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A new one-electron model for extended Hückel type molecular orbital calculations

Linkage of embedded atomic fields

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A new form of Coulomb and resonance integrals for extended Hückel type molecular orbital calculations was derived. In this model an electron moving in a molecule, when it stays in the neighborhood of the center of an atom in the molecule, sees the potential of the corresponding isolated atom. Compared with the well-known forms of Coulomb and resonance integrals, each integral derived from this model considers the influences from all atoms in the molecule, and includes the concept of atomic cell. The similarities of this model to other extended Hückel type formulations are also examined.

Key words: Molecular orbitals — Extended Hückel — Coulomb integrals — Resonance integrals

1. Introduction (effective Hamiltonian)

In the Hückel theory, the complete Hamiltonian of a molecule (the sum of kinetic energy of electrons, electron-electron interaction energy, electron-nucleus interaction, and nucleus-nucleus interaction energy) is approximated as

$$\mathscr{H}(1,2,\ldots,N)\simeq\sum_{\mu=1}^{N}\hbar(\mu),\tag{1}$$

where the summation runs over all electrons in the molecule, and $\hbar(\mu)$ is the effective one-electron Hamiltonian of the μth electron, which may consist of the kinetic energy, the nuclear attractive energy, and the repulsive energy from other electrons in the molecule [1]. The electron-electron interaction energy is counted twice on the right side of Eq. (1), and the extra part is usually compared with the nuclear term. Although the electron-electron term of the Hartree-Fock method is often a few times greater than the nuclear term in the complete Hamiltonian [2], the idea of the approximation is based on the expectation that the electron-electron energy and the inter-nuclear energy could be balanced [1, 3]. Thus one may use the approximation at least in the qualitative treatment. Considering the quantitative treatment as well, one may use the right side of Eq. (1) as an unperturbed Hamiltonian in the Møller-Plesset perturbation formalism [4].

The solutions of the Schrödinger equation for the approximate Hamiltonian on the right side of Eq. (1) are represented by Slater determinants that consist of the occupied spin orbitals selected out of the eigenfunctions of the one-electron Hamiltonian $h(\mu)$, and the eigen-energy for the configuration state function is the simple sum of the spin orbital energies, which corresponds to the rough estimation of the state function and the average energy of any electronic configuration. It is desired that the roughly calculated energies be close to the experimental values for the states with the corresponding electronic configuration. In this paper, we introduce a new form of $h(\mu)$, which is simple and may be regarded as a reasonable description of one-electron Hamiltonian in the average state of the ground and excited electronic configurations.

2. A new one-electron potential (linkage of embedded atomic fields)

In Eq. (1), $h(\mu)$ is considered as the one-electron Hamiltonian

$$h(\mu)=(-1/2)\Delta(\mu)-\sum_{\alpha=1}^{n}(Z_\alpha/r_{\mu\alpha})+u(\mu, c), \qquad (2)$$

where the first term is the kinetic energy of the μth electron, the second term is the Coulomb attraction from nuclei, and the third term $u(\mu, c)$ is the Coulomb repulsion from other electrons as a function of the coordinates of the μth electron and the electronic configuration c. The form of the third term emphasizes that the electronic repulsion term cannot be described as a function of only the coordinates of the electron under consideration. In other words, it is necessary to presume the positions or distribution of other electrons. One assumption may be the distribution of electrons in a certain configuration calculated by such an appropriate method as the Hartree-Fock method. It is also reasonable to assume that all electrons move around the center of each atom, so as to shield the nuclear charge, in the average state of the ground and excited states, as shown below.

First, one divides the total three-dimensional space into the neighborhoods of nuclei in an isolated molecule, namely, "atomic cells", $\mathfrak{C}_1, \mathfrak{C}_2, \ldots, \mathfrak{C}_n$, which satisfy the following conditions. For an arbitrary pair of different atomic cells, $(\mathfrak{C}_\alpha, \mathfrak{C}_\beta)$,

$$\mathfrak{C}_\alpha \cap \mathfrak{C}_\beta = \phi \qquad (\alpha \neq \beta), \qquad (3)$$

and for all atomic cells in the molecule,

$$\mathfrak{C}_1 \cup \mathfrak{C}_2 \cup \cdots \cup \mathfrak{C}_n = \bigcup_{\alpha=1}^{n} \mathfrak{C}_\alpha = \mathfrak{R}^3, \tag{4}$$

where $\mathfrak{R}^3$ represents the total set of position vectors of a particle and ϕ is empty set. In addition, it is assumed that each atomic cell contains a large portion of the imaginary charge of electrons of the corresponding isolated atom in the ground state, and that the space outside the molecule be appropriately included by the cells at the surface of the molecule. These cells may be analogous to the Wigner–Seitz cells in crystals.[1] Secondly, one assumes a hypothetical neutral molecule as follows, which may be the zeroth order approximation of various kinds of real neutral molecules and supermolecules (nonpolar molecules, polar molecules, charge-transfer complexes, ion pairs, etc.). In the zeroth order molecule, the net charge of the electrons and the nucleus contained in each atomic cell is zero, and electrons are moving under the zero-charge condition. In other words, when an electron, which would be described in our one-electron Schrödinger equation, migrates from an atomic cell $\mathfrak{C}_\alpha$ to an adjacent atomic cell $\mathfrak{C}_\beta$, an appropriate inter-cellular migration of other electrons occur simultaneously, so as to retain the zero-charge condition (e.g. another electron's migration from the cell $\mathfrak{C}_\beta$ to the cell $\mathfrak{C}_\alpha$). In addition, it is assumed that the electrons in this zeroth order molecule are not far apart from the molecule like those in the Rydberg excited states, but stay inside the molecule like those in the ground and valence excited states. Thus it is expected that the large portion of the potential, which the electron staying in the cell $\mathfrak{C}_\alpha$ sees, consists of the attraction from the nucleus α and the repulsion from $(Z_\alpha - 1)$ other electrons staying in the cell $\mathfrak{C}_\alpha$, because the attraction from any other nucleus β and the repulsion from Z_β electrons staying in the cell $\mathfrak{C}_\beta$ are roughly compensated each other. The above one-electron potential may be written as

