Localized Self-Consistent Field Orbitals
in Atoms and Molecules *

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Introduction

From physical, chemical as well as mathematical considerations, it is to be expected that the electronic wavefunctions of molecular systems contain certain common features. For example, wavefunctions of similar molecules should exhibit corresponding similarities. It is therefore of interest to cast the wavefunctions into forms which put these regularities in evidence. This will help interpretation in terms of chemical concepts as well as the practical determination of wavefunctions for related systems.

The regularities are of course contained in the density operator and the pair-density operator. They are therefore completely characterized by the eigenvalues and eigenfunctions of these two operators, i.e., the natural orbitals and geminals and their occupation numbers. However, these can be found only after the wavefunction of the system is known.

A fundamental regularity occurring in many systems is that the wavefunction is, to a high degree of accuracy, given as an antisymmetrized product of pairfunctions

$$\Psi = \mathcal{A} \{ \Phi_1(1,2) \Phi_{II}(3,4) \ldots \} \quad (1)$$

where the individual factors can be written in diagonal form

$$\Phi_K(i,j) = \sum_n c_{Kn} \psi_{Kn}(i) \psi_{Kn}(j) \quad (2)$$

The first term is frequently dominant and, presents the important first step in finding the $\Phi_K$'s. Limiting the pairfunctions to this dominant term, one obtains for singlet states
which yields for \( \Psi \) the Hartree-Fock determinantal form

\[
\Psi = \mathcal{A} \left\{ (\phi_1 \alpha^{(1)} (\phi_2 \beta^{(2)} \cdots (\phi_N \alpha^{(N)} (\phi_N \beta^{(2N)}) \right \}
\]

(4)

where \( \phi_1 \phi_2 \cdots \phi_N \) can be assumed mutually orthogonal and normalized.

The dominant terms can therefore be determined to good approximation by finding the best possible wavefunction \( \Psi \) of the type of Eq. (4), i.e., the self-consistent-field (SCF) wavefunction, obtained by minimizing the energy. However, even after the SCF-\( \Psi \) has been obtained, there still exists a considerable amount of freedom in the choice of the individual SCF orbitals \( \phi_i \), and the following remarks deal with the problem of using this arbitrariness to best advantage. Since the pairfunction form of Eq. (1) implies that inter-pair correlations are negligible, it stands to reason that the most appropriate SCF orbitals are those which "keep out of each others' way" as much as possible so that the electronic interactions between them are as small as possible. In other words, it is most likely that, among the various possibilities, those SCF orbitals which exhibit maximum localization will be appropriate to serve as dominant terms in pairfunction expansions. It is a most gratifying, and by no means accidental coincidence that these same localized orbitals are also those which correspond very closely to the chemist's intuitive prejudices about inner shells, lone pairs, bond orbitals etc.

**Arbitrariness of Hartree-Fock Orbitals**

While the variation principle determines \( \Psi \), it does not completely determine the individual orbitals \( \phi_n \). In fact if
defines a new set of molecular orbitals $u_1', u_2' \ldots \ldots u_N'$, then the new determinantal function

$$\Psi' = \mathcal{A}\{(u_{1\alpha})^{(1)}(u_{1\beta})^{(2)} \ldots \ldots (u_{N\beta})^{2N}\}$$

is related to the previous one by

$$\Psi = \Psi' \cdot (\text{Det} T)^2,$$

and if $T$ is an orthogonal transformation,

$$\Psi = \Psi'$$

Equation (7) is a consequence of the fact that the determinant of the product of two matrices is equal to the product of the determinants of the two matrices. Thus $\Psi$ is invariant against orthogonal transformation among the $\varphi$'s.

