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Localized Atomic and Molecular Orbitals

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INTRODUCTION

It has been pointed out by Fock[1] that a one-determinant, many-electron wave function is invariant with respect to unitary transformations among its molecular orbitals. It is completely determined by the finite-dimensional function space spanned by these orbitals and does not depend on the basis chosen within this space. In particular, the orbitals resulting from the Hartree–Fock equations represent only one of the many possible unitary bases in the *self-consistent-field space,* defined by the minimization of the energy integral. While they seem to be convenient for describing spectral transitions and ionization potentials, it appears likely that for an analysis of the intrinsic properties of a particular state, for example, the ground state, another unitary basis in the self-consistent-field space may be more effective.

This fact was used by Coulson[2] who, in discussing the dipole moment of the C-H bond, transformed the symmetry molecular orbitals of methane into localized molecular orbitals along the four bonds, which he called equivalent molecular orbitals. Later, the possibility of constructing equivalent orbitals in the presence of a *general* symmetry group was systematically analyzed by Lennard-Jones and Hall.[3] Whereas the Hartree–Fock orbitals belong to irreducible representations (as long as the Hartree–Fock operator is invariant), the equivalent orbitals span reducible representations: Certain symmetry operations transform one equivalent orbital into another.

Lennard-Jones and J. A. Pople,[4] furthermore, pointed out that the equivalent orbitals presumably *maximize the sum of the orbital self-repulsion terms* in the electronic interaction energy and, therefore, minimize the "nonclassical" off-diagonal exchange terms. Because of this property, they can be considered as that unitary orbital basis in the self-consistent-field space which exhibits maximum "localization." This characterization is of interest, because it furnishes a criterion which is applicable beyond the scope of the equivalent orbitals, namely, *within* one symmetry species as well as in the *absence* of any symmetry.[5]

Finally, Lennard-Jones and Pople[6] also suggested that such localized orbitals might be the most suitable ones for extending the wave function to take into account correlation. For, it seems reasonable to expect that they would exhibit a minimum of *inter*-orbital correlation, so that *intra*-orbital correlation would remain the essential correction.[7] Thus, Hurley, Lennard-Jones, and Pople[8] proposed to replace each doubly filled localized molecular orbital by a pair function.

In view of this interest in localized orbitals, it is remarkable that no attempts have been made to develop a method for finding them without the help of symmetry. An opinion that considerable difficulties stand in the way seems to prevail. Boys[9] has suggested approximating such orbitals by what he terms "exclusive orbitals." They are obtained by maximizing the product of the distances between the centroids of charge of all molecular orbitals, a nonlinear process carried out by consecutive iterations. There are cases, however, where the procedure is impossible as, for example, between various s orbitals on one atom. Another kind of localized molecular orbital was considered by Ruedenberg[10(a)] who defined "valence molecular orbitals" by extremizing the total overlap population of the individual molecular orbitals. The method, which involves solution of an eigenvalue problem, is again not completely general, in as much as it does not apply within an isolated atom.

In the present paper we describe an *exact method*

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[1] V. Fock, Z. Physik **61**, 126 (1930).

[2] C. A. Coulson, Trans, Faraday Soc. **38**, 433 (1942).

[3] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.* **A202**, 155 (1950).

[4] J. E. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **A202**, 166 (1950).

[5] That maximum localization might be an appropriate criterion in these cases, was first conjectured by Lennard-Jones and Pople in reference 4. Thereafter, the idea seems to have gained more and more ground.

[6] J. E. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **A210**, 190 (1951).

[7] A very readable account of these ideas was recently given by G. G. Hall, Rept. Prog. Phys., **23**, 1 (1959); and also by R. K. Nesbet, J. Chem. Phys. **36**, 1518 (1962), Sec. VII.

[8] A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953).

[9] S. F. Boys, Rev. Mod. Phys. **32**, 296 (1960).

[10(a)] K. Ruedenberg, Rev. Mod. Phys. **34**, 326 (1962).

for finding those molecular orbitals which maximize the sum of the orbital self-repulsion energies. While the process is iterative, its execution is very similar, in method as well as complexity, to the solution of an eigenvalue problem by Jacobi's method. We propose that the name "localized molecular orbitals (LMO's)" be used for these orbitals. Only in the presence of a symmetry group can they acquire properties which, under certain conditions, make them equivalent orbitals. If a distinction is required the orbitals defined here may be called "energy localized" orbitals.