$$v(\mathbf{r}) = v_\alpha(\mathbf{r}) \qquad (\text{when } \mathbf{r} \in \mathfrak{C}_\alpha), \tag{5}$$

where $\mathbf{r}$ denotes the position vector of the electron to be described and $v_\alpha(\mathbf{r})$ means the one-electron potential that is shared by all the Hartree–Fock orbitals for the ground state and the excited orbitals for the one-electron-excited state [5] of the isolated neutral atom with the nucleus α. From now on, we will call this type of potential "*linkage of embedded atomic fields* (LEAF)". Since the LEAF potential is literally described as an atomic potential in each cell, it is easy to image and understand.

3. Matrix elements of LEAF Hamiltonian

One can easily find the following property of the one-electron Hamiltonian $h_{\mathrm{LEAF}}(\mathbf{r})$ that possesses the one-electron potential (5). From Eq. (5), for an

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[1] The atomic cells in a molecule are not given definitely like Wigner–Seitz cells, while we proceed under the mathematical conditions, Eqs. (3) and (4), and the intuitive image of atomic cells

arbitrary bound-state one-electron function $f(\mathbf{r})$,

$$\begin{aligned} \hbar_{\text{LEAF}} f(\mathbf{r}) &= [-(1/2)\Delta + v)f(\mathbf{r}) \\ &= [-(1/2)\Delta + v_\alpha]f(\mathbf{r}) \\ &= \hbar_\alpha f(\mathbf{r}) \qquad (\text{when } \mathbf{r} \in \mathfrak{C}_\alpha), \end{aligned} \tag{6}$$

where $\hbar_\alpha$ denotes the one-electron Hamiltonian possessing the one-electron potential v_α. The eigenfunctions of the operator $\hbar_\alpha$ are the Hartree–Fock orbitals for the ground state and the excited orbitals for the one-electron-excited states, and specified as

$$\hbar_\alpha \phi_{\alpha i} = \varepsilon_{\alpha i} \phi_{\alpha i}, \tag{7}$$

where $\phi_{\alpha i}$ denotes the ith normalized eigenfunction of the bound state; in case that $\phi_{\alpha i}$ is a ground-state orbital, the ith eigenvalue $\varepsilon_{\alpha i}$ corresponds to the negative value of an ionization potential of the ground-state atom, and in case that $\phi_{\alpha i}$ is an excited orbital for a one-electron-excited state, the difference in energy between $\phi_{\alpha i}$ and the ground-state orbital involved in the excitation corresponds to the excitation energy [5].

Considering Eq. (6), one can easily obtain the matrix elements of $\hbar_{\text{LEAF}}$ as follows. If the atomic cells in a molecule, which satisfy Eqs. (3) and (4), are regarded as three-dimensional domains of spatial integration, the addition theorem of definite integral gives

$$\int_{\mathfrak{R}^3} = \sum_{\alpha=1}^{n} \int_{\mathfrak{C}_\alpha} . \tag{8}$$

Thus, for an arbitrary pair of bound-state one-electron functions, $f(\mathbf{r})$ and $g(\mathbf{r})$,

$$\begin{aligned} \langle f|\hbar_{\text{LEAF}}|g\rangle &\equiv \int_{\mathfrak{R}^3} f^* \hbar_{\text{LEAF}} g \, d\tau \\ &= \sum_{\alpha=1}^{n} \int_{\mathfrak{C}_\alpha} f^* \hbar_{\text{LEAF}} g \, d\tau, \end{aligned} \tag{9}$$

where $d\tau$ represents the volume element and integrations are taken in the three-dimensional domains represented by the subscripts of integral symbols. Since the variable of the integrand ($\mathbf{r}$) belongs to the cell $\mathfrak{C}_\alpha$ when the domain of integration is $\mathfrak{C}_\alpha$, from Eq. (6),

$$\int_{\mathfrak{C}_\alpha} f^* \hbar_{\text{LEAF}} g \, d\tau = \int_{\mathfrak{C}_\alpha} f^* \hbar_\alpha g \, d\tau. \tag{10}$$

