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An approach to first principles electronic structure calculation by symbolic-numeric computation

Akihito Kikuchi*

CANON INC., 30-2, Shimomaruko
3-chome, Ohta-Ku, Tokyo 146-8501-
Japan
*Email: kikuchi.akihito@canon.co.jp

ABSTRACT

This article is an introduction to a new approach to first principles electronic structure calculation. The starting point is the Hartree-Fock-Roothaan equation, in which molecular integrals are approximated by polynomials by way of Taylor expansion with respect to atomic coordinates and other variables. It leads to a set of polynomial equations whose solutions are eigenstate, which is designated as algebraic molecular orbital equation. Symbolic computation, especially, Gröbner bases theory, enables us to rewrite the polynomial equations into more trimmed and tractable forms with identical roots, from which we can unravel the relationship between physical parameters (wave function, atomic coordinates, and others) and numerically evaluate them one by one in order. Furthermore, this method is a unified way to solve the electronic structure calculation, the optimization of physical parameters, and the inverse problem as a forward problem.

Keywords: first principles electronic structure calculation, symbolic computation, Hartree-Fock-Roothaan equation, molecular integral, Gröbner bases, algebraic molecular orbital equation

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INTRODUCTION

This article is intended as an introduction of a new approach to first principles electronic structure calculation, by way of symbolic-numeric computation.[1]

There is a wide variety of electronic structure calculation cooperating with symbolic computation. The main purpose of the latter is to play an auxiliary role (but not without importance) to the former. In the field of quantum physics,[1−9] researchers sometimes have to handle complicated mathematical expressions, whose derivation seems almost beyond human power. Thus one resorts to the intensive use of computers, namely, symbolic computation.[10−16] Examples of this can be seen in various topics: atomic energy levels, molecular dynamics, molecular energy and spectra, collision and scattering, lattice spin models and so on.[16] How to obtain molecular integrals analytically or how to manipulate complex formulas in many body interactions, is one such problem. In the former, when one uses special atomic basis for a specific purpose, to express the integrals by the combination of already known analytic functions, may sometimes be very difficult. In the latter, one must rearrange a number of creation and annihilation operators in a suitable order and calculate the analytical expectation value. It is usual that a quantitative and massive computation follows a symbolic one; for the convenience of the numerical computation, it is necessary to reduce a complicated analytic expression into a tractable and computable form. This is the main motive for the introduction of the symbolic computation as a forerunner of the numerical one and their collaboration has won considerable successes. The present work should be classified as one such trial. Meanwhile, the use of symbolic computation in the present work is not limited to indirect and auxiliary part to the numerical computation. The present work can be applicable to a direct and quantitative estimation of the electronic structure, skipping conventional computational methods.

The basic equation of the first principle electronic structure calculations is the Hartree-Fock or the Kohn-Sham equation, derived from the minimum condition of the energy functional in the electron-nuclei system,[1−3] which is expressed as follows.

$$\left(-\frac{1}{2}\Delta+\sum_{a}\frac{Z_a}{|r-R_a|}+\int dr'\,\frac{\rho(r')}{|r-r'|}+V^{exc}\right)\phi_i(r)=E_i\phi_i(r). \tag{I.1}$$

The second term in the parse of the left side is the potential from nuclei with charge Z_a. The third term is the Coulomb potential generated by the charge distribution ρ. The fourth term V^{exc} is the quantum dynamical interaction operating in the many-electron system, called the "exchange and correlation". It is rewritten into the matrix eigenvalue problem, by adopting wavefunctions expanded by a certain localized basis set. This is Hartree-Fock-Roothaan (HFR) equation in Equation (I.2).

$$\mathbf{H}(\{R\},\{\Psi\},\{\zeta\},\{Q\})\,\mathbf{\Psi}(\{R\},\{\zeta\},\{Q\})=\mathbf{S}(\{R\},\{\zeta\},\{Q\})\,\mathbf{\Psi}(\{R\},\{\zeta\},\{Q\})\,\mathbf{E}(\{\zeta\},\{Q\}). \tag{I.2}$$

H is the Hamiltonian matrix, **S** is the overlap one, $\boldsymbol{\psi}$ is the wavefunction (the coefficients of the linear combination), and **E** is the eigenvalue. The variables $\{R\}$ are the positions of the nuclei, $\{\zeta\}$ are the orbital exponents that describe the special expansion of the localized base function, and $\{Q\}$ are the quantum numbers. The analytic forms of localized atomic bases are expressed by these three kinds of parameters, namely, the atomic position, the orbital exponent and quantum numbers. The HFR equation can be expressed by multi-valuable analytic functions, whose variables are $\{R\}$, $\{\zeta\}$ and $\{Q\}$. It contains transcendental functions of several kinds. This is because we conventionally adopt analytical base, such as Slater type orbital (STO) or Gaussian type orbital (GTO), to construct one-electron and two-electron molecular integrals, whose concrete expression can be derived from symbolic manipulation[4−9] by means of computer algebra systems.[10,11]

The use of analytic basis in the HFR equation is effective in the achievement of precision in numerical computation, but causes some difficulty in the mathematical operations to the equation itself, because the analytic expression is, in general, very complicated. We, however, can rewrite and approximate the HFR equation using polynomials in order to obtain much simpler expressions. The concept of polynomial approximation to the HFR equation was promoted by Yasui.[6−9] The equation becomes the set of algebraic polynomial equations expressed by atomic coordinates, orbital exponents, and quantum numbers. Based on this, we will able to unravel the relationship among parameters and clarify their dependence. This idea is be outlined here. We express a molecular orbital by the linear combination of atomic orbitals (LCAO),

$$\phi_k = \sum_{\alpha}^{\text{atom}} \sum_{i}^{\text{base}} C^{k}_{ai} \chi(R_\alpha, \{n_i, l_i, m_i\}, \zeta_i, r, \theta, \phi). \tag{I.3}$$

The variables $R_\alpha, \{n_i, l_i, m_i\}, \zeta_i$ are the atomic position, quantum numbers and the orbital exponents, respectively. The variables r,θ,ϕ are of the atom centered coordinates. The key components to the molecular orbital calculations are molecular integrals, which are the matrix elements of the each part of the Hamiltonian operator obtained by the use of LCAO, such as, kinetic energy, nuclear and electronic potentials and overlapping integrals. The approximation to molecular integrals is obtained by Taylor expansion;

$$f(x) = \sum_{p=0}^{\infty} \frac{1}{p!} \sum_{k}^{p} \begin{pmatrix} p \\ k \end{pmatrix} (x - x_0)^{p-k} f(p)(x_0) x^p \cong \sum_{i=0}^{N} A_i(x_0) x^i. \tag{I.4}$$

For example, the two-centered overlapping integral is defined as,

$$S^{ab}_{AB} \equiv \int \chi(R_A, \{n_a, l_a, m_a\}, \zeta_a, r_A, \theta_A, \phi_A) \chi(R_B, \{n_b, l_b, m_b\}, \zeta_b, r_B, \theta_B, \phi_B) dr^3. \tag{I.5}$$

The integration generates an analytic function of two orbital exponents and inter-atomic distance R. The polynomial approximation is given as,

$$S^{ab}_{AB}(\zeta_a, \zeta_b, R) \cong \sum_{P_a, P_b, P_R} A(\{n_a, l_a, m_a\}_A, \{n_b, l_b, m_b\}_B)_{P_a, P_b, P_c} \zeta_a^{p_a} \zeta_b^{p_b} R^{P_R}. \tag{I.6}$$

Other molecular integrals can be expressed in a similar way. Once the molecular integrals are approximated as polynomials, the HFR equation and the energy functional take polynomial expressions. The orbital exponents and atomic coordinates can equivalently be regarded as parameters in the calculus of variations, as well as LCAO coefficients. It will be adequate to call this multi-variable polynomial expression “algebraic molecular orbital equation,” or “algebraic molecular orbital theory.” It is not necessary to regard those equations as pure numerical eigenvalue problems. Those equations are a set of polynomials, to which both symbolic manipulations and numerical solving are applicable.

One should note some inconvenience in conventional methods, which may be surmounted by “algebraic molecular orbital equation.” The standard electronic structure calculation is a “forward problem”. We suppose the material structure, execute the electronic structure calculations, and optimize the structure so that the energy functional will be minimized. The foundation for this treatment is so-called “the adiabatic approximation”, which enables us to separate the dynamics of the nuclei and wavefunctions into two independent models, ruled by classical and quantum dynamics, respectively. The conventional method iterates two alternative computational phases, one of which are the optimization for the wavefunctions and the other for the positions of the nuclei. It is believed that this way is numerically stable. But, in view of effectiveness, this may be a lengthy and indirect, which also results in some inefficiency. Owing to the separation of the degrees of freedom of wavefunctions and nuclei, it is difficult for the conventional method to cope with cases where the dynamics of nuclei and wavefunctions are strongly coupled with each other. Meanwhile, the “inverse problem” will be to search the material structure, which shows the desirable electronic properties. To do this, the conventional method must be trial and error. At first we suppose the material structure to evaluate the electronic properties, and, by adjusting the structure, we search the direction in which the desired properties will be obtained. We have to solve forward problems repeatedly to obtain the solution of the inverse problems. The reason to this is as follows. In the conventional methods, the computation has the fixed order of numerical procedures, consisted from the eigenvalue solution, the self-consistent-field calculation and the relaxation of atomic structure, which is implemented as nested loops of independent phases of the optimizations. The unknown parameters are computed from inner loops to outer ones in order. The conventional method is obliged to determine unknown variables in a fixed order in all cases. As we will see later, the concept “algebraic molecular orbital equation” suggests a solution strategy to this circumstance.