This arbitrariness has its counterpart in the Hartree-Fock equations which, derived from $\Psi$ by the variation principle, have the form

$$\mathbf{F}(\rho) \varphi_n (x) = \sum_{m=1}^{N} \varphi_m (x) \gamma_{mn}$$

where the Hartree-Fock operator $\mathbf{F}$ depends on the solution orbitals $\varphi_1 \ldots \varphi_N$ via the density kernel (for simplicity of presentation we assume real wavefunctions)

$$\rho(x|x') = 2 \sum_{n=1}^{N} \varphi_n (x) \varphi_n (x').$$

It is readily seen that an orthogonal transformation leaves $\rho$, and hence $\mathbf{F}$, invariant and merely changes the values of the Lagrangian multipliers $\gamma_{mn} = \gamma_{nm'}$, which arise from incorporating the side conditions of
orthonormality viz.,

$$\int dx \varphi_m(x) \varphi_n(x) = \delta_{mn}. \quad (11)$$

Thus, introduction of Eq. (5) (with $T$ orthogonal), in Eqs. (8) and (10) yields

$$\mathcal{F}(\rho) u_\nu(x) = \sum_\mu u_\mu(x) \gamma'_{\mu\nu} \quad (12)$$

$$\gamma'_{\mu\nu} = \sum_{m,n} \gamma_{mn} T_{m\mu} T_{n\nu} = (T^\dagger \gamma T)_{\mu\nu} \quad (12')$$

$$\rho(x|x') = 2 \sum_\nu u_\nu(x) u_\nu(x'). \quad (13)$$

Moreover, although the orbitals $\varphi_n(x)$ have to satisfy the side conditions of orthonormality given by Eq. (11), the following argument shows that the off-diagonal elements of $\gamma_{mn}$ can be chosen arbitrarily.

The Hartree-Fock Equation (8) can be rewritten in the form

$$[\mathcal{F}(\rho) + \zeta(\varphi)] \varphi_n(x) = \gamma_{nn} \varphi_n(x) \quad (14)$$

where $\zeta(\varphi) = \zeta(\varphi_1 \cdots \varphi_N)$ is an integral operator defined by

$$\zeta(\varphi)f(x) = \int dx' G(x,x') f(x'), \quad (15)$$

$$G(x,x') = -\sum_i \sum_{k \neq k} \gamma_{ik} \varphi_k(x') \quad (15')$$

Consider now the $\gamma_{ik} = \gamma_{ki}$ ($i \neq k$) arbitrarily given. Since $G(x,x')$ is in any case symmetric, $[\mathcal{F} + \zeta]$ is a hermitean operator. Hence the solution of the pseudo-eigenvalue equation (14) can be chosen to form an orthonormal set, and thereby Eq. (14) reduces indeed to Eq. (8). Because of the orthonormality of the solutions, Eq. (14) furthermore yields the diagonality
The previous considerations show that there exist \( \frac{1}{2}N(N-1) \) arbitrary parameters in the choice of the SCF orbitals, when the SCF determinant \( \Psi \) is given. They can be chosen as the \( \frac{1}{2}N(N-1) \) parameters in the orthogonal transformations which generate other SCF orbitals from a given set. Or they can be chosen as the \( \frac{1}{2}N(N-1) \) off-diagonal Lagrangian multipliers \( \gamma_{ik} = \gamma_{ki} (k \neq i) \) in Eq. (15').

Correspondingly, a specific set of SCF orbitals can be selected in two ways:

1. By imposing \( \frac{1}{2}N(N-1) \) additional conditions on the orbitals,

\[
g_{\nu} [\phi_1(x), \phi_2(x), \ldots \phi_N(x)] \equiv 0,
\]

\( \nu = 1, 2, \ldots \frac{1}{2}N(N-1) \),

say, or

2. By imposing \( \frac{1}{2}N(N-1) \) additional conditions on the off-diagonal \( \gamma_{ik} \) (\( i \neq k \))

\[
\Gamma_{\nu} [\gamma_{12}, \ldots \gamma_{1N}, \gamma_{23}, \ldots \gamma_{2N}, \ldots \gamma_{N-1, N}] \equiv 0,
\]

\( \nu = 1, 2, \ldots \frac{1}{2}N(N-1) \).