Essentially different kinds of localized orbitals have been considered by G. Wannier and W. H. Adams.[10(b)] The Wannier transformation necessarily involves the *complete basis of all Bloch orbitals* of a band in a crystal, whereas we admit only the *incomplete sub-basis of the occupied orbitals, corresponding to the Bloch orbitals below the Fermi level.* Adams, on the other hand, has given equations for finding, within the self-consistent-field space, an orbital basis (not necessarily orthogonal) which exhibits *localization in arbitrarily chosen regions of space,* in particular around atoms, whereas we are interested in those *regions of localization which are intrinsic to a given* SCF *basis.*

DEFINITION OF LOCALIZED ORBITALS

We consider the case of a determinantal wave function of $2N$ electrons with N doubly occupied orthonormal real[10(c)] orbitals $\varphi_1\varphi_2\cdots\varphi_N$, viz.,

$$\Phi = \mathcal{A}\{(\varphi_1\alpha)^{(1)}(\varphi_1\beta)^{(2)}\cdots(\varphi_N\alpha)^{(2N-1)}(\varphi_N\beta)^{(2N)}\} \tag{1}$$

as determined by a self-consistent-field calculation. Actually, the orbitals are not uniquely determined by Φ; any unitary transformation between them will leave the wave function invariant, and we must say that Φ is associated with the N-dimensional linear space subtended by $\varphi_1\cdots\varphi_N$.

The electron interaction energy of Φ can be written

$$EI = (\Phi|\sum_{i<j} r_{ij}^{-1}|\Phi) = C - X\,, \tag{2}$$

$$\begin{aligned} C &= \tfrac{1}{2}\int dV_1 \int dV_2 r_{12}^{-1}\rho(1)\rho(2)\,,\\ &= 2\sum\nolimits_n \sum\nolimits_m [\varphi_n^2|\varphi_m^2]\,, \end{aligned} \tag{3}$$

$$\begin{aligned} X &= \tfrac{1}{4}\int dV_1 \int dV_2 r_{12}^{-1}\rho^2(1|2)\,,\\ &= \sum\nolimits_n \sum\nolimits_m [\varphi_n\varphi_m|\varphi_n\varphi_m]\,, \end{aligned} \tag{4}$$

where

$$\rho(1|2) = \sum\nolimits_n \varphi_n(1)\varphi_n^*(2)\,, \tag{5}$$

$$\rho(1) = \rho(1|1)\,,$$

$$[f|g] = \int dV_1 \int dV_2 f(1)g(2)/r_{12}\,. \tag{5$'$}$$

Since EI depends only upon Φ, it is, of course, invariant against unitary transformations among the φ's. More specifically, however, the density kernel $\rho(1|2)$ is invariant under such transformations, and so are, therefore, the "Coulomb term" C and the "exchange term" X, separately.

Such is not the case, however, for the sum of the diagonal terms

$$D(\varphi) = \sum\nolimits_n [\varphi_n^2|\varphi_n^2]\,, \tag{6}$$

which occurs in C, as well as in X. It is, therefore, a meaningful question to ask for that orthonormal basis $\lambda_1\lambda_2\cdots\lambda_N$ in the space spanned by $\varphi_1\varphi_2\cdots\varphi_N$ which minimizes $D(\varphi)$. That is, given the basis $\varphi_1\cdots\varphi_N$, find a unitary transformation

$$\lambda_\nu(x) = \sum\nolimits_n \varphi_n(x)T_{n\nu}\,, \tag{7}$$

such that

$$D(\lambda) = \sum\nolimits_\nu [\lambda_\nu^2|\lambda_\nu^2]$$

is maximum. This maximum principle defines the energy-localized SCF orbitals.

CHARACTERISTICS OF LOCALIZED ORBITALS

(1) Since $D(\varphi)$ can obviously be considered as a measure of the "over-all localization" of the basis set $\varphi_1\cdots\varphi_N$, the $\lambda_1\cdots\lambda_N$ represent, in the given linear space, that orthonormal basis which exhibits "maximum localization." They will be called *energy localized orbitals.*

(2) Because of the invariance of C and X under unitary transformations, *maximization of D* implies *minimization* of

$$C' = \sum_{\nu\neq\mu} [\lambda_\nu^2|\lambda_\mu^2]\,,$$

and

$$X' = \sum_{\nu\neq\mu} [\lambda_\nu\lambda_\mu|\lambda_\nu\lambda_\mu]\,.$$

The expression C' represents the *total of all interorbital repulsions,* and the quantity X' can be considered as the *total of the self-energies of all overlap-charge-distributions* $(\varphi_i\varphi_j)$. These minimum properties indicate that, in going beyond the SCF approximations, one is likely to find the *smallest correlation correction between different orbitals,* if one chooses the $(\lambda_1\lambda_2\cdots\lambda_N)$ as starting point.

