Generalized Method for Calculating Löwdin Orbitals

Kazuya SUZUKI, Shinsaku MARUYAMA, and Kunio ARAKI

Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki

(Received March 9, 1972)

A generalized method for numerically calculating Löwdin orbitals is proposed, the method being an application of Frobenius' theorem in algebra. Löwdin transformation matrix $\mathbf{T}=\mathbf{S}^{-1/2}$ ($\mathbf{S}$ is overlap matrix) is calculated as $\mathbf{T}=\mathbf{U}\mathbf{S}_0^{-1/2}\mathbf{U}^t$, where $\mathbf{S}_0$ is a diagonal matrix whose diagonal elements are eigen values of $\mathbf{S}$, $\mathbf{U}$ is a matrix whose column vectors are eigen vectors of $\mathbf{S}$ and $\mathbf{U}^t$ is the transposed matrix of $\mathbf{U}$. It is proved that the eigen values of the overlap matrix of $\mathbf{S}$ are always positive for any choice of linearly independent atomic orbitals and that $\mathbf{S}^{-1/2}$, the inverse square-root of $\mathbf{S}$, exists within the range of real numbers. This method is useful for computer calculation by applying Jacobi's method.

Theoretical

Löwdin's method is used for orthonormalizing a given set of atomic orbitals and the transformed orbitals, Löwdin orbitals are useful for zero differential overlap approximation[1] (ZDO). However, for the numerical calculation of the Löwdin transformation matrix $\mathbf{T}=\mathbf{S}^{-1/2}$, only an expansion formula was shown[2,3] as

$$\mathbf{S}^{-1/2}=\mathbf{I}-1/2\mathbf{D}+3/8\mathbf{D}^2-5/16\mathbf{D}^3+\cdots\cdots \quad (1)$$

where $\mathbf{S}$ is overlap matrix and an element of $\mathbf{S}$, s_{ij} is defined by

$$s_{ij}=\int x_i(v)x_j(v)\mathrm{d}v$$

x_i, x_j are atomic orbitals
$\mathbf{I}$; unit matrix
$\mathbf{D}=\mathbf{S}-\mathbf{I}$

If the value of the overlap integral s_{ij} is large, the convergence of Eq. (1) is not good. Generally, the value of overlap integral of pi orbitals is 0.20—0.30 and that of sigma orbitals 0.20—0.60. Thus, Eq. (1) is not considered to be sufficiently accurate for a detailed calculation on sigma orbitals. For other cases, in applying group theory, basic AO's are transformed into symmetry orbitals and the overlap integrals are inevitably large, if the orbitals belong to the same irreducible representation. Thus, a method for accurate calculation on the transformation matrix $\mathbf{T}=\mathbf{S}^{-1/2}$ is necessary.

In algebra, the regular matrix $\mathbf{S}$ is solved into the product of three factors:

$$\mathbf{S}=\mathbf{U}\mathbf{S}_0\mathbf{U}^t \quad (2)$$

where the matrices $\mathbf{U}$, $\mathbf{S}_0$, and $\mathbf{U}^t$ are as follows.

$$\mathbf{U}=\begin{pmatrix} u_{11} & u_{12} & \cdots\cdots & u_{1m} \\ u_{21} & u_{22} & \cdots\cdots & u_{2m} \\ \cdots & \cdots & \cdots\cdots & \cdots \\ \cdots & \cdots & \cdots\cdots & \cdots \\ u_{m1} & u_{m2} & \cdots\cdots & u_{mm} \end{pmatrix}$$

The column vector of $\mathbf{U}$, $\mathbf{u}_j(u_{1j},u_{2j},\cdots\cdots,u_{mj})$, is an eigen vector of $\mathbf{S}$. ($j=1,2,\cdots\cdots,m$)

$$\mathbf{S}_0=\begin{pmatrix} s_1 & & & 0 \\ & s_2 & & \\ & & \ddots & \\ 0 & & & s_m \end{pmatrix}$$

The diagonal element of $\mathbf{S}_0$, s_j is an eigenvalue of $\mathbf{S}$ ($j=1,2,\cdots\cdots,m$).