METHOD

In view of these circumstances, we propose the following method, named “Symbolic-numeric ab-initio molecular dynamics and molecular orbital method”.[1]

It is summarized as follows. “At first, HFR equation is approximated as a set of multi-variable polynomial Equations (Algebraic Molecular Orbital Equation), and by symbolic computation, it is rewritten into a certain form more convenient for numerical treatment. The eigenstates are evaluated by the root finding. using symbolic-numeric procedure."

The question at present is how to obtain the numerical solutions of the equations after the polynomial approximation and derive significant information. For the purpose of rewriting and solving a set of polynomial equations, several types of hybrid techniques, so-called "symbolic-numeric solving", are proposed. In them, the symbolic manipulation is applied as a preconditioning toward the set of equations to be solved. The equations are transformed into others, which have the same roots, to which the numerical computation will be easy and stable. From the form of the transformed equations, the character of the solution, such as, the existence and the geometrical structure, can be determined. Then the solving process is passed over to the numerical one. For the mathematical background, see Möller and other authors[12−15] A review of applications of symbolic computations in the field of computational chemistry is given in Barnett et al.[16]

In the present work, we make use of symbolic-numeric solving and rewriting the HFR equation, approximated as a set of polynomial equations. As a strategy, the algorithm of the "decomposition of polynomial equations into triangular sets" is applied.[12,13] In this algorithm, the following transformations are applied.

The starting equations $f_1, \ldots, f_n$

$$\begin{aligned} f_1(x_1, x_2, \ldots, x_n) &= 0 \\ f_2(x_1, x_2, \ldots, x_n) &= 0 \\ &\vdots \\ f_n(x_1, x_2, \ldots, x_n) &= 0 \end{aligned} \tag{M.1}$$

⟶ Gröbner bases with lexicographic order of $f_1, \ldots, f_n$, $\{g_i\}$

$$\begin{aligned} g_1(x_1) &= 0 \\ &\vdots \\ g_{2\_1}(x_1, x_2) &= 0 \\ &\vdots \\ g_{2\_m(2)}(x_1, x_2) &= 0 \\ g_{3\_1}(x_1, x_2, x_3) &= 0 \\ &\vdots \\ g_{n\_1}(x_1, \ldots, x_n) &= 0 \\ &\vdots \\ g_{n\_m(n)}(x_1, \ldots, x_n) &= 0 \end{aligned} \tag{M.2}$$

⟶ Triangular sets of polynomials $\{t_i\}$, each of which is given as this.

$$\begin{aligned} t_1(x_1) &= 0 \\ t_2(x_1, x_2) &= 0 \\ &\vdots \\ t_n(x_1, x_2, \ldots, x_n) &= 0 \end{aligned} \tag{M.3}$$

The algorithm in ref .12 and 13, at first, generates the Gröbner bases $\{g_i\}$ with the lexicographic monomial order from the starting set of equations $f_1, \ldots, f_n$. The generated Gröbner bases have roots identical to those of $f_1, \ldots, f_n$, and take forms which guarantee an easier numerical solving. The Gröbner bases are a set of polynomials in which the number of unknowns of each entry increases in order, from polynomials with fewer valuables to ones with more. However, the total number of polynomials in the Gröbner bases may grow more than that of the starting polynomials. Though we can search the root at this stage, we furthermore apply the decomposition to the Gröbner bases and obtain several "triangular" systems of equations $\{t_1, \ldots, t_n\}$. The first entry of which has one unknown x_1, the second has two unknowns x_1, x_2, the third three unknowns, etc, until, the last n-th has n-unknowns $x_1, x_2, \ldots, x_n$ by turns. In order to obtain all roots of the starting equations $f_1, \ldots, f_n$, we need to construct several sets of triangular sets of equations, all of which can be generated by the algorithm in ref .12 or 13. A single triangular system has fewer numbers of entries than that in the Gröbner bases before the transformation. This makes the numerical procedure easier. Once we can obtain the triangular systems of the equations, we can evaluate each unknown one by one. In the numerical solution, only a Quasi-Newton-like method, or its kindred for one variable, is necessary.

We can execute another type of the symbolic numerical solving. The foundation to this is the theorem of Stickelberger. As above, we regard the HFR equations as the set of polynomial equations expressed by unknowns $X_1, \ldots, X_m$. The set of polynomial equations constructs a zero-dimensional ideal I in the polynomial ring $R = k\,[X_1, \ldots, X_m]$, whose zeros corresponds to a residue ring $A = R/I$. Here k is the coefficient field, which, in our case, is the rational number field or the real number field. The ring A is a finite dimensional vector space over k, whose bases are expressed by monomials of $x_1, x_2, \ldots, x_m$. Thus, the multiplication by $x_1, x_2, \ldots, x_m$ on each base results in the linear combination of the bases in A. The product operations by $x_1, x_2, \ldots, x_m$ are expressed as linear transformation matrices m_h ($h = x_1, x_2, \ldots, x_m$). The bases in the residue ring $A = R/I$ and the transformation matrices are obtained by means of the Gröbner bases technique. The theorem of Stickelberger asserts that there is a one-to-one correspondence between an eigenvector $\boldsymbol{v}_\xi$ of the matrix m_h and the zero point $\xi = (\xi_1, \ldots, \xi_m)$ of the ideal I. The correspondence is given by

$$m_{x_i} \cdot \boldsymbol{v}_\xi = \xi_i \cdot \boldsymbol{v}_\xi. \tag{M.4}$$

The eigenvector $\boldsymbol{v}_\xi$ is common with all of m_{x_i}. (For details, see Sottile et al.[14] p. 101–130, "From Enumerative Geometry to Solving Systems of Polynomial Equations", by Frank Sottile.) The numerical calculations for the zeros $\xi = (\xi_1, \ldots, \xi_m)$ are executed as follows. We choose one x_i and prepare m_{x_i}. The secular equation gives us the eigenvector $\boldsymbol{v}_\xi$. If we multiply m_{x_j} ($j \neq i$) with $\boldsymbol{v}_\xi$, we can evaluate ξ_j ($j \neq i$). Thus all values of $\xi = (\xi_1, \ldots, \xi_m)$ can be obtained.

The energy functional, the normalization conditions for wavefunctions, and the HFR equation are polynomials with respect to LCAO (Linear Combination of Atomic Orbitals) coefficients and eigenvalues. Those equations are constructed from molecular integrals, which are in general, expressed as analytical functions of the included parameters, accordingly not being polynomials. Thus, the molecular integrals are replaced by approximations of polynomials of the included parameters. This means we can construct a set of polynomial equations, including not only wavefunctions and eigenvalues, but also the parameters for molecular integrals, i.e. the molecular orbital algebraic equation. If extra constraint conditions should be cast upon the HFR equation, we can prepare the polynomial equations for the constraints and add them into the set of polynomial equations. If the numerical coefficients are rationalized, we can avoid the lowering of the precision through the symbolic manipulation by means of arbitrary precision calculations of rational numbers.

One of the merits in this treatment is as follows. In the conventional method, the input data is the atomic structure and the output is the electronic structure. By contrast, in the present method, the possible input data are not limited to the atomic structures. We can select arbitrary parameters in the HFR equation and set them as the input. If the problem to be solved is properly established, we can compute other unknown variables properly. As to the properness of the problem, i.e., the existence of the roots of the set of polynomial equations, it can be judged from the ideal theory in mathematics on the condition whether its Gröbner bases have zero points set or not.

COMPUTATIONAL FLOW

The task flow is listed as follows.

1. Compute the analytic formula of the energy functional and the constraint conditions whose variables are eigenvalues, LCAO coefficients in wavefunctions, atomic coordinates, orbital exponents in molecular integrals and so on. Those analytic expressions are polynomials with respect to LCAO coefficients and eigenvalues, while the expressions are not polynomials with respect to other parameters, such as atomic coordinates and orbital exponents. Molecular integrals are rewritten by approximating polynomials with respect to the included parameters. For example, by choosing a certain point in the range of a parameter and applying the Taylor expansion around it, we can obtain the polynomial approximation. By rationalizing the numerical coefficients, we can prevent the lowering of the precision through the afterward symbolic manipulation.
2. Prepare the set of the equations to be solved, by way of the symbolic derivative, which is the minimization of the energy functional approximated by the polynomial.

3. By means of the symbolic manipulation, the above equations are transformed into others having the same roots. The initial equations are, at first, transformed into the Gröbner bases, by which we can check the existence of the solution. If the solutions are the set of isolated points, we can decompose the Gröbner bases into the triangular expression. There is an alternative way; by means of Stickelberger's theorem, the search for the solution is replaced by an eigenvalue problem.
4. By numerically solving the equations, the roots are computed and afford us the electronic structure and important information.

RESULTS

Several examples are demonstrated in this section. The units are given in atomic units. As an object, we choose the hydrogen molecule. Though we only show the examples of H_2 here, which is the simplest molecule, the applications of the present method are not limited to two-electron or two-atomic systems. The reason why we choose H_2 is as follows. Though this system is simple, it includes all kinds of quantum interactions operating in realistic materials and can be assumed as a miniature of general many-electron and polyatomic systems.

