the variational principle, MO equation is defined with the method of the Lagrangian multiplier. In this study we construct the algebraic MO equation by extending the Lagrangian function with respect to nonlinear variation and constraint condition.

By polynomial expression of molecular integrals with respect to orbital exponent of basis function, we introduce nonlinear variational parameter to the definition of the Lagrangian function. This enables the variation principle in nonlinear space. Huzinaga's book shows significant effects of nonlinear optimization to obtain better eigenstates.

The traditional MO equation, for example the HFR equation and the KS equation, is defined using the Lagrangian function with a single constraint condition. The Lagrangian function for the HFR equation consists of the total energy and a constraint condition in Eq. (2.18)

$$L_{HFR}[C] = E_{HFR}[C] + \lambda_s G_s[C], \quad (2.18)$$

where C stands for linear combinational coefficient of basis function, λ_s on the right hand side in Eq. (2.18) is the Lagrangian multiplier, and G_s means constraint condition of orthonormality of molecular orbitals. The Lagrangian function denoted by L_{HFR} in Eq. (2.18) leads the HFR MO equation by applying the variational principle

$$\frac{\partial}{\partial C} L_{HFR}[C] = 0. \quad (2.19)$$

Equation (2.19) shows that the HFR equation is defined only in the linear variational space.

While the HF equation or the KS equation is defined using the Lagrangian function with a single constraint condition, orthonormal condition of MO, we define the algebraic MO equation using the Lagrangian function with multiple constraint conditions in Eq. (2.20)

$$L_{multi}[N, n, Z, R, C, \zeta, \lambda] = E[N, n, Z, R, C, \zeta] + \sum_i \lambda_i G_i[N, n, Z, R, C, \zeta], \quad (2.20)$$

where L_{multi} on the left hand side is a Lagrangian function with multi constraint conditions, λ_i stands for the Lagrangian multiplier for the i th constraint condition, and G_i a necessary condition which is obeyed by the exact solution of the Schrödinger equation. We name the additional constraint condition in the Lagrangian function as the Schrödinger condition. We furnish the new Lagrangian function with a set of constraint conditions each of which has a different action in approaching the limit of variation. Choice of constraint condition depends on the aim. By the new Lagrangian function with nonlinear variational parameters and multiple constraint conditions, we define an algebraic MO equation on the variational principle

$$\frac{\partial}{\partial \alpha} L_{multi}[N, n, Z, R, C, \zeta, \lambda] = 0, \quad (\alpha = C, \zeta). \quad (2.21)$$

Exact eigenfunction of the molecular Hamiltonian of the Schrödinger equation should obey the Schrödinger condition, such as Kato's cusp condition, the virial theorem, the Hellmann–Feynman theorem (Feynman 1939) and the Liu–Parr–Nagy identity (Liu et al. 1995). Each condition subjects the trial function to a different action as discussed below.

The orthonormal condition of molecular orbitals is generally expressed as

$$C^*(R)S(\zeta, R)C(R) = 1. \quad (2.22)$$

At any molecular structure R , linear combination coefficient C and nonlinear orbital exponent of basis functions ζ cooperate to satisfy the orthonormal condition. In the algebraic MO theory the orthonormal condition in Eq. (2.22) is expressed by simultaneous polynomial equation. All other Schrödinger condition is the same.

Kato's cusp condition is a condition for eigenfunctions at the singular point of Coulomb interaction or in the vicinity of atomic center. In the algebraic MO theory the nuclear-electron cusp condition is adopted mainly as a local constraint condition. Three equivalent expressions for the nuclear-electron cusp condition are given as

$$\psi(0) + \frac{\psi'(0)}{Z} = 0, \quad (2.23)$$

$$\rho(0) + \frac{\rho'(0)}{2Z} = 0, \quad (2.24)$$

$$Z = -\frac{1}{2} \frac{\rho'(0)}{\rho(0)} = -\frac{1}{2} \lim_{r \rightarrow 0} d \log_e \rho(r), \quad (2.25)$$

where ψ is the eigenfunction, Z the atomic charge, $\rho(r)$ the electron charge density. The electron charge density at nucleus in Eq. (2.24) has a relation to the Fermi contact interaction. The energy of Fermi contact interaction is proportional to square of electron charge density at atomic center. Since every atomic center is a singular point of Coulomb interaction in molecule, the nuclear-electron cusp condition holds at every atom. The Eq. (2.25) means that the atomic number Z is proportional to the derivation of electron charge density over electron charge density at nucleus. The nuclear-electron cusp condition implies that the atomic positions are determined so as to satisfy the nuclear-electron cusp condition in molecule.