$\mathbf{U}^t$; transposed matrix of $\mathbf{U}$

As the matrix $\mathbf{U}$ is unitary, $\mathbf{U}^t=\mathbf{U}^{-1}$, $\mathbf{U}\mathbf{U}^t=\mathbf{I}$ and $\mathbf{U}^t\mathbf{U}=\mathbf{I}$. By means of Eq. (2), we can calculate the matrix $\mathbf{D}$ of Eq. (1):

$$\mathbf{D}=\mathbf{S}-\mathbf{I}=\mathbf{U}(\mathbf{S}_0-\mathbf{I})\mathbf{U}^t$$
$$\mathbf{D}^2=\mathbf{U}(\mathbf{S}_0-\mathbf{I})^2\mathbf{U}^t$$
$$\mathbf{D}^3=\mathbf{U}(\mathbf{S}_0-\mathbf{I})^3\mathbf{U}^t$$
$$\cdots\cdots\cdots\cdots$$
$$\mathbf{D}^n=\mathbf{U}(\mathbf{S}_0-\mathbf{I})^n\mathbf{U}^t$$

Substituting these values for those of Eq. (1), we obtain the following equation.

$$\begin{aligned}\mathbf{S}^{-1/2}&=\mathbf{I}-1/2\mathbf{U}(\mathbf{S}_0-\mathbf{I})\mathbf{U}^t+3/8\mathbf{U}(\mathbf{S}_0-\mathbf{I})^2\mathbf{U}^t \\ &\quad-5/16\mathbf{U}(\mathbf{S}_0-\mathbf{I})^3\mathbf{U}^t+\cdots\cdots \\ &=\mathbf{U}[\mathbf{I}-1/2(\mathbf{S}_0-\mathbf{I})+3/8(\mathbf{S}_0-\mathbf{I})^2 \\ &\quad-5/16(\mathbf{S}_0-\mathbf{I})^3+\cdots\cdots]\mathbf{U}^t \\ &=\mathbf{U}[\mathbf{I}+(\mathbf{S}_0-\mathbf{I})]^{-1/2}\mathbf{U}^t \\ &=\mathbf{U}\mathbf{S}^{-1/2}\mathbf{U}^t\end{aligned}$$

The matrix $\mathbf{S}_0$ is diagonal, and we have

$$\mathbf{S}^{-1/2}=\mathbf{U}\cdot\begin{pmatrix} s_1^{-1/2} & & & 0 \\ & s_2^{-1/2} & & \\ & & \ddots & \\ 0 & & & s_m^{-1/2} \end{pmatrix}\cdot\mathbf{U}^t \quad (3)$$

This is an exact and generalized expression for Löwdin transformation matrix $\mathbf{T}=\mathbf{S}^{-1/2}$, which is known in algebra as Frobenius' theorem;

Eigenvalues of matrix $F(\mathbf{A})$ are $F(\alpha_1),F(\alpha_2),\cdots\cdots,F(\alpha_m)$, where $\alpha_1,\alpha_2,\cdots\cdots,\alpha_m$ are eigenvalues of the matrix $\mathbf{A}$ and $F(x)=x^{-1/2}$.

It is proved that the eigenvalues $s_1,s_2,\cdots\cdots,s_m$ are always positive, not zero or negative. If one of the eigen values s_j is zero, the determinant of $\mathbf{S}$, Det $\mathbf{S}$ is zero (the matrix $\mathbf{S}$ is singular) and $\mathbf{S}^{-1}$, the inverse matrix of $\mathbf{S}$, does not exist. If the eigen value s_j is negative, the value of $s_j^{-1/2}$ is complex. It will be shown that no such cases exist.

1) J. A. Pople and G. A. Segal, *J. Chem. Phys.* **43**, S136, (1965)
2) P. O. Löwdin, *J. Chem. Phys*, **18**, 365, (1950).
3) P. O. Löwdin, *ibid.*, **21**, (1953).