In addition, since an arbitrary bound-state one-electron function can be expanded in terms of the descrete series of bound-state atomic orbitals on the nucleus α as

$$f = \sum_i \phi_{\alpha i} \langle \phi_{\alpha i}|f\rangle, \tag{11}$$

$$\begin{aligned} \int_{\mathfrak{C}_\alpha} f^* \hbar_\alpha g \, d\tau &= \int_{\mathfrak{C}_\alpha} \left(\sum_i \phi_{\alpha i} \langle \phi_{\alpha i}|f\rangle \right)^* \hbar_\alpha \left(\sum_j \phi_{\alpha j} \langle \phi_{\alpha g}|g\rangle \right) d\tau \\ &= \sum_i \sum_j \langle f|\phi_{\alpha i}\rangle \left(\int_{\mathfrak{C}_\alpha} \phi^*_{\alpha i} \phi_{\alpha j} \, d\tau \right) \varepsilon_{\alpha j} \langle \phi_{\alpha j}|g\rangle, \end{aligned} \tag{12}$$

where Eq. (7) is utilized and $\langle f|g\rangle$ denotes the integral

$$\int_{\Re^3} f^* g \, d\tau. \tag{13}$$

Summarizing Eqs. (9), (10), and (12), an arbitrary matrix elements of the LEAF Hamiltonian is found to be represented as

$$\langle f|\hslash_{\mathrm{LEAF}}|g\rangle = \sum_{\alpha=1}^{n} \sum_{i}\sum_{j} \langle f|\phi_{\alpha i}\rangle W(\alpha, i; \alpha, j; \mathfrak{C}_\alpha)\varepsilon_{\alpha j}\langle \phi_{\alpha j}|g\rangle, \tag{14}$$

where the function $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$ is defined as

$$W(\alpha, i; \beta, j; \mathfrak{C}_\gamma) \equiv \int_{\mathfrak{C}_\gamma} \phi^*_{\alpha i}\phi_{\beta j}\, d\tau. \tag{15}$$

Since Eq. (14) is satisfied by any pair of bound-state wave functions (f, g), one can obtain such a representation of LEAF Hamiltonian as

$$\hslash_{\mathrm{LEAF}} = \sum_{\alpha=1}^{n} \sum_{i}\sum_{j} |\phi_{\alpha i}\rangle W(\alpha, i; \alpha, j; \mathfrak{C}_\alpha)\varepsilon_{\alpha j}\langle \phi_{\alpha j}|. \tag{16}$$

4. Another representation of $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$

In this section, another representation of the function $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$ will be obtained for computation or approximation. First, a necessary condition of $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$ required by the condition of the domains of integration $\{\mathfrak{C}_\alpha\}$ (Eqs. (3) and (4)) will be derived. From the addition theorem of definite integration (Eq. (8)) as the necessary condition of Eqs. (3) and (4), the function $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$ that is defined in Eq. (15) should satisfy the condition

$$\begin{aligned}\sum_{\gamma=1}^{n} W(\alpha, i; \beta, j; \mathfrak{C}_\gamma) &= \sum_{\gamma=1}^{n} \int_{\mathfrak{C}_\gamma} \phi^*_{\alpha i}\phi_{\beta j}\, d\tau \\ &= \int_{\Re^3} \phi^*_{\alpha i}\phi_{\beta j}\, d\tau. \end{aligned}\tag{17}$$

Secondly, some sets of one-electron functions will be introduced from the set of atomic orbitals $\{\phi_{\alpha i}\}$. A set of one-electron functions $\{\bar{\phi}_{\alpha i}\}$ is defined as

$$\bar{\phi}_{\alpha i}(\mathbf{r}) \equiv \begin{cases} A_{\alpha i}\phi_{\alpha i}(\mathbf{r}) & (\mathbf{r} \in \mathfrak{C}_\alpha) \\ 0 & (\mathbf{r} \notin \mathfrak{C}_\alpha), \end{cases} \tag{18}$$

where $A_{\alpha i}$ is the normalization factor. In addition, one introduces the set $\{\overset{\circ}{\lambda}_{\alpha i}\}$, which is obtained by the symmetric orthonormalization [6] of the set $\{\bar{\phi}_{\alpha i}\}$ as

$$\boldsymbol{\lambda}^\circ = \bar{\mathbf{S}}^{-1/2}\bar{\boldsymbol{\phi}}, \tag{19}$$

where $\boldsymbol{\lambda}^\circ$ and $\bar{\boldsymbol{\phi}}$ denote the column vectors the components of which are $\overset{\circ}{\lambda}_{\alpha i}$'s and $\bar{\phi}_{\alpha i}$'s, respectively, and the $(\alpha, i; \beta, j)$-element of the square matrix $\bar{\mathbf{S}}$ is defined as

$$\bar{\mathbf{S}}_{\alpha i, \beta j} \equiv \int_{\Re^3} \bar{\phi}^*_{\alpha i}\bar{\phi}_{\beta j}\, d\tau. \tag{20}$$

If the off-diagonal elements of $\bar{\mathbf{S}}$ are sufficiently small, the matrix $\bar{\mathbf{S}}^{-1/2}$ can be expanded as

$$\bar{\mathbf{S}}^{-1/2} = \mathbf{1} - (1/2)\bar{\boldsymbol{\sigma}} + (3/8)\bar{\boldsymbol{\sigma}}^2 - + \cdots, \tag{21}$$

where $\mathbf{1}$ denotes a unit matrix and $\bar{\boldsymbol{\sigma}}$ is defined as

$$\bar{\boldsymbol{\sigma}} \equiv \bar{\mathbf{S}} - \mathbf{1}. \tag{22}$$

Thus each component of the column vector in Eq. (19) is represented as

$$\begin{aligned}\lambda^{\circ}_{\alpha i} = \bar{\phi}_{\alpha i} &- (1/2) \sum_{\beta=1}^{n} \sum_{j} \bar{\sigma}_{\alpha i,\beta j} \bar{\phi}_{\beta j} \\ &+ (3/8) \sum_{\beta=1}^{n} \sum_{j} \sum_{\gamma=1}^{n} \sum_{k} \bar{\sigma}_{\alpha i,\beta j} \bar{\sigma}_{\beta j,\gamma k} \bar{\phi}_{\gamma k} - + \cdots .\end{aligned} \tag{23}$$