These two methods of specification are of course related. In fact those SCF orbitals which satisfy the conditions (17) are obtained as solutions of the SCF equation (14), if the off-diagonal \( \gamma_{ik} \) are chosen as

\[
\int dV \phi_m(x) \left\{ \mathcal{F} + \mathcal{Q} \right\} \phi_n(x)
= \int dV \phi_m(x) \mathcal{F} \phi_n(x) + \gamma_{mn} (\delta_{mn} - 1) = \gamma_{nn} \delta_{mn}.
\]
\( \gamma_{ik} = \gamma_{ki} = \sum_{i,k} \{ g_i(\varphi), g_2(\varphi), \ldots, g_{\frac{1}{2}N(N-1)}(\varphi) \} + \int dV \varphi F \varphi_k, (i \neq k), (19) \)

where \( Q_{ik} [x_1 x_2 \cdots x_{\frac{1}{2}N(N-1)}] \) are \( \frac{1}{2} N(N-1) \) functions which vanish if and only if all arguments vanish. The proof of this contention follows from Eq. (16). The latter shows that, if the \( \gamma_{ik} \) are chosen according to Eq. (19), then

\[ Q_{ik}(g_1 g_2 \cdots) = 0 \text{ for all } i \neq k \quad (20) \]

and, because of the nature of the \( Q_{ik} \), the conditions (17) follow.

The solution of the SCF equations (14) requires, of course, iterative procedures. The particular choice of the functions \( Q_{ik} \) can presumably be made such as to favor convergence.

**Canonical SCF Orbitals**

As a first choice, we mention the canonical molecular orbitals. They arise by imposing the additional conditions \(^1\)

\[ \gamma_{mn} = \epsilon_n \delta_{mn} \quad (21) \]

leading to the canonical Hartree-Fock equations

\[ F(\rho) \varphi^0_n = \epsilon_n \varphi^0_n \quad (22) \]

This choice can also be characterized by requiring the one-electron orbital energy

\[ E(\varphi) = \int dx \varphi(x) F(\rho) \varphi(x) \quad (23) \]

to be stationary, when the density kernel \( \rho(x|x') \) is considered as known.
Externally Localized SCF Orbitals

A second possibility is the choice of an external localization criterion. Suppose we ask for those SCF MO's $\lambda_n^{i}(x)$ which exhibit maximal and minimal localization within a certain potential well $U(x)$. They are given as those solutions of the general equation (14) which result if, in Eq. (15'), one chooses the off-diagonal $\gamma_{ik}$ as

$$\gamma_{ik} = \int dV \lambda_{i}^{'}(x) \left\{ U(x) + \mathcal{F}(\rho) \right\} \lambda_{k}^{'}(x), \quad i \neq k. \quad (24)$$

This contention is proved as follows. Let $\lambda_{1}^{'}(x), \lambda_{2}^{'}(x), \ldots, \lambda_{N}^{'}(x)$ be the solutions of Eq. (14) with the choice of Eq. (24). They are then a possible set of SCF orbitals, and any other set can be expanded in terms of them, e.g.

$$\psi_{n}(x) = \sum_{\nu} \lambda_{\nu}^{'}(x) C_{\nu n}. \quad (25)$$

We are looking for those orbitals $\psi_{1} \cdots \psi_{N}$ which make the integral

$$\int dV \psi_{n}(x) U(x) \psi_{n}(x) = \sum_{\nu, \mu} c_{\nu n} c_{\mu n} \int dx \lambda_{\nu}^{'}(x) U(x) \lambda_{\mu}^{'}(x), \quad (26)$$

stationary. Because of the choice of Eq. (24), the general diagonality of Eq. (16) yields however,

$$\int dV \lambda_{m}^{'}(x) U(x) \lambda_{n}^{'}(x) = \int dV \lambda_{m}^{'}(x) \left\{ \mathcal{F} + G \right\} \lambda_{n}^{'}(x) = 0, \quad \text{for } m \neq n,$$

showing that the quadratic form (26) is in fact extremized by the $\lambda_{1}^{'}$, $\lambda_{2}^{'}$, $\ldots$, $\lambda_{N}^{'}$ themselves.