The element of overlap matrix **S** is defined by

$$s_{ij} = \int x_i(v)x_j(v)\mathrm{d}v$$

and determinant of such a matrix is Gram's determinant (Gramian), which is transformed as follows.

$$\mathrm{Det}\,\mathbf{S} = 1/m\,!\iint\cdots\int \begin{Vmatrix} x_1(v_1) & x_2(v_1) & \cdots & x_m(v_1) \\ x_1(v_2) & x_2(v_2) & \cdots & x_m(v_2) \\ \cdots & \cdots & \cdots & \cdots \\ x_1(v_m) & x_2(v_m) & \cdots & x_m(v_m) \end{Vmatrix}^2 \mathrm{d}v_1\mathrm{d}v_2\cdots\mathrm{d}v_m$$

The atomic orbitals $x_1(v)$, $x_2(v)$, $\cdots$, $x_m(v)$ are linearly independent and then Det **S** is always positive.

$$\mathrm{Det}\,\mathbf{S} > 0$$

From Eq. (2), we have

$$\begin{aligned}\mathrm{Det}\,\mathbf{S} &= \mathrm{Det}\,(\mathbf{US_0U}^t) \\ &= \mathrm{Det}\,\mathbf{S_0} \qquad (\mathbf{UU}^t=\mathbf{I}) \\ &= s_1s_2\cdots\cdots s_m\end{aligned}$$

then $s_1s_2\cdots\cdots s_m>0$

Thus it is proved that no one of the eigenvalues $s_1, s_2, \cdots\cdots s_m$ is zero and the matrix **S** is regular.

Next, it is shown all of them are positive. Considering the integral

$$Q = \int\left\{\sum_{j=1}^{m} p_jx_j(v)\right\}^2\mathrm{d}v$$

we find that Q is positive for arbitrary real numbers $p_1, p_2, \cdots\cdots, p_m$, except that the atomic orbitals $x_1(v)$, $x_2(v), \cdots\cdots, x_m(v)$ are linearly dependent (it is assumed that all the parameters p_j's are not zero). The integral Q is transformed into quadratic form:

$$\begin{aligned}Q &= \sum_{i,j=1}^{m}\int p_ip_jx_i(v)x_j(v)\mathrm{d}v \\ &= \sum_{i,j=1}^{m} p_ip_js_{ij} \\ &= (\mathbf{S}\boldsymbol{p}, \boldsymbol{p})\end{aligned}$$

where **S** is overlap matrix and $\boldsymbol{p}$ is non-zero vector $\boldsymbol{p}(p_1,p_2,\cdots\cdots p_m)$. Substituting **S** of Eq. (2), we obtain the following equation.

$$\begin{aligned}Q &= (\mathbf{US_0U}^t\boldsymbol{p}, \boldsymbol{p}) \\ &= (\mathbf{S_0U}^t\boldsymbol{p}, \mathbf{U}^t\boldsymbol{p})\end{aligned}$$

here we introduce the parameter $\boldsymbol{q}(q_1,q_2,\cdots\cdots, q_m)$, which is transformed from the former parameter $\boldsymbol{p}(p_1, p_2 \cdots\cdots, p_m)$ as $\boldsymbol{q}=\mathbf{U}^t\boldsymbol{p}$.

$$\begin{aligned}Q &= (\mathbf{S_0}\boldsymbol{q}, \boldsymbol{q}) \\ &= s_1q_1^2 + s_2q_2^2 + \cdots\cdots + s_mq_m^2\end{aligned}$$

As the integral Q is also positive for real numbers $q_1, q_2, \cdots\cdots, q_m$, all the coefficients $s_1, s_2, \cdots\cdots, s_m$ are positive *i.e.* Q is positive definite quadratic form.

$$s_1 > 0,\ s_2 > 0, \cdots\cdots s_m > 0$$

Thus, Eq. (3) is always consistent for arbitrary functional systems $x_1(v)$, $x_2(v), \cdots\cdots, x_m(v)$, except for the case in which these functions are linearly dependent, in which case at least one of the eigenvalues of overlap matrix is zero and $\mathbf{S}^{-1/2}$, the inverse square-root matrix of **S**, does not exist.