In this study the molecular electron charge density in LCAO approximation is expressed as

$$\begin{aligned} \rho[N, n, R, C, \zeta](\vec{r}) &= \sum_{\alpha}^N \rho_{\alpha, \alpha}[n, R, C, \zeta](\vec{r}) \\ &+ \sum_{\alpha \geq 2}^N \sum_{\beta (< \alpha)}^{N-1} \rho_{\alpha, \beta}[n, R, C, \zeta](\vec{r}), \end{aligned} \quad (2.26)$$

where electron charge distributions on atom or between atoms are defined as

$$\begin{aligned} \rho_{\alpha, \alpha}[n, R, C, \zeta](\vec{r}) &= \sum_p^{AO(\alpha)} \sum_q^{AO(\alpha)} \\ D_{ap, aq}[n, C] \chi_{ap}^*(\vec{r}_\alpha, \zeta_{ap}, R_\alpha) \chi_{aq}(\vec{r}_\alpha, \zeta_{aq}, R_\alpha), \end{aligned} \quad (2.27)$$

$$\rho_{\alpha,\beta}[n, R, C, \zeta](\vec{r}) = \sum_p^{AO(\alpha)} \sum_q^{AO(\beta)} D_{ap,\beta q}[n, C] \chi_{ap}^*(\vec{r}_\alpha, \zeta_{ap}, R_\alpha) \chi_{\beta q}(\vec{r}_\beta, \zeta_{\beta q}, R_\beta), \quad (2.28)$$

respectively. The sum of electron charge density at nucleus can be expressed as

$$\rho[N, n, R, C, \zeta](0) = \sum_\alpha^N \rho_{\alpha,\alpha}[n, R, C, \zeta](0) + \sum_{\alpha>2}^N \sum_{\beta(<\alpha)}^{N-1} \rho_{\alpha,\beta}[n, R, C, \zeta](0), \quad (2.29)$$

where

$$\rho_{\alpha,\alpha}[n, R, C, \zeta](0) = \sum_p^{AO(\alpha)} \sum_q^{AO(\alpha)} D_{ap,aq}[n, C] \chi_{ap}^*(0, \zeta_{ap}, R_\alpha) \chi_{aq}(0, \zeta_{aq}, R_\alpha), \quad (2.30)$$

$$\rho_{\alpha,\beta}[n, R, C, \zeta](0) = \sum_p^{AO(\alpha)} \sum_q^{AO(\beta)} \left[\chi_{ap}^*(0, \zeta_{ap}, R_\alpha) \chi_{\beta q}(R_\alpha, \zeta_{\beta q}, R_\beta) + \chi_{ap}^*(R_\beta, \zeta_{ap}, R_\alpha) \chi_{\beta q}(0, \zeta_{\beta q}, R_\beta) \right]. \quad (2.31)$$

There is another relation with respect to electron charge density at nucleus. The Liu–Parr–Nagy (LPN) identity expressed as

$$\rho(0) = -\frac{1}{4\pi} \int \frac{\nabla^2 \rho(r)}{|r|} dV, \quad (2.32)$$

has a qualification of constraint condition in the Lagrangian function. Although the LPN identity has an electron charge density at nucleus on the left hand side, it does not require the relation to the atomic charge Z on the right hand. The electron charge density at nucleus appears in Eqs. (2.24) and (2.32).