[10(b)] G. Wannier, Phys. Rev. **52**, 191 (1937); W. H. Adams, J. Chem. Phys. **37**, 2009 (1962).

[10(c)] The generalization to complex orbitals is given in the last section.

(3) If it should happen that the minimum X' vanishes identically, then this would mean that *these* localized orbitals have the properties of orthogonal *Hartree* orbitals (as opposed to *Hartree–Fock* orbitals).[11,12] *Thus, the localized orbitals* $\lambda_1\lambda_2\cdots\lambda_N$ *are those basis orbitals in the self-consistent-field space which approach most closely the behavior postulated for the Hartree orbitals.*

(4) We predict that the localized SCF orbitals are those orthonormal basis orbitals in the SCF space which closely approximate the first (N) natural orbitals (corresponding to the first $2N$ natural spin orbitals). This conjecture is based on the following line of reasoning.

Evidence has been accumulating that atomic and molecular wave functions can be remarkably well approximated by an antisymmetrized product of separated pair functions satisfying strong orthogonality conditions between them. Now the space part of each such pair function can be expressed as a natural expansion $\sum_k \psi_k(x)\psi_k^*(x')$ and, using the strong orthogonality condition, it is easily shown that each of the orbitals $\psi_k(x)$ is also a natural orbital of the *total* wave function. In view of the preceding remark (2), it is however to be expected that, for each pair function, the leading term $\psi_0(x)$ is close to one of the localized SCF orbitals. It follows, therefore, that the latter are presumably close to the first natural orbitals of the total wave function.

(5) The localized orbitals provide a quantitative basis for the qualitative chemical concepts of "localized electrons" and "delocalized electrons." Since it is always possible to construct a delocalized orbital basis from a localized orbital basis by a unitary transformation, it is obviously easy to choose *many delocalized* bases in a given SCF space. In order to see to which degree electrons act as *localized* units, one has to determine to which degree the SCF orbitals of maximal localization are restricted to certain parts of space.

CONDITIONS FOR LOCALIZED ORBITALS

An orthogonal transformation changes the basis functions $\varphi_n(x)$ into the functions

$$\varphi_n(x) + \delta\varphi_n(x) = \textstyle\sum_i \varphi_i T_{in}$$

with

$$\textstyle\sum_n T_{in}T_{jn} = \delta_{ij} .$$

Putting

$$T_{ij} = \delta_{ij} + t_{ij} ,$$

one has

$$t_{ij} + t_{ji} + \textstyle\sum_n t_{in}t_{jn} = 0 .$$

Hence, one finds, *up to first order,*

$$\delta\varphi_n = \textstyle\sum_i \varphi_i\tau_{in} , \qquad \tau_{in} + \tau_{ni} = 0 .$$

The corresponding variation of $D(\varphi)$ of Eq. (6) becomes therefore

$$\delta D = 4 \textstyle\sum_n [\varphi_n^2|\varphi_n\delta\varphi_n] = 4 \textstyle\sum_{ni} [\varphi_n^2|\varphi_n\varphi_i]\tau_{in}$$
$$\delta D = 4 \sum_{m>n} \{[\varphi_n^2|\varphi_m\varphi_n] - [\varphi_m^2|\varphi_m\varphi_n]\}\tau_{mn} . \qquad (8)$$

Now, the orthogonal matrix $\mathbf{T}$ has $\frac{1}{2}N(N-1)$ independent parameters, and so has the antisymmetric infinitesimal matrix $\boldsymbol{\tau}$. It is permissible to choose the elements $\tau_{mn}(m < n)$ as these independent parameters and, therefore, Eq. (8) represents an expansion of δD in terms of independent variations τ_{mn}.

For the localized orbitals λ_ν, $D(\lambda)$ is maximum and, hence, $\delta D(\lambda) = 0$. The localized orbitals satisfy, therefore, the condition

$$[\lambda_n^2|\lambda_n\lambda_m] = [\lambda_m^2|\lambda_n\lambda_m] \qquad (9)$$

for all pairs (n,m). This condition is clearly fulfilled by "equivalent orbitals" because of the geometrical symmetry in their definitions.

Equation (9) is, however, also fulfilled by those orbitals ψ_n which *minimize* $D(\psi)$, i.e., the orbitals of least localization. For example, in the case of one s orbital and one p orbital, one finds that

s, p = orbitals of minimal localization,
$(s \pm p)/\sqrt{2}$ = orbitals of maximal localization.

Both sets are seen to satisfy Eq. (9).

Formula (8) for the variation δD suggests the following method of steepest ascent for finding the localized orbitals λ_n.