Since $\bar{\sigma}_{\alpha i,\beta j}$ vanishes in case of $\alpha \neq \beta$ from Eq. (18), $\lambda^{\circ}_{\alpha i}$ is expressed in the form of the linear combination of $\bar{\phi}_{\alpha j}$'s as

$$\lambda^{\circ}_{\alpha i} = \bar{\phi}_{\alpha i} - (1/2) \sum_{j} \bar{\sigma}_{\alpha i,\alpha j} \bar{\phi}_{\alpha j} + (3/8) \sum_{j} \sum_{k} \bar{\sigma}_{\alpha i,\alpha j} \bar{\sigma}_{\alpha j,\alpha k} \bar{\phi}_{\alpha k} - + \cdots . \tag{24}$$

Accordingly, $\lambda^{\circ}_{\alpha i}$'s are zero outside the cell $\mathfrak{C}_\alpha$ as $\bar{\phi}_{\alpha i}$'s (Eq. 18), and an arbitrary bound-state wave function f on the domain $\mathfrak{C}_\alpha$ can be expanded in terms of $\lambda^{\circ}_{\alpha i}$'s as

$$f(\mathbf{r}) = \sum_{i} \lambda^{\circ}_{\alpha i}(\mathbf{r}) \langle \lambda^{\circ}_{\alpha i} | f \rangle \qquad (\mathbf{r} \in \mathfrak{C}_\alpha), \tag{25}$$

which is due to the completeness of the set $\{\phi_{\alpha i}\}$ on the domain $\mathfrak{C}_\alpha$ (Eq. 11). Since the variable of integrand belongs to the domain $\mathfrak{C}_\gamma$ in the integral $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$ (Eq. (15)),

$$\begin{aligned} W(\alpha, i; \beta, j; \mathfrak{C}_\gamma) &= \int_{\mathfrak{C}_\gamma} \left(\sum_{k} \lambda^{\circ}_{\gamma k} \langle \lambda^{\circ}_{\gamma k} | \phi_{\alpha i} \rangle \right)^{*} \left(\sum_{l} \lambda^{\circ}_{\gamma l} \langle \lambda^{\circ}_{\gamma l} | \phi_{\beta j} \rangle \right) d\tau \\ &= \sum_{k} \sum_{l} \langle \phi_{\alpha i} | \lambda^{\circ}_{\gamma k} \rangle \left(\int_{\mathfrak{C}_\gamma} \lambda^{\circ *}_{\gamma k} \lambda^{\circ}_{\gamma l} \, d\tau \right) \langle \lambda^{\circ}_{\gamma l} | \phi_{\beta j} \rangle \\ &= \sum_{k} \langle \phi_{\alpha i} | \lambda^{\circ}_{\gamma k} \rangle \langle \lambda^{\circ}_{\gamma k} | \phi_{\beta j} \rangle, \end{aligned} \tag{26}$$

where it is utilized that $\lambda^{\circ}_{\gamma k}$'s are the orthonormalized functions also on the domain $\mathfrak{C}_\gamma$. From the completeness of the set $\{\lambda^{\circ}_{\gamma k}\}$ on the domain $\mathfrak{R}^3$, $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$'s in the form of Eq. (26) obviously satisfy the necessary condition of atomic cells (Eq. 17).

5. Approximate forms of $\hbar_{\mathrm{LEAF}}$ and $W(\alpha, i; \beta, j; \mathfrak{C}_\alpha)$'s

As long as the atomic cells $\{\mathfrak{C}_\alpha\}$ are not definitely given, the exact $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$ cannot be obtained. Here, we will introduce the three approximations, which implicitly include the definition of atomic cells $\{\mathfrak{C}_\alpha\}$, and obtain approximate forms of $\hbar_{\mathrm{LEAF}}$ and the $W(\alpha, i; \alpha, j; \mathfrak{C}_\alpha)$'s which appear in Eq. (16).

First of all, subsets of $\{\phi_{\alpha i}\}$, G_α's, are given, each of which consists of the ground-state atomic orbitals (AO's) on the nucleus α and the excited AO's on the nucleus α with the orbital radii comparable to the longest of the ground-state AO's radii, in other words, the core and valence AO's on the nucleus α. From the assumption of the zeroth order molecule and the LEAF potential, it is reasonable to confine our attention to the one-electron-function space spanned by the elements of G_α's, namely, core and valence AO's.

Approximation A

An arbitrary one-electron function (core or valence) on the domain $\mathfrak{C}_\alpha$ is approximated as

$$f(\mathfrak{r}) \simeq \sum_{i}^{G_\alpha} \phi_{\alpha i}\langle\phi_{\alpha i}|f\rangle \qquad (\mathfrak{r}\in\mathfrak{C}_\alpha). \tag{27}$$

The introduction of *Approximation A* into Eq. (16) gives the following approximate Hamiltonian as

$$\hbar_{\text{LEAF}} \simeq \sum_{\alpha=1}^{n} \sum_{i}^{G_\alpha} \sum_{j}^{G_\alpha} |\phi_{\alpha i}\rangle W(\alpha, i; \alpha, j; \mathfrak{C}_\alpha)\varepsilon_{\alpha j}\langle\phi_{\alpha j}|, \tag{28}$$

as long as one treats core and valence orbitals.