The virial theorem in the Born–Oppenheimer approximation is expressed as

$$2T[N, n, R, C, \zeta] + V[N, n, Z, R, C, \zeta] + \sum_\alpha^N \vec{R}_\alpha \cdot \frac{\partial E[N, n, Z, R_\alpha, C, \zeta]}{\partial \vec{R}_\alpha} = 0. \quad (2.33)$$

Equation (2.33) means that the kinetic energy and the potential energy are balanced with help of the third term at any molecular geometry point on the adiabatic total energy surface (Mayer 2010). Since the exact solution of the HFR equation satisfies the virial theorem, the virial theorem can be adopted as a constraint condition in the algebraic Lagrangian function.

The Hellmann–Feynman theorem

$$\frac{\partial}{\partial \alpha} E[N, n, Z, R, C, \zeta] = \left\langle \Psi(\alpha) \left| \frac{\partial}{\partial \alpha} H[N, n, Z, R, C, \zeta] \right| \Psi(\alpha) \right\rangle, \quad (2.34)$$

can be adopted as a constraint condition in the algebraic MO Lagrangian function, where α is a parameter included in the Hamiltonian. Equation (2.34) shows the general form of the Hellmann–Feynman theorem from which specific theorem, such as the virial theorem and the electrostatic theorem, is derived.

There are mathematical conditions which are satisfied with the exact eigenfunction of the molecular Hamiltonian, for example, closure relation for quantum mechanical operators. We can select the combination of constraint conditions according to the aim.

Although it is expected that the Lagrangian function extended with nonlinear variational parameters and multiple constraint conditions would be effective, it is necessary to keep the basis set in an adequate size.

2.3 Discussion

In the previous section we proposed a method for defining an algebraic MO equation in detail. In this section we will discuss about advantage and expectation in the algebraic MO theory.

2.3.1 *Multivariable Theory for Chemistry*

It is worth constructing a multivariable theory for quantum chemistry because chemistry is a science of atoms and molecules described by many quantities associated with nucleus and electron, and parameters of external fields such as electromagnetic field and boundary conditions applied to atoms and molecules. Mechanism of chemical reaction and that of electromagnetic property of molecule are fundamentally multivariable problems.

As a methodology for multivariable problems, numerical method is inadequate because much information of molecular parameters disappears in numerical operations of addition and multiplication.

The object of chemistry is not always a forward problem. The order of searching solutions depends on the problem. It is difficult to remove the distinction between a forward problem and an inverse problem on the numerical method. On the other hand, the algebraic MO theory is adequate for multivariable problems and because many variables are expressed by symbol so that their symbolic meanings are conserved during calculation process.

The algebraic MO theory is also adequate for inverse problem because the order of searching solutions is interchangeable.

The algebraic MO is an approximate equation of the molecular Schrödinger equation in affine space (Yasui 2010, 2011). Symbolic calculation on polynomials is essential in this theory.

2.3.2 Polynomial Expression of Molecular Integrals over STFs

Most innovative part in this study is an introduction of polynomial expression of molecular integrals to molecular orbital theory. This enables to construct the algebraic molecular orbital theory in affine space. Mathematically, molecular integral expressed in polynomial plays a roll of polynomial ring, and changes the form of molecular orbital equation from matrix equation to simultaneous polynomial equation. The set of solutions of polynomial MO equation is the approximate affine variety of the Schrödinger equation. This is a basic idea of the algebraic MO theory with many variables. Molecular integral expressed in polynomial is indispensable to the algebraic quantum chemistry.

Many studies of molecular integral with STO, GTO, and other basis functions have been done in the development quantum chemistry, however, the use is confined to numerical calculations. In order to construct the algebraic MO theory, it is necessary at least that molecular integral is obtained analytically as a function of atomic configuration parameters and orbital exponents of basis function. By analytical integration, the parameters of molecular integral keep themselves in symbolic expression. In addition to that, in order to define the algebraic MO equation for the second step, it is necessary to transform molecular integral from analytical expression to polynomial one. This transformation is done by the method of Taylor expansion.