Other external localization criteria consist in requiring that the contributions of certain atomic orbitals from certain atoms be zero or minimal in an LCAO expansion, or that the overlap with certain local wavefunctions be maximized.
Intrinsically Localized SCF Orbitals

More important appears a third choice, namely the use of an intrinsic localization criterion to fix the molecular orbitals. Here we ask for those SCF orbitals which are "separated from each other" as much as possible, without stipulating in advance a location in space for them. It is obvious that the separation of two orbitals $\psi_\nu, \psi_\mu$ is best measured by an integral

$$\int dV_1 \int dV_2 \psi_\nu^2(1) \psi_\mu^2(2) f(\mathbf{r}_{12}) = [\psi_\nu^2 | \psi_\mu^2]$$

(24)

where $f(\mathbf{r}_{12})$ is a monotonic function of $\mathbf{r}_{12}$. The average interorbital separation is then given by

$$\frac{\sum_{\nu < \mu} [\psi_\nu^2 | \psi_\mu^2]}{\frac{1}{2} N(N-1)}.$$  

(25)

Intrinsically localized orbitals $\lambda_1(x), \lambda_2(x), \ldots, \lambda_N(x)$ are therefore obtained by minimizing this quantity. However, since the two expressions

$$\sum_{\nu, \mu} [\psi_\nu^2 | \psi_\mu^2] \quad \text{and} \quad \sum_{\nu, \mu} [\psi_\nu \psi_\mu | \psi_\nu \psi_\mu]$$

are easily seen to be invariant under orthogonal transformation of the $\psi$'s, the minimization of the expression (25) is clearly equivalent to the maximization of the sum

$$\sum_{\nu} [\psi_\nu^2 | \psi_\nu^2].$$

(27)

and also to the minimization of

$$\sum_{\nu < \mu} [\psi_\nu \psi_\mu | \psi_\nu \psi_\mu].$$

(28)

This intrinsic localization criterion leads to the $\frac{1}{2} N(N-1)$ conditions

$$[\lambda_i^2 | \lambda_i \lambda_j] = [\lambda_j^2 | \lambda_i \lambda_j].$$

(29)
They are obtained by introducing the infinitesimal orthogonal transformations

\[ \psi_\nu + \delta \psi_\nu = \psi_\nu + \sum \psi_\mu^t \mu_\nu , \]

\[ t_{\mu \nu} + t_{\nu \mu} = 0 , \]

into the expression (27) and requiring the variation of this sum to vanish.

It follows that intrinsically localized SCF orbitals are obtained as solutions of the general equation (14) if, in Eq. (15') one chooses \( 6 \)

\[ G(x, x') \rightarrow L(x, x') = \sum_{i \neq k}^N \lambda_i(x) \lambda_k(x') L_{ik} . \]

with

\[ (-\gamma_{ik}) \rightarrow L_{ik} = k \left[ \lambda_i^2 \lambda_k \right] - \left[ \lambda_k^2 \lambda_i \right] \]

\[ - \int dV \lambda_i(x) \mathcal{F}_\lambda_k(x) . \]

In order to show this, let \( \lambda_1 \cdots \lambda_N \) be the solution of Eq. (14) with the specification (30, 30'). As in the previous section, Eq. (16) can be deduced which, in this case, yields

\[ k \left[ \lambda_i^2 \lambda_k \right] - \left[ \lambda_k^2 \lambda_i \right] = 0 . \]

for \( i \neq k \), i.e. the conditions (29). The constant \( k \) can be adjusted to assist convergence. Its sign is related to the fact whether successive iterations will approach orbitals of maximal or of minimal localization. Both types of orbitals satisfy the conditions (29).

**Choice of Separation Function \( f(r_{12}) \)**

The following functional forms of \( f(r_{12}) \) came to mind: \( r_{12}, r_{12}^{-1}, r_{12}^2, r_{12}^{-2}, \delta(r_{12}) \). Of these \( r_{12}^2 \) and \( \delta(r_{12}) \) have the advantage that
the two-electron integrals are reduced to one-electron integrals.

The function $r_{12}^{-1}$, on the other hand, is the only one which casts the localization criterion in the form of an energy minimization. In fact, the total energy of the Hartree-Fock wavefunction of Eq. (4) has the form

$$E = \text{Kinetic Energy} + \text{Nuclear Attraction Energy} + \text{Electron Interaction Energy},$$

where

$$\text{Electron Interaction Energy} = \sum_{\mu \nu} \left\{ 2 \left[ \phi_{\mu}^2 \phi_{\nu}^2 \right] - \left[ \phi_{\mu} \phi_{\nu} \right] \left[ \phi_{\mu} \phi_{\nu} \right] \right\}$$

$$= \sum_{\mu \nu} (2 - \delta_{\mu \nu}) \left[ \phi_{\mu}^2 \phi_{\nu}^2 \right] - \sum_{\mu \nu} \left[ \phi_{\mu} \phi_{\nu} \right] \left[ \phi_{\mu} \phi_{\nu} \right]$$