To construct the algebraic molecular orbital equation

At first, we will show how to construct the algebraic molecular orbital equation and the possibility of the Self-Consistent Field (SCF) calculations. The molecular integrals needed here are generated by STO base. The energy functional is the analytic equation of the one-centered molecular integrals at hydrogen A and B, the two-centered molecular integrals and the LCAO coefficients of the wavefunctions. As the expression of the inter-atomic distance R, the molecular integrals contain transcendental functions. One of the two-centered molecular integrals is shown in (R.1).

$$\begin{aligned}
[1s(A)1s(A)|1s(B)1s(B)] &= \iint dr dr' \frac{\phi^{1s}(r-R_A;za)\phi^{1s}(r-R_A;zb)\phi^{1s}(r'-R_B;zc)\phi^{1s}(r'-R_B;zd)}{|r-r'|} \\
&= \frac{64\, za^{3/2}\, zb^{3/2}\, zc^{3/2}\, zd^{3/2}}{R(za+zb)^3(zc+zd)^3} \\
&\quad - \frac{32\, za^{3/2}\, zb^{3/2}(za+zb)zc^{3/2}\, zd^{3/2}}{E^{R(zc+zd)}(za+zb-zc-zd)^2(zc+zd)^2(za+zb+zc+zd)^2} \\
&\quad - \frac{32\, za^{3/2} zb^{3/2} zc^{3/2} zd^{3/2}(zc+zd)}{E^{R(za+zb)}(za+zb)^2(za+zb-zc-zd)^2(za+zb+zc+zd)^2} \\
&\quad - \frac{64\, za^{3/2}\, zb^{3/2}\, zc^{3/2}\, zd^{3/2}(zc+zd)(3za^2+6za\, zb+3zc^2-2zc\, zd-zd^2)}{E^{R(za+zb)}\, R(za+zb)^3(za+zb-zc-zd)^3(za+zb+zc+zd)^3} \\
&\quad + \frac{64\, za^{3/2}\, zb^{3/2}(za+zc)\, zc^{3/2}\, zd^{3/2}(-za^2-2za\, zb-3zc^2+6zc\, zd+3zd^2)}{E^{R(zc+zd)}\, R(za+zb-zc-zd)^3(zc+zd)^3(za+zb+zc+zd)^3}
\end{aligned} \tag{R.1}$$

It is the two electron repulsion between 1s orbitals and classified as "Coulombic type", denoted as [1s(A)1s(B)|1s(A)1s(B)]. Here the notation "1s (A)" and "1s (B)" meaning the atomic orbitals centered on atoms A and B. The Slater orbital takes a form $\phi^{1s}(r; z) = \frac{z^{3/2}}{\pi^{1/2}} e^{-zr}$. There are other repulsion integrals, classified as the "exchange type" [1s(A)1s(B)|1s(A)1s(B)] and the "hybrid type" [1s(A)1s(A)|1s(A)1s(B)]. In general, the molecular integrals have more complicated expressions than (R.1). If STO is used, these integrals take more lengthy expressions, including transcendental functions, such as exponentials or exponential integrations, and infinite series summations.[5] In spite of this complicacy, we can treat them easily after the symbolic processing, by approximating them as finite degree polynomials by means of the Taylor expansion. It is noted here that the STO base can describe the physical property of the localized atomic wavefunction more precisely than by GTO (Gaussian Type Orbital) base, both in the neighborhood of the nucleus and in the remote region from it. Thus, the STO base becomes more advantageous for the purpose of expressing the molecular equations as the polynomials of the atomic coordinates. This is the reason why STO is adopted here. However, the following recipes are also applicable to the GTO calculations, and possibly, to semi-empirical calculations, such as AM1 (Austine Model 1)[17] and PM3 (Parameterized Model number 3),[18] or tight-binding model, where the matrix elements are given as analytic formulas.

As an example of a forward problem in the first principles molecular dynamics, the optimization of the structure (the distance between two hydrogen atoms) and the UHF electronic structure calculation are simultaneously executed.

We execute the Unrestricted Hartree-Fock (UHF) calculations in which the trial wavefunctions for up- and down-spins are defined as in (R.2) and (R.3). The corresponding eigenvalues are denoted as ev and ew. It is noted here: these trial functions with the bases of the orbital exponent 1 are too primitive to assure good agreements with experiments: for accuracy, we must optimize the orbital exponent to a suitable value. It is only to reduce the computational cost in the symbolic computation that we adopt such primitive trial functions. Here, the positions of hydrogen A and B are denoted as $\mathrm{R_A}$ and $\mathrm{R_B}$. The inter-atomic distance is $\mathrm{r} = \mathrm{R_A} - \mathrm{R_B}$. We use the notation, such as $\mathrm{X_A} = |\mathrm{x} - \mathrm{R}_A|$ and $X_B = |x - R_B|$.

$$\phi_{up}(x) = (a \exp(-x_A) + b \exp(-x_B))/\sqrt{\pi} \tag{R.2}$$

$$\phi_{down}(x) = (c \exp(-x_A) + d \exp(-x_B))/\sqrt{\pi} \tag{R.3}$$

The energy functional is transformed into the polynomial form by way of the fourth order Taylor expansion of the inter-atomic distance *r*, centered at the position of $R_o = 7/5$ atomic unit. The functional is generated in a standard way of molecular orbital theory, which is the total energy of the electron-nuclei system (given in the atomic units) with the constraint condition of the ortho-normality of the wavefunctions. The Lagrange multipliers are eigenvalues. The coefficients of real numbers are truncated to third decimal places and approximated as rational numbers, as is shown in (R.4). The LCAO coefficients for the up-spin electron are (a,b), (c,d) are those for the down-spin electron, ev is the eigenvalues of the up-spin electron, ew is that of the down-spin electron and *r* is the inter-atomic distance. It is rather a rough approximation to use numerical coefficients truncated to third decimal places, which causes the computational error (the order of a few percents) by the present method, compared to the conventional way with the double precision calculation. This approximation is only intended to reduce the computational cost in the symbolic processing. In this sense, examples in this section are mock-ups for realistic calculations, the aim of which is to illustrate the application of the present method, aside from the accuracy.

$$\begin{aligned}
&\Omega[\{\phi_\mathrm{i}(\xi);\ \text{the occupied orbital i},\ \xi \equiv (\mathrm{r}, \sigma_\mathrm{spin})\}] \\
&\quad = \sum_i \int \mathrm{d}\xi \phi_\mathrm{i}(\xi) \left(-\frac{1}{2}\nabla^2 + \sum_a \frac{\mathrm{Z_a}}{|\mathrm{r} - \mathrm{R_a}|} \right) \phi_\mathrm{i}(\xi) \\
&\quad + \frac{1}{2} \sum_{\mathrm{i,\,j}} \iint \mathrm{d}\xi \mathrm{d}\xi' \frac{\phi_\mathrm{i}(\xi)\phi_\mathrm{i}(\xi)\phi_\mathrm{j}(\xi')\phi_\mathrm{j}(\xi')}{|\mathrm{r} - \mathrm{r}'|} \\
&\quad - \frac{1}{2} \sum_{\mathrm{i,\,j}} \iint \mathrm{d}\xi \mathrm{d}\xi' \frac{\phi_\mathrm{i}(\xi)\phi_\mathrm{j}(\xi)\phi_\mathrm{j}(\xi')\phi_\mathrm{i}(\xi')}{|\mathrm{r} - \mathrm{r}'|} + \frac{1}{2} \sum_{\mathrm{a,b(a \neq b)}} \frac{\mathrm{Z_a Z_b}}{|\mathrm{R_a} - \mathrm{R_b}|} \\
&\quad - \sum_{\mathrm{i,\,j}} \lambda_\mathrm{ij} \left(\int \mathrm{d}\xi \phi_\mathrm{i}(\xi)\phi_\mathrm{j}(\xi) - \delta_\mathrm{ij} \right)
\end{aligned} \tag{R.4}$$