The aim of quantum chemistry is various. In some studies, the precise calculation is needed. In other studies, it is important to grasp the essence of chemistry neither too much nor too little in accuracy. For these aims, polynomial molecular integral is extremely advantageous especially for large molecules. The accuracy of polynomial molecular integral is controllable in a wide range of variables by using adequate expansion centers. On the controllability of accuracy, it is possible to make a seamless approximation or an effective Hamiltonian on the first principle.

With respect to calculation error, there is no mixing of numerical errors in symbolic polynomial calculation because the coefficients of polynomial ring are expressed by rational numbers in this study.

While the algebraic MO theory is constructed in real-space in this study, we can define it in momentum-space by using the Shibuya-Wolfman integral which is molecular integral of exponential type basis function in momentum space (Shibuya and Wulfman 1965; Avery 2000).

2.3.3 *Advantage of Extension of the Variational Principle*

The effectiveness of variational principle depends on the set of trial functions, the set of variational parameters, and the constraint conditions. In principle, LCAO-MO theory is defined by the set of linear parameters and nonlinear parameters, however, in most traditional MO theory, nonlinear variational parameters are omitted. On the other hand, in the algebraic MO equation, orbital exponent is introduced as a nonlinear variational parameter in the definition of MO equation through polynomial expression of molecular integrals. In the algebraic MO theory compatibility of linear variational parameter and nonlinear variational parameter is attained. The action of orbital exponent as a nonlinear variational parameter is effective, which is described in Huzinaga's book. In case of atomic collision, for example, overlap of wave functions between atoms begins to contact with their tails of wave functions in the asymptotic region determined by the orbital exponent of basis functions. Contact of wave function brings about initial separation of molecular energy level in the same symmetry, and works to stabilize total electronic energy of atomic system. Using linear parameters and nonlinear parameters, trial functions fit precisely the details of variational active space of the molecular Hamiltonian so as to approach local minimum of total electronic energy under the set of Schrödinger conditions. In addition to accurate eigenenergy in the algebraic MO equation, more precise eigenfunction will be obtained by the extend variational method for degenerated state or quasidegenerated state of the Hamiltonian.

The set of the Schrödinger condition acts to extend variational function space in which each condition takes a different action to minimize total electronic energy in molecule. Thanks to polynomial expression of molecular integrals, we can extend the Lagrangian function without difficulty.

The orthonormal condition is a nonlocal constraint condition. In the algebraic MO theory the orthonormal constraint condition in Eq. (2.22) works not only in linear variational space through the density matrix but also in nonlinear variational space through the overlap matrix. On the other hand, in the traditional MO theory, nonlinear orbital exponents in overlap matrix are fixed in numerical value so that it is difficult to optimize MOs at arbitrary molecular geometrical point.

Atomic center is a singular point of Coulomb potential in molecule. By Kato's nuclear-electron cusp condition expressed in several form in Eqs. (2.23), (2.24) and (2.25), wave functions of the Schrödinger equation is able to avoid the divergence at atomic centers. As described in Eq. (2.29), atomic charge at atomic center includes contributions from the outer region. This means that cusp and tail of basis functions hold Kato's nuclear-electron cusp condition. Exact wave functions or exact electron charge densities, which obey Kato's nuclear-electron cusp condition, distribute in molecule so as to determine molecular structure, in other words, it might be said that Kato's nuclear-electron cusp condition gives a principle to determine molecular structure.

While the LPN identity in Eq. (2.32) includes electron charge density at atomic center, it does not require atomic number Z in the definition. Since electron charge density at atomic center appears both in Kato's nuclear-electron cusp condition and the LPN identity conditions, these conditions are intrinsically the same. By this reason, the LPN identity is approximately applicable to non-exponential basis functions, such as Gauss type functions.