Since any atomic cell $\mathfrak{C}_\alpha$ contains a large portion of any core or valence AO on the nucleus α, the following approximation may be appropriate, considering Eq. (18).

Approximation B

$$\bar{\phi}_{\alpha i} \simeq \phi_{\alpha i}, \tag{29}$$

where $\phi_{\alpha i}$ belongs to the G_α.

If one introduces *Approximation B* into the $W(\alpha, i; \alpha, j; \mathfrak{C}_\alpha)$'s in Eq. (15), considering Eq. (18),

$$\begin{aligned} W(\alpha, i; \alpha, j; \mathfrak{C}_\alpha) &= \int_{\mathfrak{R}^3} (\bar{\phi}_{\alpha i}/A_{\alpha i})(\bar{\phi}_{\alpha j}/A_{\alpha j})\, d\tau \\ &\simeq (A_{\alpha i}A_{\alpha j})^{-1} \int_{\mathfrak{R}^3} \phi_{\alpha i}\phi_{\alpha j}\, d\tau \\ &= (A_{\alpha i})^{-2}\delta_{ij} \\ &= W(\alpha, i; \alpha, i; \mathfrak{C}_\alpha)\delta_{ij} \qquad (\phi_{\alpha i}\in G_\alpha \text{ and } \phi_{\alpha j}\in G_\alpha), \end{aligned} \tag{30}$$

where it is noted that the factor $(A_{\alpha i})^{-2}$ is identical with $W(\alpha, i; \alpha, i; \mathfrak{C}_\alpha)$ from the definition of $A_{\alpha i}$, and real forms of AO's are used. From now on, only the real one-electron functions will be considered.

Introducing *Approximation B*, the complete orthonormal set $\{\lambda^\circ_{\alpha i}\}$ in Eq. (23) may be approximated by the orthonormal set $\{\lambda_{\alpha i}\}$, each element of which is defined as

$$\begin{aligned}\lambda_{\alpha i} \equiv \phi_{\alpha i} &- (1/2) \sum_{\beta=1}^{n} \sum_{j}^{G_\beta} \sigma_{\alpha i,\beta j}\phi_{\beta j} \\ &+ (3/8) \sum_{\beta=1}^{n} \sum_{j}^{G_\beta} \sum_{\gamma=1}^{n} \sum_{k}^{G_\gamma} \sigma_{\alpha i,\beta j}\sigma_{\beta j,\gamma k}\phi_{\gamma k} \\ &- + \cdots \qquad (\phi_{\alpha i} \in G_\alpha),\end{aligned} \tag{31}$$

where

$$\sigma_{\alpha i,\beta j} \equiv \int_{\Re^3} \phi_{\alpha i}\phi_{\beta j}\, d\tau - \delta_{\alpha\beta}\delta_{ij}. \tag{32}$$

The $\lambda_{\alpha i}$'s localization in the cell $\mathfrak{C}_\alpha$ is supported by the theorem that the symmetric orthonormalization minimizes the sum of squared distances (in Hilbert space) between each initial function and a corresponding function of the linearly transformed set [7]. In addition, the theorem also justifies the approximation that any core or valence orbital on the domain $\mathfrak{C}_\alpha$ could be expanded in terms of $\lambda_{\alpha i}$'s like $\phi_{\alpha i}$'s in *Approximation A*. The matrix representation of Eq. (31) is

$$\begin{aligned}\boldsymbol{\lambda}_G &= \boldsymbol{\phi}_G - (1/2)\boldsymbol{\sigma}_G\boldsymbol{\phi}_G + (3/8)\boldsymbol{\sigma}_G^2\boldsymbol{\phi}_G - + \cdots \\ &= (\mathbf{1} + \boldsymbol{\sigma}_G)^{-1/2}\boldsymbol{\phi}_G,\end{aligned} \tag{33}$$

where $\boldsymbol{\phi}_G$ denotes the column vector, the components of which are all the elements of the subset

$$G \equiv G_1 \cup G_2 \cup \cdots \cup G_n = \bigcup_{\alpha=1}^{n} G_\alpha, \tag{34}$$

each component of $\boldsymbol{\lambda}_G$ is $\lambda_{\alpha i}$ in Eq. (31), and the symmetric matrix $\boldsymbol{\sigma}_G$ has the elements $\sigma_{\alpha i,\beta j}$'s defined in Eq. (32). From the representation of $W(\alpha, i; \beta, j; \mathfrak{C}_\gamma)$ in Eq. (26), the use of $\lambda_{\beta j}$'s in place of $\lambda^\circ_{\beta j}$'s gives approximate $W(\alpha, i, \alpha, i; \mathfrak{C}_\beta)$'s as

$$\begin{aligned}W(\alpha, i; \alpha, i; \mathfrak{C}_\beta) &\simeq \sum_{j}^{G_\beta} \langle \phi_{\alpha i}|\lambda_{\beta j}\rangle\langle\lambda_{\beta j}|\phi_{\alpha i}\rangle \\ &= \sum_{j}^{G_\beta} [\langle \boldsymbol{\phi}_G|{}^t\boldsymbol{\lambda}_G\rangle]_{\alpha i,\beta j}[\langle\boldsymbol{\lambda}_G|{}^t\boldsymbol{\phi}_G\rangle]_{\beta j,\alpha i} \\ &= \sum_{j}^{G_\beta} |[(\mathbf{1} + \boldsymbol{\sigma}_G)^{1/2}]_{\alpha i,\beta j}|^2,\end{aligned} \tag{35}$$