$$\Downarrow$$

```
Ω = (3571 − 1580*a^2 − 3075*a*b − 1580*b^2 − 1580*c^2 + 625*a^2*c^2 +
1243*a*b*c^2 + 620*b^2*c^2 − 3075*c*d + 1243*a^2*c*d + 2506*a*b*c*d +
1243*b^2*c*d − 1580*d^2 + 620*a^2*d^2 + 1243*a*b*d^2 + 625*b^2*d^2 + 1000*ev −
1000*a^2*ev − 1986*a*b*ev − 1000*b^2*ev + 1000*ew − 1000*c^2*ew −
1986*c*d*ew − 1000*d^2*ew − 5102*r + 332*a^2*r + 284*a*b*r + 332*b^2*r +
332*c^2*r + 43*a*b*c^2*r + 20*b^2*c^2*r + 284*c*d*r + 43*a^2*c*d*r +
80*a*b*c*d*r + 43*b^2*c*d*r + 332*d^2*r + 20*a^2*d^2*r + 43*a*b*d^2*r −
63*a*b*ev*r − 63*c*d*ew*r + 3644*r^2 + 75*a^2*r^2 + 724*a*b*r^2 + 75*b^2*r^2 +
75*c^2*r^2 − 401*a*b*c^2*r^2 − 124*b^2*c^2*r^2 + 724*c*d*r^2 −
401*a^2*c*d*r^2 − 1372*a*b*c*d*r^2 − 401*b^2*c*d*r^2 + 75*d^2*r^2 −
124*a^2*d^2*r^2 − 401*a*b*d^2*r^2 + 458*a*b*ev*r^2 + 458*c*d*ew*r^2 −
1301*r^3 − 69*a^2*r^3 − 303*a*b*r^3 − 69*b^2*r^3 − 69*c^2*r^3 +
146*a*b*c^2*r^3 + 42*b^2*c^2*r^3 − 303*c*d*r^3 + 146*a^2*c*d*r^3 +
618*a*b*c*d*r^3 + 146*b^2*c*d*r^3 − 69*d^2*r^3 + 42*a^2*d^2*r^3 +
146*a*b*d^2*r^3 − 139*a*b*ev*r^3 − 139*c*d*ew*r^3 + 185*r^4 + 12*a^2*r^4 +
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39*a*b*r^4 + 12*b^2*r^4 + 12*c^2*r^4 − 17*a*b*c^2*r^4 − 4*b^2*c^2*r^4 +
39*c*d*r^4 − 17*a^2*c*d*r^4 − 86*a*b*c*d*r^4 − 17*b^2*c*d*r^4 + 12*d^2*r^4 −
4*a^2*d^2*r^4 − 17*a*b*d^2*r^4 + 13*a*b*ev*r^4 + 13*c*d*ew*r^4)/1000

The precision of this approximation should be checked initially. The values of the original energy functional and the polynomial approximation at a = b = c = d = 1 and ev = ew = 0 are plotted in Figure 1 as the function of inter-atomic distance. It shows sufficient agreement in the range of r = 1−2 atomic unit. However, if the r goes out of this region, the polynomial approximation is not appropriate and we must try another center of the expansion R_0. By increasing the maximum degree of the Taylor expansion, we can enlarge the range of r where the polynomial approximation is valid.

We can make use of the symmetry in H_2 and express the wavefunctions as the linear combination of the symmetric and asymmetric ones, as in (R.5) and (R.6).

$$\phi_{up}(x) = \mathrm{t}(\exp(-x_A) + \exp(-x_B))/\sqrt{\pi} + \mathrm{s}(\exp(-x_A) - \exp(-x_B))/\sqrt{\pi} \tag{R.5}$$

$$\phi_{down}(x) = \mathrm{u}(\exp(-x_A) + \exp(-x_B))/\sqrt{\pi} + \mathrm{v}(\exp(-x_A) - \exp(-x_B))/\sqrt{\pi} \tag{R.6}$$

This is the transformation by (R.7).

$$a = \mathrm{t} + \mathrm{s}, b = \mathrm{t} - \mathrm{s}, c = \mathrm{u} + \mathrm{v}, d = \mathrm{u} - \mathrm{v} \tag{R.7}$$

Then, the HFR equation is given by the set of equations in (R.8), where (t, s) is the LCAO coefficient for up-spin, (u, v) is that for down spin, ev is the eigenvalue for up spin, ew is that for down spin, and *r* is the inter-atomic distance.

$$① \; \frac{\partial\Omega}{\partial a} + \frac{\partial\Omega}{\partial b} = 0 \longrightarrow \tag{R.8}$$

32*s*u*v*r^4 − 336*s*u*v*r^3 + 992*s*u*v*r^2 − 160*s*u*v*r + 40*s*u*v − 324
*t*u^2*r^4 + 2572*t*u^2*r^3 − 6448*t*u^2*r^ 2 + 584*t*u^2*r + 19936*t*u^2 +
156*t*v^2*r^4 − 1068*t*v^2*r^3 + 2248*t*v^2*r^2 − 80*t*v^2*r − 32*t*v^2
+26*t*ev*r^4 − 278*t*ev*r^3 + 916*t*ev*r^2 − 126*t*ev*r − 7972*t*ev + 126*t*r
^4 − 882*t*r^3 + 1748*t*r^2 + 1896*t*r − 12470*t = 0

$$② \; \frac{\partial\Omega}{\partial a} - \frac{\partial\Omega}{\partial b} = 0$$

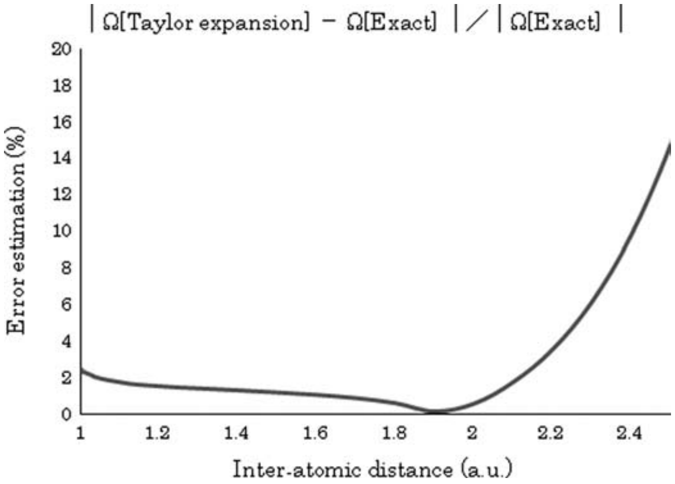

Figure 1. **Shows the deviation between the exact energy functional Ω and its polynomial approximation, |Ω(Taylor expansion) − Ω(Exact)|/|Ω(Exact)| v.s. the interatomic distance r, given in percentage.**

→156*s*u^2*r^4 − 1068*s*u^2*r^3 + 2248*s*u^2*r^2 − 80*s*u^2*r − 32*s*u^2
− 52*s*v^2*r^4 + 236*s*v^2*r^3 − 32*s*v^2*r^2 − 104*s*v^2*r + 48*s*v^2
− 26*s*ev*r^4 + 278*s*ev*r^3 − 916*s*ev*r^2 + 126*s*ev*r − 28*s*ev − 30*s*r^4
+ 330*s*r^3 − 1148*s*r^2 + 760*s*r − 170*s + 32*t*u*v*r^4 − 336*t*u*v*r^3
+992*t*u*v*r^2 − 160*t*u*v*r + 40*t*u*v = 0

$$③ \quad \frac{\partial\Omega}{\partial c}+\frac{\partial\Omega}{\partial d}=0$$

→156*s^2*u*r^4 − 1068*s^2*u*r^3 + 2248*s^2*u*r^2 − 80*s^2*u*r − 32*s^2*u
+ 32**t*v*r^4 − 336*s*t*v*r^3 + 992*s*t*v*r^2 − 160*s*t*v*r + 40*s*t*v
− 324*t^2*u*r^4 + 2572*t^2*u*r^3 − 6448*t^2*u*r^2 + 584*t^2*u*r + 19936*t^2*u
+ 26*u*ew*r^4 − 278*u*ew*r^3 + 916*u*ew*r^2 − 126*u*ew*r − 7972*u*ew
+126*u*r^4 − 882*u*r^3 + 1748*u*r^2 + 1896*u*r − 12470*u = 0

$$④ \quad \frac{\partial\Omega}{\partial c}-\frac{\partial\Omega}{\partial d}=0$$

→ − 52*s^2*v*r^4 + 236*s^2*v*r^3 − 32*s^2*v*r^2 − 104*s^2*v*r + 48*s^2*v
+ 32*s*t*u*r^4 − 336*s*t*u*r^3 + 992*s*t*u*r^2 − 160*s*t*u*r + 40*s*t*u
+ 156*t^2*v*r^4 − 1068*t^2*v*r^3 + 2248*t^2*v*r^2 − 80*t^2*v*r − 32*t^2*v
− 26*v*ew*r^4 + 278*v*ew*r^3 − 916*v*ew*r^2 + 126*v*ew*r − 28*v*ew
−30*v*r^4 + 330*v*r^3 − 1148*v*r^2 + 760*v*r − 170*v = 0

$$⑤ \quad \frac{\partial\Omega}{\partial(\mathrm{ev})}=\left\langle\phi_{up}\middle|\phi_{up}\right\rangle-1=0$$

→ − 13*s^2*r^4 + 139*s^2*r^3 − 458*s^2*r^2 + 63*s^2*r − 14*s^2 + 13*t^2*r^4
−139*t^2*r^3 + 458*t^2*r^2 − 63*t^2*r − 3986*t^2 + 1000 = 0

$$⑥ \quad \frac{\partial\Omega}{\partial(\mathrm{ew})}=\langle\phi_{down}|\phi_{down}\rangle-1=0$$

→13*u^2*r^4 − 139*u^2*r^3 + 458*u^2*r^2 − 63*u^2*r − 3986*u^2 − 13*v^2*r^4
+139*v^2*r^3 − 458*v^2*r^2 + 63*v^2*r − 14*v^2 + 1000 = 0

⑦ $\dfrac{\partial\Omega}{\partial r} = 0$

→312*s^2*u^2*r^3 − 1602*s^2*u^2*r^2 + 2248*s^2*u^2*r − 40*s^2*u^2
− 104*s^2*v^2*r^3 + 354*s^2*v^2*r^2 − 32*s^2*v^2*r − 52*s^2*v^2
− 52*s^2*ev*r^3 + 417*s^2*ev*r^2 − 916*s^2*ev*r + 63*s^2*ev − 60*s^2*r^3
+ 495*s^2*r^2 − 1148*s^2*r + 380*s^2 + 128*s*t*u*v*r^3 − 1008*s*t*u*v*r^2
+ 1984*s*t*u*v*r − 160*s*t*u*v − 648*t^2*u^2*r^3 + 3858*t^2*u^2*r^2
− 6448*t^2*u^2*r + 292*t^2*u^2 + 312*t^2*v^2*r^3 − 1602*t^2*v^2*r^2
+ 2248*t^2*v^2*r − 40*t^2*v^2 + 52*t^2*ev*r^3 − 417*t^2*ev*r^2 + 916*t^2*ev*r
− 63*t^2*ev + 252*t^2*r^3 − 1323*t^2*r^2 + 1748*t^2*r + 948*t^2 + 52*u^2*ew*r^3
− 417*u^2*ew*r^2 + 916*u^2*ew*r − 63*u^2*ew + 252*u^2*r^3 − 1323*u^2*r^2
+ 1748*u^2*r + 948*u^2 − 52*v^2*ew*r^3 + 417*v^2*ew*r^2 − 916*v^2*ew*r
+ 63*v^2*ew − 60*v^2*r^3 + 495*v^2*r^2 − 1148*v^2*r + 380*v^2 + 740*r^3

−3903*r^2 + 7288*r − 5102 = 0

To solve the algebraic molecular orbital equation by symbolic-numeric computation
At first, we assume $r = 7/5$ to see the possibility of actual first principles calculations. The entry as is shown by $\partial\Omega/\partial \mathrm{r} = 0$ in (R.8) is replaced by (R.9).

$$5r - 7 = 0 \tag{R.9}$$

The lexicographic order Gröbner bases are shown in (R.10) with the monomial ordering of s < t < u < v < ev < ew < r. (Hereafter this monomial ordering is kept in the following computations.) In the entries of the Gröbner bases, those variables show themselves in the reverse order of r, ew, ev, v, u, t, s, by turns. The relationships among those variables, which are ambiguous in the expression of HFR equation, may be extracted there.

J[1] = r − 1.4 (R.10)

J[2] = 0.000000000000000044923679950280179834153752545837120050869800531719*ew^6
+ 0.000000000000000083784847684948917991823061663879813241022968255965*ew^5
+ 0.000000000000000055224314065899427802789765894852689587104815167352*ew^4
+ 0.000000000000000014691161157734078517931578598749996418029499346849*ew^3
+ 0.0000000000000000011979351185242681597299140874114661346717404726834*ew^2
− 0.0000000000000000000083986996356237445246657340658569895849354776549449*ew
− 0.00000000000000000000037230409053155950263983522183691557632339096670694

J[3] = 0.00000000013962876535705715746622071381953097719892118070071*ev
+ 0.00000032173656936235047932064238004296019881075131225526*ew^5
+ 0.00000033291652477736005207182034309098081628696594819331*ew^4
+ 0.00000006589110323648302126095620051055593446942561498025 1*ew^3
− 0.0000000145021947963247304958954925854495404878708307549*ew^2
− 0.00000000258966394703031452768238081492650376302930226169 44*ew
+ 0.00000000005081919751322588124435323091396968621359149411 8136

J[4] = 0.0035337421249281116351414330877752843125543561935616*v*ew^4
+ 0.0021801710635532512041192523955501421176113052868825*v*ew^3
+ 0.00024683412076704120861849546037854544501562730166012*v*ew^2
− 0.0000014554651684258252511501850703694711773679621730295*v*ew
− 0.00000007520336491246198410768915301515145627392367086 0722*v

J[5] = 0.00000000000002469182263912597327197080785436650088580523083 8289*v^2
− 0.000000000047190217319792339322638580120931177672487391351614*ew^5
− 0.000000000074233725861437012556372485089134912758173742859754*ew^4
− 0.000000000037044087563918384281802854504031102187085751576865*ew^3
− 0.0000000000055056937948011551503818116670012263028105621886299*ew^2
+ 0.0000000000000289247109748205722101525546739216874984857506225 16*ew
− 0.0000000000000485199500275950858789604761685291061709957821 84575

J[6] = 0.00082444529533914000480121749252034857614275087163634*u*ew^4
+ 0.0015402471286109903529960234596133438365658562434456*u*ew^3
+ 0.0010186155101412674041097562139745242960275920262626*u*ew^2
+ 0.00027330147151793449108809755546973584926704784843595*u*ew
+ 0.000023152649811839442946188162579039171063101525686031*u

J[7] = 0.15500652085373657278272155048840425269081666861422*u*v*ew^2
+ 0.096124486745923798453025086330083252761630136665135*u*v*ew
+ 0.011178119900970398824611330746954877639528183070683*u*v

J[8] = 0.0000000000000024691822639125973271970807854366500885805230838289*u^2

+ 0.000000000000661854196219566262518458693577537389005453156961 92*ew^5

+ 0.00000000000104114593559623870281793809899690868803363016919 08*ew^4

+ 0.000000000000519552275700609620984987581216899088839593845151 93*ew^3

+ 0.0000000000000772186853155438576293540302694999396484080162796 23*ew^2

− 0.0000000000000004056760578869777434741548572196422923655933747 5379*ew

− 0.00000000000000002336874149055445010614708278861304342621920416 8902

J[9] = 0.0619709181331632165671838700351535038880015135145 67*t*ew^4

+ 0.0778696729851536106601989192087910586233444646828 8*t*ew^3

+ 0.0295292875457438087096204472450619269508636195133 21*t*ew^2

+ 0.0032178375021467349512602370986204354827641359493411*t*ew

+ 0.000043456853031823070001289851734608283302642795735406*t

J[10] = 0.0518741366729778499986886699102483527457785030856 6*t*v*ew^3

+ 0.0329814165688916253656643121212067736852468257601 42*t*v*ew^2

+ 0.0042447701517134049943862889216523608128280851170331*t*v*ew

+ 0.000058600461674134415884220932579569266784799169692295*t*v

J[11] = 0.0217917033542653598802626469372919880768213136857 22*t*u*ew^3

+ 0.0270410377833077439842866167839432112120824559894 42*t*u*ew^2

+ 0.0099601988616932931997530597003570949767046400427524*t*u*ew

+ 0.00097550648450924773054739454162691886820402290190827*t*u

J[12] = 0.0000000000000024691822639125973271970807854366500885805230838289*t^2

− 0.00000000000198971010605196521073951254782084998209238102702 69*ew^5

− 0.00000000000170255700897566555354942878105283795981196597736 02*ew^4

− 0.0000000000000234835922003041993487421509254127188129940598659 64*ew^3

+ 0.000000000000196737278128084850157481822936643807630855116924 87*ew^2

+ 0.0000000000000197860784570238330525920261811058210268663905357 66*ew

− 0.0000000000000004421907929073940449226936063716746614280127929 5227