Application of Eq. (3) to computer calculation is simple. In order to solve the secular equation of symmetric matrix **H** (Hamiltonian) or **F** (Hartree-Fock matrix), usually Jacobi's method is used. It is often preliminarily arranged as a subprogram. By using this, we can obtain the transformation matrix **T** as follows; eigen values and eigen vectors of **S** are calculated by Jacobi's method and then the diagonal elements $s_1, s_2, \cdots\cdots, s_m$ are substituted in Eq. (2) for the inverse square-root $s_1^{1/2}, s_2^{-1/2}\cdots\cdots, s_m^{-1/2}$. The process is easy programming. We might find the order of eigen values and eigen vectors, obtained by Jacobi's method, is indefinite and variable, depending on the diagonalizing operations. Nevertheless, the product of the matrices $\mathbf{S}=\mathbf{US_0U}^t$ and $\mathbf{S}^{-1/2}=\mathbf{US_0}^{-1/2}\,\mathbf{U}^t$ are uniquely determined. In other words, the matrices **S** and $\mathbf{S}^{-1/2}$ are invariable against the permutation of arbitrary eigenvalues and eigenvectors of **S**.

We have for an element of **S**, s_{pq}

$$\begin{aligned}s_{pq} &= \sum_{i,j=1}^{m} u_{pi}\delta_{ij}s_ju_{qj} \\ &= \sum_{j=1}^{m} u_{pj}s_ju_{qj}\end{aligned}$$

and similarly, for an element of $\mathbf{S}^{-1/2}$,

$$(\mathbf{S}^{-1/2})_{pq} = \sum_{j=1}^{m} u_{pj}s_j{}^{-1/2}u_{qj}$$

$$\mathbf{U} = \begin{array}{c} \\ \\ \\ p> \\ \\ q> \\ \\ \end{array}\begin{pmatrix} & & & \boldsymbol{u}_j & & \boldsymbol{u}_i & \\ u_{11} & u_{12} & \cdots & u_{1j} & \cdots & u_{1i} & \cdots \\ u_{21} & u_{22} & \cdots & u_{2j} & \cdots & u_{2i} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ u_{p1} & u_{p2} & \cdots & u_{pj} & \cdots & u_{pi} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ u_{q1} & u_{q2} & \cdots & u_{qj} & \cdots & u_{qi} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}$$

As the summation is taken over all the elements of p-th row and q-th row, the total sum is invariant against permutation of arbitrary eigenvafues s_i, s_j and the corresponding column vectors u_i, u_j. Thus, the matrices **S** and $\mathbf{S}^{-1/2}$ are invariable against the change of the order of eigenvalues and eigenvectors.

Combination with group theory is also simple.[4] The basic AO's are at first transformed into symmetry orbitals and then ortho-normalized by the Löwdin transformation.

$$\begin{aligned}&\boldsymbol{x}_s = \mathbf{O}\boldsymbol{x}_a \quad (\boldsymbol{x}_s, \boldsymbol{x}_a, \text{ column vectors}) \\ \text{or}\quad &\boldsymbol{x}_s = \boldsymbol{x}_a\mathbf{O}^t \quad (\boldsymbol{x}_s, \boldsymbol{x}_a, \text{ row vectors}) \\ &\boldsymbol{x}_L = \boldsymbol{x}_s\mathbf{S}^{-1/2}\end{aligned}$$

where **O** is a unitary matrix determined from the symmetry of molecules. The vectors $\boldsymbol{x}_a$, $\boldsymbol{x}_s$, and $\boldsymbol{x}_L$ are the array of basic AO's, symmetry orbitals and ortho-normalized orbitals, respectively. The merit of these transformations lies in the invariability of the Hamiltonian and Hartree-Fock matrix.

4) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys*, **43**, S 129, (1965).

Examples

Some examples of the Löwdin transformation matrix $\mathbf{T}=\mathbf{S}^{-1/2}$ are given as follows.