where the square bracket with the subscript $(\alpha i, \beta j)$ denotes the $(\alpha, i; \beta, j)$-element of the matrix in the bracket, and ${}^t\mathbf{M}$ means the transposed matrix of $\mathbf{M}$. Substituting i and j for subscripts (α, i) and (β, j), respectively, each term in Eq. (35) is rewritten as

$$\begin{aligned}|[(\mathbf{1}+\boldsymbol{\sigma}_G)^{1/2}]_{ij}|^2 &= |[\mathbf{1}+(1/2)\boldsymbol{\sigma}_G-(1/8)\boldsymbol{\sigma}_G^2+\cdots]_{ij}|^2\\ &= |\delta_{ij}+(1/2)\sigma_{ij}-(1/8)\sum_p^G \sigma_{ip}\sigma_{pj}+\cdots|^2\\ &= (\delta_{ij})^2+\delta_{ij}\sigma_{ij}+(1/4)(\sigma_{ij})^2-(1/4)\delta_{ij}\sum_p^G(\sigma_{ip})^2+\cdots, \end{aligned} \tag{36}$$

where only the terms up to second order of σ are described. Summarizing Eqs. (35) and (36) yields

$$W(\alpha, i; \alpha, i; \mathfrak{C}_\alpha) \simeq 1-(1/4)\sum_{\beta=1}^{n}\sum_{j}^{G_\beta}(\sigma_{\alpha i,\beta j})^2+\cdots, \tag{37}$$

and

$$W(\alpha, i; \alpha, i; \mathfrak{C}_\beta) \simeq (1/4)\sum_{j}^{G_\beta}(\sigma_{\alpha i,\beta j})^2+\cdots \qquad (\alpha \neq \beta). \tag{38}$$

Considering the definition of $\sigma_{\alpha i,\beta j}$ in (32), the approximate values of $W(\alpha, i; \alpha, i; \mathfrak{C}_\beta)$'s in (37) and (38) seem to satisfy the necessary condition of atomic cells in Eq. (17). Actually, the satisfaction can be proved in the form of Eq. (35) as

$$\begin{aligned}\sum_{\beta=1}^{n} W(\alpha, i; \alpha, i; \mathfrak{C}_\beta) &\simeq \sum_{\beta=1}^{n}\sum_{j}^{G_\beta}[(\mathbf{1}+\boldsymbol{\sigma}_G)^{1/2}]_{\alpha i,\beta j}[(\mathbf{1}+\boldsymbol{\sigma}_G)^{1/2}]_{\beta j,\alpha i}\\ &= [\mathbf{1}+\boldsymbol{\sigma}_G]_{\alpha i,\alpha i}\\ &= 1. \end{aligned} \tag{39}$$

Introducing the approximation in (30) into Eq. (28), one obtains the approximate form of $\hbar_{\text{LEAF}}$ as

$$\hbar_{\text{LEAF}} \simeq \sum_{\alpha=1}^{n}\sum_{k}^{G_\alpha}|\phi_{\alpha k}\rangle W(\alpha, k; \alpha, k; \mathfrak{C}_\alpha)\varepsilon_{\alpha k}\langle\phi_{\alpha k}|. \tag{40}$$

However, if one successively introduces *Approximations A* and *B*, the invariance of the one-electron Hamiltonian with respect to the rotation of $\phi_{\alpha k}$'s around the nucleus α is not guaranteed. In order to retain the invariance, we define an average value as

$$W_{\alpha\tilde{n}l} \equiv (2l+1)^{-1}\sum_{i}^{\{\alpha,\tilde{n},l\}} W(\alpha, i; \alpha, i; \mathfrak{C}_\alpha), \tag{41}$$

where the summation runs over all the AO's which have the center α, the principal number $\tilde{n}$, and the azimuthal number l. In addition, we introduce the following approximation.

Approximation C

Each $W_{\alpha\tilde{n}l}$ is substituted for $(2l+1)$ corresponding $W(\alpha, i; \alpha, i; \mathfrak{C}_\alpha)$'s in (40).

Approximation C yields

$$\hbar_{\mathrm{LEAF}} \simeq \sum_{\alpha=1}^{n} \sum_{\{\alpha,\tilde{n},l\}}^{G_\alpha} W_{\alpha\tilde{n}l}\varepsilon_{\alpha\tilde{n}l} \sum_{k}^{\{\alpha,\tilde{n},l\}} |\phi_{\alpha k}\rangle\langle\phi_{\alpha k}|, \tag{42}$$

where the AO sets $\{\alpha, \tilde{n}, l\}$ are the subsets of G_α, $\varepsilon_{\alpha\tilde{n}l}$ denotes the orbital energy shared by the AO's which belong to the set $\{\alpha, \tilde{n}, l\}$. Introducing the approximation in (35) or (37) into Eq. (41), one finds the approximate form of $W_{\alpha\tilde{n}l}$ as follows.

$$\begin{aligned} W_{\alpha\tilde{n}l} &\simeq (2l+1)^{-1} \sum_{i}^{\{\alpha,\tilde{n},l\}} \sum_{j}^{G_\alpha} |[(\mathbf{1}+\boldsymbol{\sigma}_G)^{1/2}]_{\alpha i,\alpha j}|^2 \\ &= (2l+1)^{-1} \sum_{i}^{\{\alpha,\tilde{n},l\}} \left\{1-(1/4)\sum_{\beta=1}^{n}\sum_{j}^{G_\beta}(\sigma_{\alpha i,\beta j})^2+\cdots\right\}. \end{aligned} \tag{43}$$

Considering that the symmetric matrix $(\mathbf{1}+\boldsymbol{\sigma}_G)^{1/2}$ is transformed into

$$\mathbf{R}(\mathbf{1}+\boldsymbol{\sigma}_G)^{1/2}\,{}^t\mathbf{R} \tag{44}$$

by the atomic rotation that is represented by the orthogonal matrix $\mathbf{R}$, it is obvious that the approximate forms of $W_{\alpha\tilde{n}l}$ in (43) and $\hbar_{\mathrm{LEAF}}$ in (42) are invariant against the atomic rotation.