(32)

with $f(r_{12}) = r_{12}^{-1}$. The last sum on the right hand side is minimized by the localized orbitals, so that the total electron interaction energy comes as close as it is possible to the first sum on the right hand side, which is in fact the energy expression for the Hartree product function

$$\psi_H = (\phi_1 \alpha)^{(1)} (\phi_1 \beta)^{(2)} \cdots (\phi_N \beta)^{(2N)}$$

Thus, intrinsic localization with the choice $f(r_{12}) = r_{12}^{-1}$ generates orbitals which come as close as possible to the situation where orbitals can be identified with electrons.\(^5,6\)

In the following this choice will be assumed.

Construction of Localized Orbitals from an Arbitrary Set of SCF Orbitals.

A frequent situation is the case, that a set $\phi_1, \phi_2, \cdots \phi_N$, of SCF orbitals is known, in particular the canonical set. The problem is then to construct from them the intrinsically localized orbitals
\[ \lambda_{\nu}(x) = \sum_n \phi_n(x) T_{n\nu} \]  

(33)

This problem is easily solved in the case of two orbitals. Writing

\[ \lambda_1 = \varphi_1 \cos \theta + \varphi_2 \sin \theta, \]  

(34)

\[ \lambda_2 = \varphi_1 \sin \theta + \varphi_2 \cos \theta, \]  

one finds that

\[ \sum_n [\lambda_n^2 | \lambda_n^2] - \sum_n [\varphi_n^2 | \varphi_n^2] = A_{12} + \sqrt{A_{12}^2 + B_{12}^2} \cos 4(\theta - \alpha) \]  

(35)

is the function to be maximized, where

\[ A_{12} = [\varphi_1 \varphi_2 | \varphi_1 \varphi_2] - \frac{1}{4} [\varphi_1^2 - \varphi_2^2 | \varphi_1^2 - \varphi_2^2], \]  

(36)

\[ B_{12} = [\varphi_1^2 - \varphi_2^2 | \varphi_1 \varphi_2]. \]  

(37)

\[ \cos 4\alpha = -\frac{A_{12}}{\sqrt{A_{12}^2 + B_{12}^2}}, \]  

(38)

\[ \sin 4\alpha = \frac{B_{12}}{\sqrt{A_{12}^2 + B_{12}^2}}. \]  

(38')

The maximum is obtained by choosing \( \theta = \alpha \).

In the case of \( N \) orbitals, the total maximization is achieved by a sequence of 2 \( \times \) 2 maximizations. Choosing sequentially all \( m-n \) combinations, one iterates until the sum \( \sum_n [\varphi_n^2 | \varphi_n^2] \) cannot be increased further within the desired accuracy. 6
Localized Orbitals and Molecular Symmetry

In molecules, whose symmetry group admits multi-dimensional irreducible representations, there exists a close relationship between symmetry and localized orbitals. If the density kernel $\rho(x|x')$ of Eq. (10) is invariant against all group operations, so is the Hartree-Fock operator $\mathbf{T}$ of Eq. (8) and, hence, the canonical molecular orbitals belong to irreducible representations. The localized orbitals, on the other hand, frequently span reducible representations which are characterized by the fact that the group operations merely permute the localized orbitals among each other. Under these conditions the localized orbitals are called equivalent orbitals.\(^{5,7,8}\)