The virial theorem in Eq. (2.33) holds at any molecular structure in the stationary state. Equation (2.33) means that kinetic energy and potential energy are balanced exactly with a help of the third term, which is an inner product of atomic position vector and gradient vector of the electronic total energy surface. It is interesting that the kinetic energy and the potential energy are global quantities but the third term is a summation of local quantities. Since the kinetic energy is always positive and the potential energy is always negative, the third term has to work as an adjuster to hold the virial theorem. This suggests that the third term needs accuracy. In the third term expressed in polynomial, first derivation of electronic total energy with respect to atomic position vector is obtained analytically. At any molecular geometrical point, the kinetic energy, the potential energy and the third term are able to take a balance among themselves by optimizing linear variational parameters and nonlinear variational parameters in this study.

It is well recognized that the fulfillment of the Hellmann–Feynman theorem is difficult by poor basis functions. This suggests that the Hellmann–Feynman theorem works as a strong constraint condition for defining a precise MO equation. It is expected that the Hellmann–Feynman theorem expressed in polynomials with respect to linear parameters and nonlinear parameters will play an effective roll as a strong constraint condition in the Lagrangian function.

Compared with a single constraint condition, the set of constraint conditions will generate more precise constraint condition as a whole. Multiple constraint condition increases a degree of freedom of trial function in variational active space.

By the cooperative effect by nonlinear variational parameter and multiple constraint condition in the Lagrangian function, the algebraic MO equation will provide more accurate eigenenergies and MOs than the traditional MO equation does.

2.3.4 Advantage in Calculation of Electron Correlation

Since the Schrödinger equation includes the electron correlation or the many body effect completely, electron correlation energy is defined by the total energy difference between the HF equation and the Schrödinger equation. Both the HF theory and the algebraic MO theory is based on the one-body model, however, the latter is superior in the variational principle as described in this chapter. This means that the total energy difference between the algebraic MO equation and the Schrödinger is expected to be smaller than in the case of the HF theory.

The eigenstate obtained by the algebraic MO calculation includes the electron correlation in some degree because the Lagrangian function adopts the Schrödinger conditions as constraint conditions. Electron correlation or electron many-body effect appears in coincident collision among electrons over two particles. Electron correlation appears not only in the stable eigenstate but also in the transition process. Electronic polarizability and multielectron transition, for example, are sensitive to the electron correlation on the ground state and during the transition process, respectively. The algebraic MO theory is useful in the calculation of electronic properties in which many-body interactions are active.

Having size consistency, many-body perturbation theory (MBPT) is valid for calculation of electronic correlations, particularly for large molecules. For a long time, various variation theory and perturbation theory of electronic correlation have been studied on the base of the traditional MO theory with orbital exponents of basis functions being fixed. For this reason, it is difficult for the traditional MO theory to achieve a high accuracy of electron correlation energy. On the other hand, it is expected that the algebraic MO theory will lead a rapid convergence in MBPT.

In a case when nonadiabatic interaction and electron correlation is close in energy, or in a critical region where a drastic reorganization of electronic configurations occurs, it may be difficult to analyze those complex interaction. For these cases, mathematics of polynomial will be useful for disentangling the complex.

2.3.5 Integer Variables in Quantum Chemistry

Number of atom, atomic number and number of electron is a basic information in chemistry. The Schrödinger equation includes atomic number Z , number of atom and number of electron as integer parameter. This means that there exists at least a relation between the integer parameter and the quantum eigenstate in molecule. However, it is impossible to know the relation from the HFR calculations because atomic number Z is dealt as a numerical value. The traditional theoretical chemistry has no awareness to solve MO equation with respect to those integers. It is interesting that Kato's nuclear-electron cusp condition connects directly atomic number Z and wave function at atomic centers in molecule.

2.3.6 Advantage of Polynomial Equation

M.P. Barnett informed us many papers about applications of polynomial equation in the field of chemistry except quantum chemistry (Barnett et al. 2004). M. Minimair and M.P. Barnett explained how to solve polynomial equations by using Gröbner bases (Minimair and Barnett 2004). Algebraic computational theory of polynomials has been developed in recent years (Cox et al. 2007), however, there has been no algebraic method in the development of quantum chemistry.