```
    J[13] = 0.0560848331751266786864948113251063854255183697836O4*s*ew^2
                + 0.034127439269225675895016122448171947840127214030889*s*ew
                − 0.00066282300441698232705078773127382486945402101120119*s
                − 0.040893885020249465973553191938478590309960079399638*t*u*v*ew
                − 0.029010301971762382682320743416650072000710482565746*t*u*v

J[14] = 0.021791703354265359880262646937291988076821313685722*s*v*ew
            − 0.00041052862271488237533112188857801258113775891824163*s*v − t*u*ew^2
            − 0.91523243331780979308516147067869265402585316644918*t*u*ew
            − 0.18279835739609284049315718860436264109118081404686*t*u

 J[15] = 0.082689621743132526006561521010847989515268982874621*s*u*ew
             + 0.051874136672977849998688669910248352745778503O8566*s*u + t*v*ew^2
             + 0.45088158483424862414602508768019029048144708971225*t*v*ew
             + 0.0068176823481038061179522681529012450074191772534997*t*v

     J[16] = 0.061970918133163216567183870035153503888001513514567*s*u*v
                 + 7.54843402550665153673201812730961379367248454713989*t*ew^3
                 + 9.2977596625794358858261233928027031703300204455612*t*ew^2
                 + 2.93333692208165449675224101101090746851954196539922*t*ew
                 + 0.043698233453379147442339681621264612101282386252875*t

   J[17] = 0.15500652085373657278272155048840425269081666861422*s*t − u*v*ew
               − 0.31006594502119821790385986369248662988955022236O5*u*v

J[18]=0.0000000000000024691822639125973271970807854366500885805230838289*s^2
          +0.000000000014186637003179206604978647501193712331871881329982*ew^5
          +0.000000000012139234851393709326934898047082480718477074921104*ew^4
          +0.00000000000016743805897305182765540212510939603762998421893102*ew^3
          −0.0000000000014027371833250135761788614236060225048185772213358*ew^2
          −0.000000000000141074778648629063444287891909984518147600123O8984*ew
          −0.0000000000000018657929453315597187256856909000195939743454954377
```

The triangular decomposition to (R.10) is shown in (R.11), which involves five decomposed sets of equations. One decomposed set includes seven entries, into each of which, the seven variables is added one by one, with the order of r, ew, ev, v, u, t, s.