6. Coulomb and resonance integrals

From the approximate form of LEAF Hamiltonian (42), one can derive several types of extended Hückel Hamiltonian by the following approximations.

Approximation 1

The differential overlaps ($\phi_{\alpha i}\phi_{\beta j}$'s) between core and valence orbitals are neglected.

From the chemical standpoint, we are interested in the valence orbitals. If one introduces *Approximation 1*, the valence part of $\hbar_{\mathrm{LEAF}}$ can be treated independently of the core terms of the Hamiltonian, because the resonance integrals between valence and core AO's are zero with respect to the $\hbar_{\mathrm{LEAF}}$ in the form of Eq. (42). Thus the valence block of the approximate matrix of $\hbar_{\mathrm{LEAF}}$ can be separated as an independent matrix. Each element of the matrix is represented as

$$\begin{aligned} H_{rs} &= \sum_{\alpha=1}^{n} \sum_{\{\alpha,\tilde{n},l\}}^{V_\alpha} W_{\alpha\tilde{n}l}\varepsilon_{\alpha\tilde{n}l} \sum_{k}^{\{\alpha,\tilde{n},l\}} \langle\chi_r|\phi_{\alpha k}\rangle\langle\phi_{\alpha k}|\chi_s\rangle \\ &= \sum_{k} S_{rk}W_k\varepsilon_k S_{ks}, \end{aligned} \tag{45}$$

where the summation with respect to k runs over all the valence AO's in the molecule, χ_r's denote the valence AO's as basis functions, S_{rk} is the (r, k)-element of the matrix $\mathbf{1}+\boldsymbol{\sigma}_G$, and W_k and ε_k are the $W_{\alpha\tilde{n}l}$ and the $\varepsilon_{\alpha\tilde{n}l}$ of ϕ_k, respectively. From Eq. (45), one can see that each matrix element (Coulomb or resonance integral) of the valence LEAF one-electron Hamiltonian includes the influences from all the atoms ($\alpha = 1, \ldots, n$) in a molecule.

Approximation 2

W_k's, which are near and less than unity, are taken as unity.

If one introduces *Approximation 2* into Eq. (45), the formula will be identical with that of the energy weighted maximum overlap (EWMO) model, which was developed in a Green's function or propagator formulation [8], and was derived and analyzed by the density functional theory [9]. The EWMO model doesn't have any concept of such atomic cells as given in the LEAF model. However, there is one characteristic that is possessed by both EWMO and LEAF and that arises from the common form

$$H_{rs} = \sum_k S_{rk} F_k S_{ks}, \tag{46}$$

where F_k's are all negative. This characteristic is that all the MO energies calculated from the matrix elements H_{rs}'s in Eq. (46) are negative. It can be easily proved with the real quadratic form of the matrix $\{H_{rs}\}$. This property is reasonable because the one-electron state function represented by an LCAO function describes a state of an electron bound by a molecule, the state function of which is characterized by the equation

$$\lim_{|r|\to\infty} \psi(r) = 0^{2}. \tag{47}$$

Approximation 3

The AO's as basis functions are replaced by the symmetrically orthogonalized energy weighted atomic orbitals, each of which is close to the corresponding original atomic orbital [9].

If one introduces *Approximation 3* in addition to *Approximation 2*, one obtains the formula

$$H_{rs} = -S_{rs}\sqrt{H_{rr}H_{ss}}, \tag{48}$$

where S_{rs} denotes the overlap between the corresponding original AO's ϕ_r and ϕ_s [9]. This formula has the form similar to that which was proposed by Ballhausen and Gray [10].

Approximation 4

In Eq. (45), each W_k, which is near and less than unity, is replaced by the average value of all the W_k's, and the second-order terms of the overlaps that are not equal to unity are neglected.

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[2] If the energy of a state represented by an LCAO were positive, the corresponding solution of the Schrödinger equation in the region sufficiently far apart from the molecule would have the form

$$\psi(r) \simeq A \exp(\pm ik \cdot r),$$

since both the Coulomb attractive and repulsive terms would be sufficiently small. This solution contradicts Eq. (47)

If one employs *Approximation 4* after *Approximation 1*, one finds

$$H_{rs}=\begin{cases} W\varepsilon_r & (r=s) \\ WS_{rs}(\varepsilon_r+\varepsilon_s) & (r\neq s), \end{cases} \tag{49}$$

where W denotes the average value of all the W_k's in Eq. (45). From the Eq. (49), one finds the Wolfsberg-Helmholz-type relationship [11] between resonance and Coulomb integrals,

$$H_{rs}=(K/2)S_{rs}(H_{rr}+H_{ss}), \tag{50}$$

where the parameter K is equal to 2. However, there's a definite inequality between the Coulomb integrals in Eq. (45) and Eq. (49) as

$$|\sum_k W_k\varepsilon_k S_{kr}^2| \simeq |W\sum_k \varepsilon_k S_{kr}^2 > |W\varepsilon_r|. \tag{51}$$

Thus it is more reasonable that the Coulomb integral in Eq. (45) should be estimated by the inequality

$$|H_{rr}| \gtrsim |W\varepsilon_r|. \tag{52}$$

In this case, which is closer to the LEAF formalism (Eq. 45), the K parameter is near and less than 2 in the Wolfsberg-Helmholz relationship (Eq. 50). It is interesting that the previously recommended value of the parameter K is 1.75 [1], which is near and less than 2 as expected by the LEAF formalism.