The simplest example is that of the atomic configuration \({(s)^2 (2px)^2}\) whose wavefunction $\Psi$ can be written

$$\Psi = \left\{ (s\alpha) (s\beta) (2px\alpha) (2px\beta) \right\}$$  \hspace{1cm} (39)

or

$$\Psi = \left\{ (d_+\alpha) (d_+\beta) (d_-\alpha) (d_-\beta) \right\} ,$$  \hspace{1cm} (39')

where $d_+$ and $d_-$ are the digonal hybrid orbitals

$$d_+ = \left\{ (s) + (2px) \right\} / \sqrt{2} ,$$  \hspace{1cm} (40)

$$d_- = \left\{ (s) - (2px) \right\} / \sqrt{2} .$$

The symmetry orbitals $s$, $2px$ belong to the irreducible representations $\Sigma$, $\Pi$ of the rotation group, whereas $d_+$ and $d_-$ are equivalent orbitals.
The latter are the localized orbitals, if (s) and (2px) are of equal spatial extension, as is the case for (s) = (2s), since then (d+) and (d−) penetrate each other less. However, if one of the two symmetry orbitals is considerably smaller than the other, such as is the case for (s) = (1o), then the roles are reversed, and the symmetry orbitals represent the localized pair.

In a similar way, one s orbital and three p orbitals combine to form three trigonally equivalent hybrids, which are localized if the orbitals are of comparable spatial extension.

The case of one s orbital and four p orbitals, finally, occurs in the Neon configuration \( \{(1s)^2 (2s)^2 (2px)^2 (2py)^2 (2pz)^2\} \) which can also be written as the configuration \( \{(1s)^2 t_1^2 t_2^2 t_3^2 t_4^2\} \), where the \( t_k \) are the localized tetrahedral hybrid orbitals

\[
\begin{align*}
t_1 &= \frac{1}{2} \left\{ 2s + 2px + 2py + 2pz \right\} \\
t_2 &= \frac{1}{2} \left\{ 2s + 2px - 2py - 2pz \right\} \\
t_3 &= \frac{1}{2} \left\{ 2s - 2px + 2py - 2pz \right\} \\
t_4 &= \frac{1}{2} \left\{ 2s - 2px - 2py + 2pz \right\}
\end{align*}
\]

(41)

Quite analogous are the self-consistent-field orbitals in Methane, \( \text{CH}_4 \). The canonical orbitals are
and belong to the representations $A_1$ and $T_2$ respectively. The localized orbitals are

\[
\begin{align*}
\varphi_1 &= a \,(C\,2s) + b \, \frac{1}{2} \left[ H_1 + H_2 + H_3 + H_4 \right], \\
\varphi_2 &= a' \,(C\,2px) + b' \, \frac{1}{2} \left[ H_1 + H_2 - H_3 - H_4 \right], \\
\varphi_3 &= a' \,(C\,2py) + b' \, \frac{1}{2} \left[ H_1 - H_2 + H_3 - H_4 \right], \\
\varphi_4 &= a' \,(C\,2pz) + b' \, \frac{1}{2} \left[ H_1 - H_2 - H_3 + H_4 \right],
\end{align*}
\]

(42)

and essentially concentrated around the four equivalent bonds, since 

\[(a - a') \quad \text{and} \quad (b - b') \quad \text{are small as compared to} \quad a' \quad \text{and} \quad b'.\]

Localized Orbitals in the Absence of Symmetry

While in the presence of molecular symmetry, the localized orbitals are readily constructed as equivalent orbitals, an explicit numerical evaluation is required in the absence of symmetry.

The simplest example is that of the configuration $(1\,s)^2 (2\,s)^2$, where $(2\,s)$ is Schmidt-orthogonalized to $(1\,s)$. For all atoms in the second row of the periodic table, one finds very nearly the same localized ''inner'' and ''outer'' $s$-orbitals, namely 6
(inner orbital) = 0.995 (1 s) - 0.10 (2 s)
(outer orbital) = 0.10 (1 s) + 0.995 (2 s)

It is easily seen that the inner orbital is more contracted towards the nucleus than the (1 s) orbital, and that the orthogonal outer orbital has less of an (1 s) admixture, than the Schmidt orthogonalized (2 s) orbital. The exchange integral between the two orbitals is reduced by a factor of about 5. In oxygen, for example, it decreases from 2 eV to 0.4 eV.

A simple molecular example would be the BH molecule. If one localizes the three canonical orbitals \(1\sigma, 2\sigma, 3\sigma\), one finds an inner shell orbital (iB) on Boron, a lone pair (\(2\sigma_B\)) on Boron and a bonding orbital (b\(\sigma_{BH}\)). Execution of the localization for the [Minimal-Basis-Set] - [Best-Molecule] - LCAO-SCF-MO's, obtained by B. J. Ransil, yields the following results.

