Study of LCAO-MO calculation by using completely numerical basis functions

Katsumi Nakagawa
3-1-1-201 Hiyoshi-Honcho, Kohoku-ku, Yokohama, Kanagawa 223-0062 Japan
nakagawa.katsumi@nifty.com

Abstract. Choice of basis functions is decisive in LCAO-MO method to calculate accurately MOs of a molecule under complicated electric/magnetic potential. For such situation, calculating basis functions analytically is generally difficult. To obtain them, the new numerical calculating method based on matrix operation and the new sample point system based on FCC lattice were proposed. Further LCAO-MO calculation using basis functions calculated by this method was applied for small molecules under inner electric potential and showed reasonable results. Finally, two challenges to apply this method for arbitrary magnetic potential are clarified.

1. Introduction
The author has studied calculation of NMR spectrum.[1],[2] In his study, he experienced that calculating nuclear spin-spin coupling(J) accurately is more difficult than the case of chemical shift(\(\delta\)). For \(\delta\), uniform magnetic field \(H\) is applied, \(H\) induces current in a molecule and the current causes anti-magnetic field, which shifts the resonance peak. Here the current can be calculated by using MOs of the molecule.[3] In this paper basis function is substantially atomic orbital, so the term “AO” will be used instead of “basis function”. For LCAO-MO calculation under uniform \(H\), analytically accurate AO, often called “London atomic orbital”, is known.[4] It is very effective to obtain accurate MOs but works only for uniform \(H\). On the other hand, J is caused by interaction between nuclear magnetic moments of neighboring atoms via MOs. J causes splitting of the resonance peak. \(H\) caused by nuclear magnetic moments is generally very complicated and analytically accurate AO is unknown. The author imputes poorer accuracy of J to poorer quality of AO under complicated \(H\).

To obtain high quality AO \(\chi\), solve numerically for example Hartree-Fock-Slater equation including potential \(\rho(r)\) for each atom. In the case that \(\rho(r)\) is electrical potential, it is like eq.(1).

\[
\frac{1}{2}v^2 - ZA + \int r - \frac{\rho(r)}{r^12} dv^2 - 3\alpha \left[ \frac{3}{4\pi} \rho \sigma(r) \frac{1}{3} + \phi(r) \right] \chi = \epsilon \chi \quad (\sigma = \alpha, \beta)
\]  

(1)

This is the similar as conventional DV-X\(\alpha\) method.[5] But we can’t use spherical harmonic functions as \(\chi\) because \(\phi(r)\) can creates extreme spherically asymmetric circumstances. We need new strategy.
2. Completely numerical AO

In quantum mechanics, wave functions can be obtained by two ways, differential equation and matrix operation. The former is popular but the latter is more powerful in this case. In matrix operation, physical quantity \( P \) is represented by matrix \([P]\) and wavefunction \( \psi \) is represented by vector \([\psi]\). \([P]\) act on \([\psi]\) like eq.(2), where \( \psi(r_i) \) is value of \( \psi \) at sample point \( r_i \) in 3D space.

\[
[P][\psi] = \begin{bmatrix}
P_{11} & P_{12} & \cdots & P_{1n} & \psi(r_1) \\
P_{21} & P_{22} & \cdots & P_{2n} & \psi(r_2) \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
P_{n1} & P_{n2} & \cdots & P_{nn} & \psi(r_n)
\end{bmatrix}
\]

(2)

A new sample point system for AO calculation was developed. Firstly, arrange sample points (= SP) like FCC lattice points and let’s call them imaginary SPs, each of which occupies the same volume or weight \( \omega_0 \) and has equivalent 12 neighboring points except peripheral area of the system. Designate one of imaginary SP as the origin and express coordinate of imaginary SP as \( (x, y, z) \). This system is very convenient for numerical calculation but its uniform point distribution is inappropriate for AOs. Concentrate SPs toward the origin to calculate precisely around the nucleus. After this transformation, let’s call them real SPs. and express coordinate of real SP as \( (X, Y, Z) \). Although the direction of each SP around the origin is preserved, the distance from the origin \( r = \sqrt{x^2 + y^2 + z^2} \) is modified to \( R = \sqrt{X^2 + Y^2 + Z^2} \). If the probability of appearance of real SP at \( R \) is assumed to be like eq.(3)

\[
P(R) = R^{-\lambda} \quad (0 < \lambda < 3),
\]