Ex. (1). *Pi Orbitals of Ethylene.*

C_1—C_2 the distance C_1—C_2; 1.34Å the value of overlap integral

$2p_{z1}$ $2p_{z2}$ $s_{12}=0.270$

The overlap matrix is as follows.

$$\mathbf{S}=\begin{bmatrix}1 & s\\ s & 1\end{bmatrix} \qquad s_{12}=s_{21}=s$$

By applying Eq. (2), the matrix **S** is transformed as

$$\mathbf{S}=\begin{bmatrix}1/\sqrt{2} & 1/\sqrt{2}\\ -1/\sqrt{2} & 1/\sqrt{2}\end{bmatrix}\begin{bmatrix}1+s & 0\\ 0 & 1-s\end{bmatrix}\begin{bmatrix}1/\sqrt{2} & -1/\sqrt{2}\\ 1/\sqrt{2} & 1/\sqrt{2}\end{bmatrix}$$

Then, by means of Eq. (3), we obtain

$$\mathbf{S}^{-1/2}=\begin{bmatrix}1/\sqrt{2} & 1/\sqrt{2}\\ -1/\sqrt{2} & 1/\sqrt{2}\end{bmatrix}\begin{bmatrix}1/\sqrt{1+s} & 0\\ 0 & 1/\sqrt{1-s}\end{bmatrix}\begin{bmatrix}1/\sqrt{2} & -1/\sqrt{2}\\ 1/\sqrt{2} & 1/\sqrt{2}\end{bmatrix}$$

Substituting s=0.270,

$$\mathbf{S}^{-1/2}=\begin{bmatrix}1.029 & -0.141\\ -0.141 & 1.029\end{bmatrix}$$

The same values are obtained also by Eq. (1).

Ex. (2). *Pi Orbitals of Allyl Radical.*

C_1 C_2 C_3 the distance C_1-C_2; 1.39Å
$<C_1C_2C_3=120°$

$2p_{z1}$ $2p_{z2}$ $2p_{z3}$ $s_{12}=0.246$
$s_{13}=0.035$

The overlap matrix **S** is as follows.

$$\mathbf{S}=\begin{bmatrix}1.000 & 0.246 & 0.035\\ 0.246 & 1.000 & 0.246\\ 0.035 & 0.246 & 1.000\end{bmatrix}$$

From C_{2v} symmetry of allyl radical the symmetry orbitals are obtained as $\Gamma=A_2+2B_1$

A_2; $1/\sqrt{2}\cdot 2p_{z1}-1/\sqrt{2}\cdot 2p_{z3}$

B_1; $2p_{z2}$, $1/\sqrt{2}\cdot 2p_{z1}+1/\sqrt{2}\cdot 2p_{z3}$

The overlap matrices of the symmetry orbitals are calculated to be

$$\mathbf{S}_{A2}=0.965$$

$$\mathbf{S}_{B1}=\begin{bmatrix}1.035 & 0.348\\ 0.348 & 1.035\end{bmatrix}$$

Then, the transformation matrices are obtained as follows.

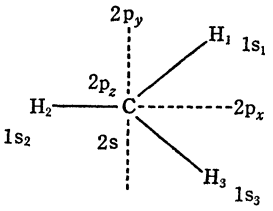
$$\mathbf{S}_{A2}{}^{-1/2}=1.018$$

$$\mathbf{S}_{B1}{}^{-1/2}=\begin{bmatrix}1.030 & -0.183\\ -0.183 & 1.030\end{bmatrix}$$

The transformation matrix of AO basis is calculated by Eq. (3) as follows.

$$\mathbf{S}^{-1/2}=\begin{bmatrix}1.024 & -0.130 & 0.006\\ -0.130 & 1.048 & -0.130\\ 0.006 & -0.130 & 1.024\end{bmatrix}$$

Ex, (3) Sigma Orbitals of Methyl Radical.



the distance C-H
1.08 Å
$<HCH=120°$

The radical $CH_3\cdot$ is assumed to be planar of C_{3v} symmetry.

The overlap matrix is as follows.