Orthogonal transformation from canonical to localized SCF orbitals:

<table>
<thead>
<tr>
<th></th>
<th>(1\sigma)</th>
<th>(2\sigma)</th>
<th>(3\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iB</td>
<td>0.99260</td>
<td>-0.08955</td>
<td>-0.08199</td>
</tr>
<tr>
<td>(2\sigma_B)</td>
<td>0.10882</td>
<td>0.35659</td>
<td>0.92790</td>
</tr>
<tr>
<td>b(\sigma_{BH})</td>
<td>-0.05386</td>
<td>-0.92996</td>
<td>0.36370</td>
</tr>
</tbody>
</table>

Expansion of localized molecular orbitals in terms of Schmidt orthogonalized Slater orbitals:

<table>
<thead>
<tr>
<th></th>
<th>B (k)</th>
<th>B (s)</th>
<th>B (p)</th>
<th>H (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iB</td>
<td>0.99491</td>
<td>-0.09958</td>
<td>0.03124</td>
<td>-0.01494</td>
</tr>
<tr>
<td>(2\sigma_B)</td>
<td>0.11176</td>
<td>0.90638</td>
<td>-0.46229</td>
<td>-0.18413</td>
</tr>
<tr>
<td>b(\sigma_{BH})</td>
<td>-0.00972</td>
<td>-0.27730</td>
<td>-0.44348</td>
<td>-0.55833</td>
</tr>
</tbody>
</table>
Matrix of exchange integrals for the canonical orbitals:

\[
\begin{array}{ccc}
1\sigma & 2\sigma & 3\sigma \\
1\sigma & 2.91124 & 0.02286 & 0.02234 \\
2\sigma & 0.02286 & 0.53855 & 0.06011 \\
3\sigma & 0.02234 & 0.06011 & 0.50444 \\
\end{array}
\]

Matrix of exchange integrals for the localized orbitals:

\[
\begin{array}{ccc}
iB & \delta\sigma B & \delta\gamma BH \\
iB & 2.97315 & 0.00756 & 0.00435 \\
\delta\sigma B & 0.00756 & 0.53801 & 0.01030 \\
\delta\gamma BH & 0.00435 & 0.01030 & 0.60929 \\
\end{array}
\]

It is seen that the sum of the six off diagonal exchange integrals is reduced from 30 eV to about 5.5 eV.

In most molecules, one finds of course a mixed situation; the localized orbitals are determined partly by symmetry and partly by further numerical localization. As examples, we quote here the localized orbitals for the isoelectronic series N₂, CO, BF, which are given in Table 1.¹⁰

Comparison of these molecules shows that the composition of the inner shells is about constant and that the s-p hybridization of lone pair and bonding orbitals varies systematically with the ratio of the number of lone pair electrons to the number of bonding electrons. Schematic diagrams indicating the nature of localized molecular orbitals in other
Table I. Localized Minimal-Basis-Set LCAO-SCF Molecular Orbitals in N₂, CO, BF.

<table>
<thead>
<tr>
<th></th>
<th>N₂</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>N k</td>
<td>N s</td>
<td>N pσ</td>
<td>N pπ</td>
<td>N' k</td>
<td>N' s</td>
<td>N' pσ</td>
<td>N' pπ</td>
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|       | CO   |       |       |       |       |       |       |       |       |
|-------|------|-------|-------|-------|-------|-------|-------|-------|
|       | C k  | C s   | C pσ  | C pπ  | C pπ  | O k   | O s   | O pσ  | O pπ  |
| iC    | -0.996 | 0.099 | -0.037 | 0.000 | 0.000 | -0.001 | 0.004 | 0.026 | 0.000 |
| iO    | -0.003 | -0.002 | 0.020 | 0.000 | 0.000 | -0.003 | 0.115 | -0.027 | 0.000 |
| tσC   | -0.119 | -0.003 | 0.467 | 0.000 | 0.000 | 0.017 | 0.129 | 0.126 | 0.000 |
| tσO   | -0.006 | -0.144 | -0.208 | 0.000 | 0.000 | 0.117 | 0.788 | -0.651 | 0.000 |
| bt1CO | 0.009 | -0.101 | -0.173 | -0.259 | -0.282 | -0.030 | -0.315 | -0.261 | -0.427 |
| bt2CO | 0.009 | -0.101 | -0.173 | 0.365 | -0.030 | -0.315 | -0.261 | -0.188 | 0.601 |
| bt3CO | 0.009 | -0.101 | -0.173 | 0.373 | -0.084 | -0.030 | -0.315 | -0.261 | 0.614 |