(3)

\( R \) can be related to \( r \) by eq.(4), because imaginary SPs exist uniformly.

\[
4\pi r^2 P(R) dR = 4\pi r^2 dr
\]

(4)

Therefore

\[
\frac{11}{-1C} \lambda R = C^3 - \lambda r C \quad \text{or} \quad r = C^3 R (C = 1 - 3)
\]

(5)

where a parameter \( \lambda \) seems to be appropriate around 2.0.

In matrix operation, each term in eq.(1) has to be replaced by a matrix. Matrix form of Laplacian \( \nabla^2 \) was obtained as follows. Poisson equation (6) is solved like eq.(7).

\[
\nabla^2 f(r) = g(r)
\]

(6)

\[
f(r) = -1 \int_{4\pi(r^2)} g(r) dx
\]

(7)

Eq.(7) is transformed to numerical integration and represented as matrix operation like eq.(8).

\[
[f] = -1 \sum g(r_j) w = -1[R][w][g]
\]

(8)

where \( r_{ij} \) is the distance between point \( r_i \) and point \( r_j \) and \( \omega_i \) is weight of real SP \( r_i \). \([g]\) is solved like eq.(9) and matrix form of \( \nabla^2 \) is found to be eq.(10) by comparing eq.(9) with eq.(6).[6]

\[
[g] = -4\pi[[R][\omega]]^{-1}[f] = -4\pi[\omega]^{-1}[R]^{-1}[f]
\]

(9)

\[
[\nabla^2] = -4\pi[\omega]^{-1}[R]^{-1}
\]

(10)

Eq.(10) is the expression for real SPs, but it is modified like eq. (11) for imaginary SPs.

\[
-\frac{1}{2} \frac{1}{1} v = -4\pi[w_2][R][w_2]
\]

(11)

Diagonal elements of \([R]\) were set to be 0 to avoid infinity. To include contribution from diagonal element, correcting term should be added to kinetic term in eq.(1) like eq.(12).
\[-1 - \frac{1}{2} + [\nu_2] + 2(4\pi \times 9)[\omega^3] = 2\pi [w_2][R][w_2] + 2.41798793[w_3]\]

Eq. (12) is easier to handle, because it is Hermitian operator. But obtained \(\psi(r_i)\) by using eq. (12) includes factor of \(\sqrt{\omega_i}\). It has to be corrected to \(\psi(r_i)/\sqrt{\omega_i}\) in real 3D space, where we set the molecule. Other terms in the left side of eq. (1) are diagonal matrices, whose diagonal element is the value of each potential at each SP. So every matrices in eq. (1) can be written down easily and eq. (1) becomes simple numerical eigen-value problem, which can be solved by ordinary mathematical routine, even if potential \(\phi(r)\) has very complicated form. Therefore, we can calculate easily accurate AOs under arbitrary electric potential.

**Table 1** shows energies of lower 9 orbitals of Ar atom calculated by this method. AO#3-5 and #7#9 are perfectly degenerated.

| AO  | Energy(a.u.) |
|-----|--------------|
| #1  | -114.681094  |
| #2  | -11.136150   |
| #3  | -8.760035    |
| #4  | -8.760035    |
| #5  | -8.760035    |
| #6  | -1.045049    |
| #7  | -0.498346    |
| #8  | -0.498346    |
| #9  | -0.498346    |

![Fig. 1 Pictures of AO#7-9 of Ar atm in Table 1 illustrated by VESTA](image)

Fig. 1 shows pictures of AO#7-9 by VESTA[7]. They seem to be 3p orbitals. Although spherical harmonics functions weren’t used explicitly, they appeared spontaneously.