	$2p_z$	2s	$2p_x$	$2p_y$	$1s_1$	$1s_2$	$1s_3$
$2p_z$	1.000	0.000	0.000	0.000	0.000	0.000	0.000
2s	0.000	1.000	0.000	0.000	0.576	0.576	0.576
$2p_x$	0.000	0.000	1.000	0.000	0.233	−0.456	0.233
$2p_y$	0.000	0.000	0.000	1.000	0.403	0.000	−0.403
$1s_1$	0.000	0.576	0.233	0.403	1.000	0.256	0.256
$1s_2$	0.000	0.576	−0.465	0.000	0.256	1.000	0.256
$1s_3$	0.000	0.576	0.233	−0.403	0.256	0.256	1.000

The symmetry orbitals are determined to be $\Gamma=3A_1+2E$.

A_1; $2p_z$

2s

$1/\sqrt{3}\ (1s_1+1s_2+1s_3)$

E; $2p_x$

$1/\sqrt{6}\ (1s_1-2s_2+1s_3)$

$2p_y$

$1/\sqrt{2}\ (1s_1-1s_3)$

and their overlap matrices are calculated as

$$\mathbf{S}_{A1}=\begin{bmatrix}1.000 & 0.000 & 0.000\\ 0.000 & 1.000 & 0.998\\ 0.000 & 0.998 & 1.512\end{bmatrix}$$

$$\mathbf{S}_{E}=\begin{bmatrix}1.000 & 0.570 & 0.000 & 0.000\\ 0.570 & 0.744 & 0.000 & 0.000\\ 0.000 & 0.000 & 1.000 & 0.570\\ 0.000 & 0.000 & 0.570 & 0.744\end{bmatrix}$$

Using Eq. (3), we can obtain the following transformation matrices.

$$\mathbf{S}_{A_1}^{-1/2} = \begin{bmatrix} 1.000 & 0.000 & 0.000 \\ 0.000 & 1.563 & -0.699 \\ 0.000 & -0.699 & 1.204 \end{bmatrix}$$

$$\mathbf{S}_{E}^{-1/2} = \begin{bmatrix} 1.233 & -0.505 & 0.000 & 0.000 \\ -0.505 & 1.460 & 0.000 & 0.000 \\ 0.000 & 0.000 & 1.233 & -0.505 \\ 0.000 & 0.000 & 0.505 & 1.460 \end{bmatrix}$$

As for the transformation matrix of AO basis, the following result is obtained.

$$\mathbf{S}^{-1/2} = \begin{array}{c} \\ 2p_z \\ 2s \\ 2p_x \\ 2p_y \\ 1s_1 \\ 1s_2 \\ 1s_3 \end{array} \begin{array}{c} \begin{array}{ccccccc} 2p_z & 2s & 2p_x & 2p_y & 1s_1 & 1s_2 & 1s_3 \end{array} \\ \begin{bmatrix} 1.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 1.564 & 0.000 & 0.000 & -0.405 & -0.405 & -0.405 \\ 0.000 & 0.000 & 1.232 & 0.000 & -0.205 & 0.411 & -0.205 \\ 0.000 & 0.000 & 0.000 & 1.232 & -0.356 & 0.000 & 0.356 \\ 0.000 & -0.405 & -0.205 & -0.356 & 1.373 & -0.083 & -0.083 \\ 0.000 & -0.405 & 0.411 & 0.000 & -0.083 & 1.373 & -0.083 \\ 0.000 & -0.405 & -0.205 & 0.356 & -0.083 & -0.083 & 1.373 \end{bmatrix} \end{array}$$

From the three examples, we see that the transformation matrix deviates largely from unit matrix, especially in the case of sigma orbital (Ex. 3). Thus, it seems necessary to examine the parameters used in NDO method. As an example, Hartree-Fock matrix **F** and core Hamiltonian **H** are transformed as follows by the Löwdin transformation.

$$\mathbf{F}' = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}$$

$$\mathbf{H}' = \mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2}$$

Usually, the symbol β_{ij} is used for i, j element of H'_{ij} which is determined from the spectroscopic data. By means of Eq. (3), one can calculate the value of β_{ij} and compare it with experimental one.