```
[1] :                                                                      (R.11)
      _[1]  =  r − 1.4
      _[2] = 0.082689621743132526006561521010847989515268982874621
         *ew + 0.05187413667297784999868866991024835274577850308566
      _[3] = 0.00000000013962876535705715746622071381953097719892118070071
         *ev + 0.00000000000021872894505215127104699976329395744001395648217513
      _[4]  =  v
      _[5] = 0.00000000000000024691822639125973271970807854366500885805230838289
         *u^2 − 0.000000000000000703872760120252538315069754210795
         41060390364383305
      _[6]  =  t
      _[7] = 0.00000000000000024691822639125973271970807854366500885805230838289
         *s^2 − 0.00000000000000050186141759442129979160381879133091558873472043949
 [2]:
      _[1]  =  r − 1.4
      _[2]  =  ew − 0.018838757853893431115706795065601087293579573640499
      _[3]  =  ev − 0.018838757853893431115706795065601087293579573640499
      _[4]  =  v^2 − 2.03250049593012100694952569568426974696181825868366
      _[5]  =  u
      _[6]  =  t
      _[7] = 0.00000000000000024691822639125973271970807854366500885805230838289
         *s^2 − 0.00000000000000050186141759442129979160381879133091558873472043949
 [3]:
      _[1]  =  r − 1.4
      _[2]  =  ew^2 + 0.620131890042396435807719727384973259779100444721
         *ew + 0.072113868754708844917382916961852739039135803532834
      _[3]  =  ev − ew
      _[4]  =  v^2 − 14.80995023428197133951905921507729315089177369253934
         *ew − 5.77765333933354558148702071632256029046854951290411
      _[5]  =  u^2 + 2.07713129226284416025022121618132789954954241021854
         *ew + 0.52526673231711754540325634713814260954516716824085
      _[6]  =  t^2 + 2.07713129226284416025022121618132789954954241021854
         *ew + 0.52526673231711754540325634713814260954516716824085
      _[7]  =  s + 8.55670765807561749977207690461050758297371934231746
         *t*u*v*ew + 6.24834985328317561951025512690840116358160281553919*t*u*v
 [4]:
      _[1]  =  r − 1.4
      _[2]  =  ew + 0.62075494398358690094167914213207711792332315380224
      _[3]  =  ev + 0.62075494398358690094167914213207711792332315380224
      _[4]  =  v
      _[5]  =  u^2 − 0.28506310384917288370291954789447830487339321330884
      _[6]  =  t^2 − 0.28506310384917288370291954789447830487339321330884
      _[7]  =  s
 [5]:
      _[1]  =  r − 1.4
      _[2]  =  ew + 0.015665034671961754863974784720813826678603082481373
      _[3]  =  ev + 0.6273355178007699660610156274085545071738486487756
      _[4]  =  v^2 − 2.03250049593012100694952569568426974696181825868366
      _[5]  =  u
      _[6]  =  t^2 − 0.28506310384917288370291954789447830487339321330884
      _[7]  =  s
```

There are numerical coefficients that are very lengthy due to a problem in the algorithm in the Gröbner bases generation.[19–21] The computational procedure applies the Buchberger's algorithm, in which the addition, subtraction, multiplication and division are iterated to the polynomial system.

In the intermediate expression through the computation, some polynomials with huge degrees may arise, some of whose coefficients have extreme difference in the numerical scale compared to others. This difference in the scale of coefficients will remain in the final result. To assure the numerical accuracy, we must resort to the computations with arbitrary precision.

Though the solutions include complex ones, the physically admissible real solutions are shown in Table 1. We obtain four combinations, where the two electrons of up- or down-spins are located the symmetric or asymmetric wavefunctions. This means we obtain both the ground and the excited states.

Table 1. Shows the solutions for Equations (R.11). The electron 1 and 2 lie in the up- and down- spin, respectively.

	Solution 1	Solution 2	Solution 3	Solution 4
s (the coefficient for electron 1)	0.00000	− 1.42566	0.00000	− 1.42566
t (the coefficient for electron 1)	− 0.53391	0.00000	− 0.53391	0.00000
u (the coefficient for electron 2)	− 0.53391	− 0.53391	0.00000	0.00000
v (the coefficient for electron 2)	− 0.53391	0.00000	− 1.42566	− 1.42566
ev (the eigenvalue for electron 1)	− 0.62075	− 0.01567	− 0.62734	0.01884
ew (the eigenvalue for electron 2)	− 0.62075	− 0.62734	− 0.01567	0.01884
r (the inter-atomic distance)	1.40000	1.40000	1.40000	1.40000
The total energy	− 1.09624	− 0.49115	− 0.49115	0.15503
electron1	symmetric orbital	asymmetric orbital	symmetric orbital	asymmetric orbital
electron2	symmetric orbital	symmetric orbital	asymmetric orbital	asymmetric orbital

Atomic and electronic structural optimization executed simultaneously

The inter-atomic distance, r, and the wavefunctions can be optimized at the same time, as is done in Car-Parrinello method. In this case the inter-atomic distance, r, is an unknown to be determined, not a fixed constant.

In order to obtain the ground state alone, we add Equation (R.12) into the equations in (R.8).

$$s = v = 0 \tag{R.12}$$

(This method is applicable to this example only. In general, the ground state is given as a solution where the sum of the total occupied eigenvalue becomes a minimum of one. To specify the ground state, it is enough to compute eigenvalues alone. For this purpose, in making the triangular decomposition of the equations, we can prepare the equations including only eigenvalues as unknowns. We have only to solve them). With this treatment, we can replace the equation to be solved with a simpler one. The part of the equation including r is shown in Equation (R.13), whose real solutions are shown in Table 2. To determine the inter-atomic distance, we have only to solve this part of the equation.

Table 2. Shows the real solutions in the Equations (R.13).

	Solution1	Solution2	Soultion3
r	− 1.812	1.652	6.010
ev	− 6.675	− 0.578	− 17.585
t	0.846	0.545	0.983

[1]: (R.13)