3. LCAO-MO calculation by using new AOs

For LCAO-MO calculation, Fock Matrix \(F_{RS}\) is necessary. It corresponds to an interaction between AO \(\chi_F\) and \(\chi_S\). As \(F\) is an operator in the left side of eq. (1), \(F_{RS}\) is integrated numerically like (13).

\[F_{RS} = \int \chi \star F \chi \, dv \rightarrow \sum \chi \star (r)F(r)\chi (r)wr_{rs}\]

Eq. (13) should be integrated at all SPs of all atoms. Two problems appeared and were solved. Firstly, atom A and atom B have their proper SP systems constructed independently. SPs of both atoms overlap in the molecule and their weights \(\omega\) have to be unified. It was done in the same way as conventional DV-Xα method[5] like eq. (14).

\[1/\omega = 1/\omega_A + 1/\omega_B\]
where \( \omega_A \) is weight when only atom A exists and \( \omega_B \) is weight when only atom B exists. Secondly, if \( \chi \) belongs to atom A, value of \( \chi \) is given only at SP of atom A. Values of \( \chi \) at SP of atom B were interpolated by using values of \( \chi \) at surrounding SPs of atom A. Interpolation was executed as follows.

Let \( r_B \) be any SP of atom B. Find the SP of atom A nearest to \( r_B \). Designate it \( r_A^0 \) and set \( r_A^0 \) to be the origin. Expand \( \chi \) to the second order around \( r_A^0 \) like (15).

\[
\chi_{xx} \chi_{yy} \chi_{zz} = \chi(0) + \chi_x x + \chi_y y + \chi_z z + x^2 + y^2 + z^2 + \chi_{xy} yz + \chi_{xz} zx + \chi_{yz} xy
\]

(15)

Select SPs of atom A around \( r_A^0 \) and designate them \( r_{Ai} \) \((i = 1,2,\ldots,n)\). By substituting \( r_{Ai} = (x_i, y_i, z_i) \) into eq.(15), simultaneous equations (16) are obtained.

As number of unknown coefficients is 9, they can be uniquely solved if condition number \( n = 9 \) or can be estimated by the method of least squares if \( n > 9 \). Even if \( n < 9 \), they can be reasonably estimated by using Moore-Penrose pseudo-inverse matrix.[8] As a lattice point of FCC, each point has 12 equivalent SPs neighboring around it in the space of imaginary SPs, like

\[
(a, 0, 0), (0, a, 0), (−a, 0, 0), (0, −a, 0), (a, 0, −a), (0, a, −a), (−a, 0, −a), (0, −a, −a), (a, a, 0),
\]

\[
(−a, a, 0), (−a, −a, 0), (a, −a, 0),
\]

where \( a \) is a half of lattice constant. If all 12 SPs are used, or \( n = 12 \), the method of least squares is applicable. But the author used only 8 SPs from the top of (17) and apply Moore-Penrose pseudo-inverse matrix for 9 coefficients. It’s because using small number of SPs is advantageous in peripheral area of SP system. Fig. 2 shows example of interpolation by this method for a N\(_2\) molecule which is composed with atom A and atom B. Values of 2s orbitals of atom A at SPs of atom A (= real values) is shown by solid curve as a function of distance from atom A nucleus and its interpolated values for SPs of atom B is shown by open circles. They seem to be interpolated but not perfectly. In this method, AOs and MOs are calculated alternatively by SCF method. After one step of AO-SCF and Fock Matrix calculation, one step of MO-SCF proceeds. Then information of orbital populations analyzed from MOs flows to the next AO-SCF calculation and adjusts each AO’s occupation number. This is the same process as conventional DV-X\(_\alpha\) method.[5]. In AO-SCF calculation, eigen-value problem is heavy, because the dimension of its matrix \((= n)\) is number of SPs of a atom and time for eigen-value problem calculation is proportional to \(n^3\). In MO-SCF process, \( n \) is small but Fock Matrix calculation is rather heavy. The cost of AO-SCF is roughly proportional to the number of atoms \((= m)\) and that of MO-SCF is proportional to \(m^2\). As Fock matrix between distant atoms can be neglected in large molecule, total cost of calculation in this method may be \(O(m^2)\).