|       | BF   |       |       |       |       |       |       |       |       |
|-------|------|-------|-------|-------|-------|-------|-------|-------|
|       | B k  | B s   | B pσ  | B pπ  | B pπ  | F k   | F s   | F pσ  | F pπ  |
| iB    | 0.995 | -0.098 | 0.037 | 0.000 | 0.000 | -0.001 | 0.000 | -0.020 | 0.000 |
| iF    | -0.003 | -0.005 | 0.014 | 0.000 | 0.000 | -0.003 | 0.126 | -0.020 | 0.000 |
| tσB   | 0.111 | 0.930 | -0.390 | 0.000 | 0.000 | -0.013 | 0.126 | -0.020 | 0.000 |
| tσF   | -0.001 | -0.121 | -0.211 | 0.000 | 0.000 | 0.101 | 0.671 | -0.751 | 0.000 |
| bt1BF | -0.009 | 0.048 | 0.124 | 0.236 | -0.038 | 0.050 | 0.407 | 0.255 | 0.721 |
| bt2BF | -0.009 | 0.048 | 0.124 | -0.086 | 0.227 | 0.050 | 0.407 | 0.255 | 0.264 |
| bt3BF | -0.009 | 0.048 | 0.124 | -0.155 | -0.185 | 0.050 | 0.407 | 0.255 | -0.475 |

AO's:  k = 1s,  s = 2s,  pσ = 2pz,  pπ = 2px,  pπ = 2py.
LMO's: i = inner shell,  tσ = σ-lone pair,  bt = trigonal bond orbital,  tσ = bond orbital,  bt = trigonal bond orbital.
molecules are given in the Figure 1.\textsuperscript{11}

Fig. 1. Schematic Diagrams of Localized Orbitals.

Localized Molecular Orbitals in Delocalized Electronic Systems

As was mentioned in the introduction, the localized SCF orbitals are most useful in molecules whose electronic configuration naturally divides
in reasonably separated pairs. A classic example is the water molecule where the localized orbitals are the inner shell on Oxygen, a bonding orbital along each OH bond and two lone pair orbitals on Oxygen which, together with the bond orbitals form a distorted tetrahedral hybrid set.

On the other hand, localized orbitals are probably not quite as useful in typical delocalized systems, such as pi-electrons in aromatic molecules. Nevertheless, they may give interesting insights also in these cases. It is not unlikely that they may establish a closer correspondence between molecular orbital theory and the classical chemical concept of Kekulé structures. For it seems likely that in such systems there are in general several sets of localized orbitals, i.e. that the self-energy sum has several relative maxima. Each set of localized orbitals corresponds to one of the possible Kékulé structures, with each double bond corresponding to one localized orbital which is mainly concentrated in that region. Such localized orthogonal Kékulé MO's are therefore a possible way of interpreting a self-consistent-field wavefunction. This result of localization has been found in benzene although, there, it is possible to choose the two mutually orthogonal localized MO's in many different ways. In any event, these results show that the "mesomerism" between Kékulé structures can be understood as merely representing different ways of interpreting the same molecular orbital determinant and that, in contrast to the Valence Bond approach, this mesomerism can be discussed without reference to resonance or correlation effects.
References

1. This invariance was first pointed out by V. Fock, Z. Physik 61, 126 (1930).


7. Historically, equivalent orbitals were discussed much earlier than general localized orbitals. See, F. Hund, Z. Physik 73, 1 (1931) and 73, 565 (1932); C. A. Coulson, Trans. Far. Soc. 38, 433 (1942).


11. The explicit results are given in reference 10.
12. K. Ruedenberg, to be published.

13. C. Edmiston and K. Ruedenberg to be published.