```
  8942144364*r^23 − 435341589039*r^22 + 9813157241157*r^21 − 134458128500631
*r^20 + 1251986164962728*r^19 − 8584760758387395*r^18 + 48176522279858253
*r^17 − 254992901607817871*r^16 + 1360184656773665254*r^15 − 6685412705413184235
*r^14 + 26848712421674517351*r^13 − 82265960807423324641*r^12 + 185370
480318135661708*r^11 − 295651827763150999108*r^10 + 307426892321213994312
*r^9 − 148683667595876075980*r^8 − 97338526988608612178*r^7 + 245772518836579791529
```

*r^6 − 200002425723099153061*r^5 + 47298638179277635737*r^4 + 46006348188804187952
*r^3 − 41646082527529600720*r^2 + 13118922400543578496*r − 1869747053688110592 = 0

[2]:
10313892*r^15 − 376866027*r^14 + 6245669754*r^13 − 61144647973*r^12 + 387764699571
64699571*r^11 − 1646957525797*r^10 + 4691411679124
*r^9 − 8760215434992*r^8 + 10281598671237*r^7 − 7316755042677*r^6 + 3784010771997
*r^5 − 2194016637700*r^4 − 299532295668*r^3 + 1482785614608*r^2 − 746000940352
*r + 36100845312 = 0

[3]:
10313892*r^15 − 376866027*r^14 + 6245669754*r^13 − 61144647973*r^12 + 378596795571
96795571*r^11 − 1405917509797*r^10 + 1917133055124
*r^9 + 9044372533008*r^8 − 55118065080763*r^7 + 103464
030245323*r^6 + 92432281739997*r^5 − 770797010005700*r^4 + 1063674493728332
*r^3 + 652030557238608*r^2 − 2854269358708352*r + 1954998898509312 = 0

The solutions include the positive and negative real valued ones and the imaginary valued ones. The admissible solutions (r > 0) are two in number, as in Table 2. However, the solution which lies in the valid range of the Taylor expansion is only that of r ∼ 1.6. The discrepancy between the solution and the experimental value (r ∼ 1.4) is due to the numerical error caused by the roughness of the fourth order Taylor expansion and the rationalization of the numerical coefficients, being truncated. In addition, it is also due to the not-optimized orbital exponent in the trial wavefunctions.

A recipe for an inverse problem

It is demonstrated here how to solve a related inverse problem. Suppose a problem, where the energy difference between the occupied and the unoccupied states has a certain value; we should evaluate the inter-atomic distance, r, at which the energy difference shows this value. This example is a miniature of the inverse problem to find the lattice constants at which the band gap shows the desired width. In this case, we execute Restricted-Hartree-Fock (RHF) calculations. The wavefunctions of the occupied and the unoccupied are given in (R.14) and (R.15). The eigenvalues are denoted as e_{occ}, e_{unocc}.

$$\phi_{occ}(x) = s(\exp(-x_A) + \exp(-x_B))/\sqrt{\pi} \tag{R.14}$$

$$\phi_{unocc}(x) = t(\exp(-x_A) + \exp(-x_B))/\sqrt{\pi} \tag{R.15}$$

The required equations are presented in (R.16), whose details are omitted here. The set of the equations for the occupied state can be obtained the same way as was done with the example of the UHF calculation. The orthogonality condition to the occupied and the unoccupied states is added to it.

$$\begin{aligned}
&\tfrac{\partial\Omega}{\partial s} = 0\\
&\tfrac{\partial\Omega}{\partial t} = 0\\
&\tfrac{\partial\Omega}{\partial(e_{occ})} = \langle\phi_{occ}|\phi_{occ}\rangle - 1 = 0\\
&\langle\phi_{unocc}|\phi_{unocc}\rangle = 1\\
&\langle\phi_{occ}|\phi_{unocc}\rangle = 0\\
&e_{occ} - e_{unocc} = E_{gap}
\end{aligned} \tag{R.16}$$

For example, let us compute r, which gives $\mathrm{E}_{\mathrm{gap}} = \mathrm{e}_{\mathrm{unocc}} - \mathrm{e}_{\mathrm{occ}} = 0.9$. The real solutions are those at r = −1.103, 0.307, 1.643, 3.958. The solution in the valid range of the Taylor expansion is only that at r = 1.643. The eigenvalues of the occupied and the unoccupied states are shown in Figure 2 as the function of R. It shows this result is accurate.

Then, in this case, is the structure stable? If we evaluate the inter-atomic forces, it can be easily judged. On the other hand, with the view of symbolic-numeric solving, we can use the following judgment. To do this, in the set of the equations in (R.16) we insert the condition of Equation (R.17),

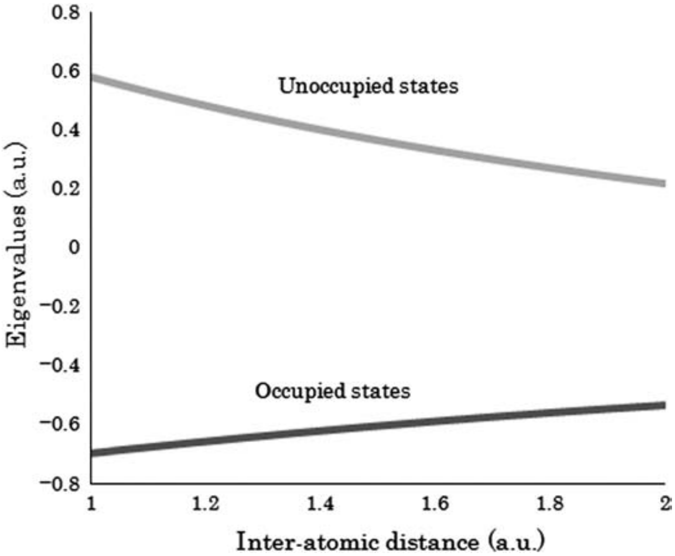

Figure 2. Shows the dependence of occupied and unoccupied eigenvalues on the inter-atomic distance. Eigenvalues of the occupied and the unoccupied states are shown by the real and broken lines, respectively.

the minimization condition of the energy functional with respect to the inter-atomic distance, r.

$$\frac{\partial \Omega}{\partial r} = 0 \tag{R.17}$$

The computed Gröbner base is {1} (as a set of polynomials). It includes only a constant polynomial “1”. The zeros of the Gröbner bases provide us with the solution to the equations. However, the term {1}, as a polynomial, does not become zero. Thus, we can conclude that the supposed problem does not have a solution with a stable structure.

The electronic and atomic structure optimization rewritten in a single matrix eigenvalue problem

Here we show another numerical method by means of Stickelberger’s theorem. The electronic and atomic structure optimization is rewritten in a single matrix eigenvalue problem. The example is the optimization of inter-atomic distance in H_2, where the RHF calculation is executed. The trial wavefunction is given as Equation (R.18).

$$\phi_{occ}(x) = t(\exp(-x_A) + \exp(-x_B))/\sqrt{\pi} \tag{R.18}$$

The eigenvalue is denoted as ev and the inter-atomic distance is *r*. The HFR equation becomes the set of polynomials expressed by t, ev, and r. This set of equations, in the mathematical sense, constructs a zero-dimensional ideal, I, in the polynomial ring A = R[t, ev, r], the zeros of which correspond to a residue ring A/I. (R means the rational number field.) A/I is a finite-dimensional vector space over R. Its base is represented by monomials of t, ev, and r, which are shown in (R.19).

b[1] = t*ev*r^3 b[2] = t*r^4 b[3] = t^3*ev b[4] = t*ev^3 b[5] = t^3*r
b[6] = t*ev^2*r b[7] = t*ev*r^2 b[8] = t*r^3 b[9] = ev*r^3 b[10] = r^4
b[11] = t^3 b[12] = t^2*ev b[13] = t*ev^2 b[14] = ev^3 b[15] = t^2*r
b[16] = t*ev*r b[17] = ev^2*r b[18] = t*r^2 b[19] = ev*r^2 b[20] = r^3
b[21] = t^2 b[22] = t*ev b[23] = ev^2 b[24] = t*r b[25] = ev*r
b[26] = r^2 b[27] = t b[28] = ev b[29] = r b[30] = 1

(R.19)

The transformation matrix corresponding to the multiplication by the variable, t, is shown in (R.20).

$$
\begin{array}{ccccccccccccccccccc}
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 1. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 1. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 1. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 1. & 0. & 0. & 0. & 0. & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 1. & 0. & 0. & 0. & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 1. & 0. & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 1. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
2.46857 & 0.250358 & 0.000433932 & -0.519297 & 0.000905017 & -0.229989 & 0.400711 & 0.0592776 & 0. & 0. & 0.00037686 & 0. & -0.0488928 & 0. & 0. & 0.0253457 & 0. & 0.0106224 & 0. \\
2.85865 & 1.8302 & 0.010766 & -3.25489 & 0.00562066 & 0.195796 & 0.755874 & 0.513375 & 0. & 0. & -0.0000321824 & 0. & 0.188933 & 0. & 0. & 0.177659 & 0. & 0.101971 & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
-3.28726 & 16.9846 & 0.815632 & -68.3604 & 0.199106 & -6.99935 & 17.2255 & 12.5718 & 0. & 0. & 0.010156 & 0. & 2.94616 & 0. & 0. & 8.19509 & 0. & 3.31843 & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
1.10471 & 0.0541875 & 0.0005962 & -0.43266 & 0.000241163 & 0.0161693 & 0.169585 & 0.0191714 & 0. & 0. & 4.36536\times 10^{-6} & 0. & 0.00658837 & 0. & 0. & 0.0121792 & 0. & 0.00422577 & 0. \\
-41.1091 & 92.4474 & 0.457252 & -248.171 & 0.949199 & 7.93844 & -9.06291 & 33.1339 & 0. & 0. & 0.0550604 & 0. & 7.29159 & 0. & 0. & -1.91674 & 0. & 7.47555 & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
0.381952 & -0.482168 & -0.00366255 & 1.05379 & -0.00214058 & -0.266467 & 0.0658373 & -0.170307 & 0. & 0. & -0.0000384651 & 0. & -0.0484318 & 0. & 0. & 0.00667468 & 0. & -0.0375156 & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
-13.5886 & -1.50329 & 0.000693225 & 2.88068 & -0.00965266 & 1.64897 & -2.25783 & -0.319754 & 0. & 0. & -0.00357141 & 0. & 0.303898 & 0. & 0. & -0.125453 & 0. & -0.05279 & 0. \\
-9.85681 & -9.15049 & -0.0964526 & 22.4732 & -0.0359414 & -1.57568 & -3.20362 & -3.05264 & 0. & 0. & 0.00102063 & 0. & -1.41532 & 0. & 0. & -1.22295 & 0. & -0.657454 & 0. \\
480.008 & -277.275 & -3.39938 & 331.95 & 0.518864 & -172.803 & 89.1965 & -51.8746 & 0. & 0. & 0.670983 & 0. & -36.5975 & 0. & 0. & 14.0368 & 0. & 1.13365 & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
7.34299 & 6.6392 & 0.00938662 & -17.0623 & 0.0147453 & 1.43466 & 1.18689 & 1.56243 & 0. & 0. & -0.000518309 & 0. & 0.363976 & 0. & 0. & 0.111898 & 0. & 0.278794 & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
15.2609 & -1.665537 & -0.0325943 & 4.78209 & -0.0255023 & -8.07839 & 2.60648 & -0.91568 & 0. & 0. & 0.00589181 & 0. & -0.519365 & 0. & 0. & 0.0343565 & 0. & -0.229064 & 0. \\
4.37903 & 18.2502 & 0.31662 & -48.1151 & 0.0770211 & 4.75029 & 3.82373 & 7.43136 & 0. & 0. & -0.0068586 & 0. & 3.54526 & 0. & 0. & 3.3935 & 0. & 1.7193 & 0. \\
0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. & 0. \\
176.488 & 32.4122 & 0.0776154 & -62.9606 & 0.177886 & -12.346 & 26.5689 & 7.04326 & 0. & 0. & -0.0170918 & 0. & -5.2778 & 0. & 0. & 1.56207 & 0. & 1.18349 & 0. \\
-21.5227 & -39.0633 & -0.494407 & 121.758 & -0.355958 & 0.576694 & -5.67678 & -17.58 & 0. & 0. & -0.00940279 & 0. & -3.59933 & 0. & 0. & -4.92509 & 0. & -4.18857 & 0. \\
22.4313 & 97.9958 & 1.19706 & -159.224 & 0.120322 & 24.8872 & 3.17625 & 23.7835 & 0. & 0. & -0.11519 & 0. & 0.58433 & 0. & 0. & 1.73174 & 0. & 2.14857 & 0.
\end{array}
\tag{R.20}
$$

The other transformation matrices are calculated in similar ways. We can evaluate the eigenvector, $\boldsymbol{v}_{\xi}$, of the matrix, $\mathrm{m_t}$ and can obtain eigenvalues corresponding to variables t and ev by means of the relations in (R.21) and (R.22). The values for t and ev are computed as ξ_t and ξ_{ev}. The real valued solutions are identical to those in Table 2, given in the previous example.

$$\mathrm{m_t} \cdot \mathrm{v}_{\xi} = \xi_t \cdot \boldsymbol{v}_{\xi} \tag{R.21}$$

$$\mathrm{m_{ev}} \cdot \mathrm{v}_{\xi} = \xi_{\mathrm{ev}} \cdot \boldsymbol{v}_{\xi} \tag{R.22}$$

DISCUSSION

The advantages of the present method are recapitulated here.