![Fig. 2 Interpolation of 2s orbital of N atom at SPs of another N atom in N\(_2\) molecule.](image)

![Fig. 3 Pictures of typical MOs of N\(_2\) molecule in Table 2.](image)
4. Examples of MOs calculated by this method

Table 2: Energies of MOs \( N_2 \) molecules and their symmetry

| MO   | Energy (a.u.) |
|------|---------------|
| #1   | -14.1297 \( 1\sigma_g \) |
| #2   | -14.1292 \( 1\sigma_u \) |
| #3   | -1.0443 \( 2\sigma_g \) |
| #4   | -0.4022 \( 2\sigma_u \) |
| #5   | -0.3936 \( 1\pi_u \) |
| #6   | -0.3916 \( 1\pi_u \) |
| #7   | -0.2627 \( 3\sigma_g \) |
| #8   | 0.0102 \( 1\sigma_g \) |
| #9   | 0.0123 \( 1\pi_g \) |
| #10  | 0.7252 \( 3\sigma_u \) |

one of \( \sigma \) or \( \pi \) orbitals. MO#5-#6 and MO#8-#9 are degenerated, but their accuracy are not so perfect as the case of AOs of \( \text{Ar} \) atom. (See Table 1) Relatively poor accuracy of interpolation causes it. Fig.3 shows pictures of typical AOs in Table 2 illustrated by VESTA. Fig.4 shows total energy (atomic unit) of \( N_2 \) molecule as a function of inter-nuclear distance \( R \) (relative unit). The curve has the minimum around \( R=1.0 \), which means experimental equilibrium distance.

Table 3 shows energies of lower

| MO   | Energy (a.u.) |
|------|---------------|
| #1   | -19.0250 \( A_1 \) |
| #2   | -18.7845 -- |
| #3   | -18.7838 -- |
| #4   | -1.2039 \( A_1 \) |
| #5   | -0.9330 \( B_1 \) |
| #6   | -0.5906 \( A_1 \) |
| #7   | -0.4680 \( B_2 \) |
| #8   | -0.4246 \( B_1 \) |
| #9   | -0.4210 \( A_1 \) |
| #10  | -0.2238 \( A_2 \) |
| #11  | -0.1839 \( B_1 \) |
| #12  | -0.1594 \( A_1 \) |
| #13  | -0.1162 \( B_2 \) |
| #14  | 0.1297 \( A_1 \) |
| #15  | 0.2268 \( B_1 \) |
15 orbitals of \textbf{O3 molecule} calculated by this method. This molecule has C_{2v} symmetry and Table 4 is its irreducible representation table. Fig.5 is pictures of typical MOs. Each of MOs except MO#2,#3 corresponds to one of representations (A_1,A_2,B_1,B_2). MO#2 and #3 are just 1s orbitals of atom O_2 or atom O_3 in Fig.5. MO#7 corresponds to 3-centered- bond composed with 3 2p orbitals.

Table 4 Irreducible representation table of C_{2v}

|     | \(E\) | \(C_2\) | \(\sigma_p(xz)\) | \(\sigma_p'(yz)\) |
|-----|-------|---------|----------------|------------------|
| \(A_1\) | 1     | 1       | 1              | 1                |
| \(A_2\) | 1     | 1       | -1             | -1               |
| \(B_1\) | 1     | -1      | 1              | -1               |
| \(B_2\) | 1     | -1      | -1             | 1                |

Table 5 shows energies of lower 8 orbitals of \textbf{NH3 molecule} calculated by this method. MO#3,#4 and MO#7,#8 are degenerated. This molecule has C_{3v} symmetry and degenerated representation \(E\). \(\psi_a\) and \(\psi_b\) in eq.(18) are MOs corresponding to \(E\) composed by 1s of \(H_1, H_2, H_3\) in Fig.6. MO#3,#4 in Fig.6 show same characteristic as \(\psi_a\) and \(\psi_b\) but include component of 2p of N atom slightly.