There are several mathematical advantages in solving a simultaneous algebraic equation. Firstly, it is possible to identify the existence of solutions rigorously even if it is difficult to solve the equation under a difficult condition. Secondly, identification of the number of solutions is possible. Lastly, it is possible to identify the relations among variables. In some cases, there is a remarkable possibility to find a useful relation among molecular variables. In addition to that, there is a great advantage in the algebraic method, that is, there is no distinction between forward problem and inverse problem. We can obtain solutions in any sequence of variables from polynomial equation.

The SCF iterative technique is a standard method for solving a nonlinear MO equation by regarding it as a linear equation. For small molecules SCF iterative technique is useful, however, it is inconvenient in case when a quasidegenerate electronic state exists. In some cases, quasidegenerate state cannot be solved by the SCF iterative technique. On the other hand, the algebraic MO equation needs no SCF iterative technique because nonlinear polynomial MO equation is solved algebraically. This is a great practical advantage of the algebraic MO equation.

2.3.7 Advantage in the Born-Oppenheimer Approximation

Study of nonadiabatic interaction between electron and nucleus is interesting as a fundamental interaction in chemistry. There are two interesting problems after obtaining PESs on the BO approximation. The one is to solve nuclear eigenstates on PES by using NAC. The another is to solve nonadiabatic electron transition probability between PESs by using NAC.

In the BO approximation, total molecular wave function is expressed by the sum of product of electronic wave function and nuclear wave function. The phase of electronic wave functions and that of nuclear wave functions cancel each other in the stationary state. This cancelation mechanism is a hidden nature in the nuclear Schrödinger equation. Nuclear quantum state is sensitive to NAC and PES because energy separation between nuclear quantum states is much smaller than that of electronic adiabatic PESs. In order to give a reliable description for nuclear state, it is better to express NAC and PES by continuous parameters, not by discrete numerical parameters. Owing to the method of polynomial expression of NAC, the nuclear Schrödinger equation will be solved in high accuracy. Construction of the coupled Schrödinger equation for electrons and nuclei is a fundamental problem not only for nonadiabatic process but also for molecular dynamics on the BO approximation in a wide range of time.

Within the adiabatic approximation, the time-dependent electronic wave function has the dynamical phase and the Longuet-Higgins/Berry phase which are acquired by the eigenenergy of electronic state and NAC, respectively. Acquisition of NAC and the Longuet-Higgins/Berry phase needs consistency in solving the nuclear Schrödinger equation. Acquisition of electronic eigenstate and nuclear eigenstate on the BO approximation is a multivariable problem. In symbolic

calculation of NAC and the Longuet-Higgins/Berry phase, polynomial method will be useful. NAC and the Longuet-Higgins/Berry phase expressed as a multivariable function will play an important role as a reciprocal relation in the Born-Oppenheimer molecular dynamics.

Nonadiabatic electron transition appears in fundamental process in many fields of molecular science, such as chemical reaction, especially important in photochemistry, slow atomic collision, spectroscopy for electron and nucleus, surface science, solid-state physics. The nonadiabatic electron transition probability is a time-dependent problem. In slow atom-atom collision, the transition near the avoided crossing region of adiabatic electronic states obeys a selection rule different from that for dipole transition. To discover a region where the nonadiabatic electron transition occurs between PESs is an interesting problem.

Conclusion

In this chapter we proposed a method for defining an algebraic molecular orbital equation in order to construct a multivariable symbolic quantum theory for molecular science. We defined the algebraic MO equation as a simultaneous multivariable polynomial equation on the nonlinear variational principle by introducing polynomial expression of molecular integrals over STFs with respect to atomic configuration parameters and nonlinear orbital exponents of basis functions. In this algebraic theory there is no need of SCF iterative technique and there is no distinction between forward problem and inverse problem. The algebraic MO theory is beyond the Hartree-Fock theory in spite of one-body model because our theory includes electron correlation by adoption of the Schrödinger condition as constraint condition in the Lagrangian function. Using controllability of polynomial molecular integral accuracy, a seamless effective Hamiltonian can be defined without lack of the first principle in a wide range of physical dimension. This study brings a new practical method on the first principle for large molecules with accordance to the aim of study.

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