7. Molecular orbital energies of H_2O

In this section the MO energies of H_2O, which are calculated under the valence LEAF formalism and the popular Wolfsberg-Helmholtz (WH) formalism, will be presented. The geometry of H_2O is taken as O-H distance = 0.9575 Å and ∠HOH = 104.5° under C_{2v} symmetry. The used valence AO's are Slater-type orbitals ($\zeta(\mathrm{H}, 1s)=1.0000$, $\zeta(\mathrm{O}, 2s)=2.2458$, $\zeta(\mathrm{O}, 2p)=2.2266$) [12] and the used AO energies (ε_k's in LEAF, H_{rr}'s in WH) are the negative values of VOIP's ($\varepsilon(\mathrm{H}, 1s)=-13.60$ eV, $\varepsilon(\mathrm{O}, 2s)=-32.34$ eV, $\varepsilon(\mathrm{O}, 2p)=-15.80$ eV) [13], each of which is near the corresponding Hartree-Fock AO energy [14]. The parameter K is taken as 1.75 in the WH formalism, and in the valence LEAF formalism (Eq. 45), based on *Approximation 1*, W_k is given as

$$W_k=W_{\alpha\tilde{n}l}=(2l+1)^{-1}\sum_{i}^{\{\alpha,\tilde{n},l\}}\sum_{j}^{V_\alpha}|[(\mathbf{1}+\boldsymbol{\sigma}_V)^{1/2}]_{\alpha i,\alpha j}|^2, \tag{53}$$

where $\mathbf{1}+\boldsymbol{\sigma}_V$ denotes the matrix of the overlaps between valence AO's.

Table 1 shows the valence MO energies of H_2O, which were calculated under the above condition, and the measured ionization potentials corresponding to the valence MO's [15]. If one adopts the independent-particle model in the analysis of the electronic states of a molecule, the MO energies can be compared with the negative values of experimental ionization potentials. The agreement between the calculated (in both LEAF and WH) and experimental values is good. However it should be noted that the LEAF MO energies are given for the average

Table 1. Valence molecular orbital energies of H_2O (in eV)

MO	LEAF[a]	WH[b]	I_p[c]
$2b_2$	−4.64	+4.03	—
$4a_1$	−6.28	+9.95	—
$1b_1$	−15.40	−15.80	12.61
$3a_1$	−16.52	−16.26	14.73
$1b_2$	−18.09	−17.52	18.55
$2a_1$	−36.98	−33.40	32.19

[a] Calculated under the valence LEAF formalism
[b] Wolfsberg-Helmholtz formalism with $K = 1.75$
[c] Ionization potentials of H_2O in the ground state [15]

state of the ground and valence-excited configurations, in contrast with the Koopmans theorem for the Hartree-Fock MO energies which are given for a single state, usually for the ground state.

The energies of $4a_1$ and $2b_2$ MO's are negative in the LEAF formalism while those in the WH formalism are positive. These differences are connected with not only the property of one-electron Hamiltonian but also the estimation of excitation energies. If the complete Hamiltonian is approximated by the simple sum of the one-electron Hamiltonians for core and valence electrons as in Eq. (1), the excitation energy to promote an electron from a valence MO to another valence MO can be estimated with the difference in energy between the involved valence MO's. The excitation energies estimated by the LEAF formalism are 9.12 and 10.76 eV for the $(1b_1 \rightarrow 4a_1)$ and $(1b_1 \rightarrow 2b_2)$ excitations, respectively. These values are near the CI-calculated excitation energies from the ground state to the singlet $(1b_1 \rightarrow 4a_1)$ and $(1b_1 \rightarrow 2b_2)$ excited states (12.46 and 12.40 eV, respectively) [16]. On the other hand, the WH formalism estimated the $(1b_1 \rightarrow 4a_1)$ and $(1b_1 \rightarrow 2b_2)$ excitation energies to be 25.75 and 19.83 eV, which are far apart from the CI results.

The above discussion suggests that the LEAF Hamiltonian is suitable for the zeroth order description of the complete Hamiltonian for the ground and valence-excited states (Eq. 1), and therefore, that the LEAF MO's may be somehow useful in the CI calculations of the ground and valence-excited states.

8. Conclusion

A new model for extended Hückel type molecular orbital calculations with the concept of atomic cells was proposed and new forms of Coulomb and resonance integrals were derived from this model. Previous forms of Coulomb and resonance integrals (Wolfsberg-Helmholtz, Ballhausen-Gray, and EWMO) were also derived with several approximations from the new form. In the similarity to the EWMO model, the negative definite property of the energies of LCAO molecular orbitals was emphasized. In the comparison with the Wolfsberg-Helmholz form, the magnitude of the parameter K was discussed. Finally, it was found that the zeroth order estimation of valence excitation energies of H_2O in the LEAF formalism was in good agreement with the CI results.

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