Table 5 Energies of MOs of NH_3 molecule calculated by this method.

| MO  | Energy(a.u.) |
|-----|--------------|
| #1  | -13.9865 \(A_1\) |
| #2  | -0.7106 \(A_1\) |
| #3  | -0.3631 \(E\) |
| #4  | -0.3628 \(E\) |
| #5  | -0.1269 \(A_1\) |
| #6  | 0.2197 \(A_1\) |
| #7  | 0.2881 \(E\) |
| #8  | 0.2900 \(E\) |

\[
\psi_a = \frac{1}{\sqrt{6}}(2x_1 - x_2 - x_3)
\]

\[
\psi_b = \frac{1}{\sqrt{6}}(x_2 - x_3)
\]  

(17)
5. Inner potential and its effect

Table 6 Ionization charge (Z-Q) of atoms in O\textsubscript{3} molecule (Fig.5) and in NH\textsubscript{3} molecule (Fig.6).

|   | O\textsubscript{3} |   |   | NH\textsubscript{3} | N | H\textsubscript{1} | H\textsubscript{2} | H\textsubscript{3} |
|---|---|---|---|---|---|---|---|---|
| Z  | 8.000 | 8.000 | 8.000 | 8.000 | 1.000 | 1.000 | 1.000 |
| Q  | 7.646 | 8.182 | 8.171 | 7.502 | 0.830 | 0.834 | 0.834 |
| Z-Q | 0.354 | -0.182 | -0.171 | -0.502 | 0.170 | 0.166 | 0.166 |

The sum of orbital populations of the same atom is called as an atomic population (Q). The difference between atomic number (Z) and Q is regarded as ionization of the atom in the point charge approximation. As examples, table 6 shows Z, Q, Z-Q of O\textsubscript{3} molecules. Z-Q will form electric potential \( \phi(r) \) and \( \phi(r) \) will act on electrons in other atoms. Let’s call the sum of \( \phi(r) \) inner (electric) potential \( \phi_i(r) \). \( \phi_i(r) \) will reproduce real potential in each atom for AO calculation and completely numerical AOs will be able to reflect such potential. To see its effect, electric dipole moment \( \vec{\mu}_e \) was calculated according to eq.(19).

\[
\vec{\mu}_e = \sum Z_A \vec{R}_A - \int \sum \psi^* r \psi_i \, dv
\]

where \( Z_A \) is atomic number of atom A and coordination vector of a nucleus of atom A.

Table 7 Effect of \( \phi_i \) on dipole moments of CO, O\textsubscript{3}, NH\textsubscript{3} molecules

|   | Dipole moment \( |\mu_i| \) (Debye) |
|---|---|
| CO | Calculation | experimental |
| without | 0.2990 | 0.1098 |
| with | 0.3020 | |
| O\textsubscript{3} | without | 0.5948 | |
| with | 0.3938 | 0.5337 |
| NH\textsubscript{3} | without | 1.7763 | 1.4718 |
| with | 1.3613 | |

Table 7 shows calculated \( |\mu_i| \) of CO, O\textsubscript{3}, NH\textsubscript{3} molecules and experimental ones for comparison. In case of O\textsubscript{3}, NH\textsubscript{3}, \( \phi_i \) seems to reduce \( |\mu_i| \). In these calculations, only 1s, 2s and 2p orbitals were used. \( \phi_i \) may distort them and shorten substantial distance between ionization charges. But corrected \( |\mu_i| \) do not necessarily get closer to experimental ones. This may be the result of insufficient accuracy of \( \phi_i(r) \) due to rough approximation of ionized charges.

6. Summary and the next challenges

a. In AOs by the new method, spherical harmonic functions were not used explicitly but appeared spontaneously in spherically symmetric circumstance.

b. MOs by the new method showed symmetries agreeing with the point group theory.

c. Inner electric potential distorts AOs, and modify electron distributions reasonably.

But to include magnetic vector potential \( A(r) \) to kinetic energy term (20), there remain two challenges.

\[
\frac{1}{2}(\mathbf{v}^2 - aA(r)) = -\frac{1}{2}v^2a2\mathbf{i}v.A(r) - A(r).\mathbf{v} + \frac{a^2}{2}A(r)^2
\]

(19)

d. As gradient \( \nabla \) appears alone, \( \nabla \) has to be represented as a matrix operator.

e. As imaginary number \( \mathbf{i} \) appears, operation has to treat complex wave functions.
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