In the present method, the fundamental Equation (the HFR equation and the constraints) is expressed as a set of polynomial Equations (algebraic molecular orbital equation), combined with each other seamlessly. In the conventional method, the loop for eigenvalue solutions, that of Self Consistent Field (SCF) procedure, and that of the optimization calculation are nested with one another. By contrast, in the present method, those nested loops are unified in a flow of the search for roots in a set of polynomial equations, which afford us a clear view in the numerical computation and a shortcut to the necessary information. The roots of the triangulated equations are obtained one by one numerically. The eigenvalue solutions for multi-dimensional matrix and the iterative approximation for the mean field, where the difficulty in the convergence generally occurs, are not needed. It is not necessary to iterate the independent optimization toward the atomic structure and the wavefunctions. Concerning the structural optimization, by means of the elimination of the variables, we can obtain a set of equations with only atomic coordinates. The roots are the stable optimized structure. It means that the “pseudo” atomic interactions are obtained without SCF calculations. In the optimization of other parameters there are similar merits. The present method will simulate the cases where the dynamics of the wavefunctions and that of the nuclei are strongly coupled with each other, beyond the adiabatic approximation.

The algebraic molecular orbital equation, expressed as polynomial sets, informs us of the relationships between unknown variables. Thus, in order to evaluate those unknowns, we can divide suitable parts of them into prepared inputs and expected outputs, respectively. The calculation is not confined to the conventional framework, such as, those where the input is the structure and the output is the electronic states. The distinctions between forward and inverse problems are eradicated, and we can treat all of them as forward problems in a unified way. In order to cope with the inverse problem, we should check whether it is well-posed or not. The present method affords us a key to this. After the transformation from the fundamental equation to the Gröbner bases, the present method can inspect the 'properness' of the problem, i.e. the existence of the solutions. Based on the mathematical ideal theory, it can judge the existence of a solution, which provides us the zeros of the Gröbner bases. If the solutions exists, it can also be determined whether these are isolated points or sets with more than one dimension. If the solutions are isolated, the numbers of the solutions, in the range of the real or complex numbers, can be known (see references on symbolic numeric computations).

The computations in the previous section, showed how we fixed the orbital exponent, z, at unity and converted molecular integrals into polynomials of inter-atomic distance R alone. The algebraic molecular equations can be extended to a more general case. We can make multi-variable Taylor expansions for the atomic coordinates and orbital exponents in order to prepare polynomials of those two kinds of variables. If this is done, the equation includes both parameters and we could optimize atomic coordinates and orbital exponents simultaneously.

This present work is at a primitive stage. At present, this study does not necessarily afford us a sufficiently precise calculation. One reason is the constraint of access to the hardware. The cost in the symbolic computation tends to be so massive (especially on memory usage) that we are obliged to use simplified molecular integrals, reduce the degrees of the approximating polynomial and rationalize numerical coefficients in lower accuracies. As for the overall computation cost in the explanatory calculations in the previous section, the generation of the molecular integrals, especially for two-electron repulsion integrals, are the most demanding. Using a desktop pc (2.0 GHz dual core CPU, 2.0GB memory), in the case of 1s STO (with the assumption four orbital exponents in the integrand are all equal), the computational time for a two-electron repulsion integral by Mathematica (version 8) reaches approximately $100 \sim 1000$ s. The memory usage for the most complex case (the exchange type two-electron repulsion integral) amounts to $0.5 \sim 1$GB. If orbital exponents are taken to be different to each other, the computational time amounts to hours, being accompanied with an increase in memory usage. (One should note that this is the result of a symbolic computation program, which is still under development by the author's research group; there is plenty room for optimization.)
The construction of exact and approximate energy functional by Mathematica can be done in a few minutes. As for the symbolic-numeric solving, in the same computational environment, the numerical solution in the examples can be obtained in $1 \sim 10$ s, and the memory usage is $0.5 \sim 1$MB, when the computations are processed by Computer algebra system SINGULAR (version 3). This quickness is because of the simplicity of the problem setting. If polynomial equations are more complicated than those in the above explanatory calculations, for example, with longer integer numerical coefficients and an increased number of symbols, the cost on the computational time and memory usage grows so large that the symbolic-numeric computation becomes difficult in an insufficient computational environment. In the simple computation of H_2, as above, the structural optimization by UHF without artificial symmetrization to wavefunctions results in a demanding calculation that requires large cpu-time and memory usage. The reinforcement to the computer memory seems to be indispensable to effective computation.

There is also a fundamental problem on the theoretical side. As seen in the starting polynomial equation of (R.8), the scales of the numerical coefficients are similar. Meanwhile, after the symbolic computations, in the generated Gröbner bases, the scales of the coefficients show great discrepancies. The extreme growth of coefficients results in larger computational costs and a decrease in accuracy in the numerical procedure. Thus, one of the major interests in the field of symbolic computation is how to avoid such inconveniences, many strategies have now been proposed.[19 – 21] For example, Brickenstein proposes the "slimgb" algorithm in order to keep the intermediate expressions as slim as possible, by regularly replacing a swelled polynomial with a shorter, equivalent one.[19] Lichtblau, based on an empirical study, discusses important points that should be handled carefully when using approximate arithmetic for coefficients.[20] Arnold presents modular algorithms for the purpose of limiting the enormous growth in rational-numbered coefficients.[21] These strategies, as well as others with the same intention, will be of importance in more complex calculations.

Other difficulties will arise in the application to more complex systems.

First, the generation of the molecular integrals must be burdensome. The shown example, using a hydrogen molecule is a very simple one. We need only one- or two-centered integrals. The molecular integrals are computed from the 1s orbital alone, so that the integrals take the simplest expressions. For a more complex molecule, we must use more general and more complicated atomic basis, which give more complex molecular integrals. Besides, we have to evaluate three- or four-centered two-electron repulsion integrals. Here we have a problem: as for the analytic expression of multi-centered repulsion integrals, the derivation by the STO is a formidable one. For this reason, the STO has not been widely used in quantum chemistry. But, as there are several merits in STO, studies to obtain analytic expressions for multi-centered repulsion integrals by means of STO are still pursued.[22] At present, it is more pragmatic to employ GTO, the de facto standard, in which the analytic technique for the derivation of multi-centered integrals has been well established.

Secondly, in the explanatory numerical computations given above, we can evaluate both ground and excited states. This means that we must confront all possible electronic configurations and single out the necessary one from the solutions. It is in contrast to the conventional computations, where it is trivial work to get a ground state; one has only to compute the necessary number of lower occupied eigenvalues in ascending order from the bottom and put an electron in each; in the iterative minimization of the total energy functional, one can gather occupied states only, omitting the calculation of unoccupied states. On the other hand, in the polynomial equations, if one solves them without care, the whole eigenstates (including both of necessary and unnecessary ones, and as many as the matrix dimension) will appear in the set of solutions indiscriminately. The number of unnecessary configurations shall grow enormously in more complex systems, where more electrons and a larger basis set are included. In order to sift out the ground states, we can pick up the configuration in which the total sum of the eigenvalues in the occupied states becomes minimal, by firstly solving the equations for energy spectrum, obtained by polynomial triangulations. This tactic will be of use for sorting and indexing excited states. Also, to impose certain point group symmetry on wave function will be effective in the reduction of computational cost. The RHF structural optimization for a hydrogen molecule in the previous section, in which the ground state is extracted from the symmetrized wavefunction, is a clumsy example of this. The switching between symmetrized and asymmentrized wavefunctions lead to the selection of ground or excited states.

Thirdly, the polynomial approximation to the exact functional causes nonsensical solutions, which should be checked with care. In more complicated cases, this situation will be troublesome. The admissible solutions must lie in a range where the polynomial approximation, through the Taylor expansion, is quantitatively valid: if the solution appears to be dubious, one must re-examine it by another polynomial approximation with a different center point of the Taylor expansion. One can also use polynomials of higher degrees for this purpose.

In summary, the present work shows that the concept of the “molecular orbital algebraic equation” by means of the “polynomial approximation to molecular integrals” is applicable to the realistic first principles electronic structure calculation, as well as its potential in several fundamental problems, which are difficult to handle by the conventional method. We recognize that the difficulties to be overcome are large. However, improvement in computer architecture is so rapid that we can expect the achievement of sufficient accuracy by the present method and its application to complex and large material in future, spurred by the refinement of the symbolic computation theory.

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