Since the particular infinitesimal transformation

$$\tau_{mn} = \epsilon F_{mn} = \epsilon\{[\varphi_n^2|\varphi_n\varphi_m] - [\varphi_m^2|\varphi_n\varphi_m]\} , \qquad \epsilon > 0 , \qquad (10)$$

guarantees that

$$\delta D = \sum_{m<n} \epsilon(F_{mn})^2 > 0 , \qquad (11)$$

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[11] As "orthogonal Hartree orbitals" we define those orbitals which minimize the energy of a Hartree product of *orthogonal* orbitals. The resulting equations differ from the Hartree-Equations by having *off-diagonal* Lagrangian multipliers λ_{ij}. It can be shown that orbitals which satisfy these modified Hartree equations also satisfy the condition (9), below, and hence represent the localized orbital basis in their function space (which is, of course, not identical with the Hartree–Fock space).

[12] Hartree's functions satisfy the equations which result by discarding the off-diagonal λ_{ij} mentioned in reference 11. This introduces some nonorthogonality. But frequently, the Hartree functions and the orthogonal Hartree functions are not too different. *Both exhibit localized character. This localized character is entirely lost, however, if one introduces into the Hartree equations the common additional averaging process over the electron-interaction potential.* Under these conditions, one obtains nonlocalized symmetry orbitals.

construct the orthogonal matrix $T = \exp(\epsilon F)$. This is achieved by solving the eigenvalue problem[13]

$$\textstyle\sum_n F_{mn}a_{nk} = f_k a_{nk}\,, \qquad (12)$$

and then forming

$$T_{mn}(\epsilon) = \textstyle\sum_k e^{\epsilon f_k} a_{mk}a^*_{nk}\,. \qquad (13)$$

Then calculate

$$D(\epsilon) = \textstyle\sum_{ij}\sum_{kl}[\varphi_i\varphi_j|\varphi_k\varphi_l]T_{in}T_{jn}T_{kn}T_{ln}$$

as functions of the parameter ϵ. Because of Eq. (11), this function will first increase in value. Find that new set of orbitals

$$\epsilon_k = \textstyle\sum_n \varphi_n T_{nk}(\epsilon) \qquad (14)$$

for which $D(\epsilon)$ is maximum. Then determine the new antisymmetric matrix

$$F'_{jk} = [\epsilon_k^2|\epsilon_j\epsilon_k] - [\epsilon_j^2|\epsilon_j\epsilon_k]\,,$$

and start all over again.

The method described in the subsequent section is, however, simpler.

DETERMINATION OF LOCALIZED ORBITALS

Two-Dimensional Space

The localization problem can be solved explicitly in the two-dimensional case. Let the transformation from (φ_1,φ_2) to another basis (u_1,u_2) be given by

$$\begin{aligned} u_1(x) &= \cos\gamma\varphi_1(x) + \sin\gamma\varphi_2(x)\,,\\ u_2(x) &= -\sin\gamma\varphi_1(x) + \cos\gamma\varphi_2(x)\,. \end{aligned} \qquad (15)$$

It is readily found that, in this case,

$$D(u) = D(\varphi) + A_{12} + (A_{12}^2 + B_{12}^2)^{\frac{1}{2}}\cos 4(\gamma - \alpha)\,, \qquad (16)$$

where

$$A_{12} = [\varphi_1\varphi_2|\varphi_1\varphi_2] - \tfrac{1}{4}[\varphi_1^2 - \varphi_2^2|\varphi_1^2 - \varphi_2^2]\,, \qquad (17)$$

$$B_{12} = [\varphi_1^2 - \varphi_2^2|\varphi_1\varphi_2]\,. \qquad (18)$$

and 4α is defined by

$$\left.\begin{aligned} \cos 4\alpha &= -A_{12}/(A_{12}^2 + B_{12}^2)^{\frac{1}{2}}\,,\\ \sin 4\alpha &= B_{12}/(A_{12}^2 + B_{12}^2)^{\frac{1}{2}}\,,\\ \tan 4\alpha &= -B_{12}/A_{12}\,. \end{aligned}\right\} \qquad (19)$$

Concomitantly, one finds for the exchange integral

$$[u_1u_2|u_1u_2] = [\varphi_1\varphi_2|\varphi_1\varphi_2] - \tfrac{1}{2}A_{12} - \tfrac{1}{2}(A_{12}^2 + B_{12}^2) \times \cos 4(\gamma - \alpha)\,. \qquad (20)$$

From Eq. (16) it is obvious that $D(u)$ reaches the same maximum for the values

$$\gamma_{\max} = \alpha\,,\quad \alpha + \tfrac{1}{2}\pi\,,\quad \alpha + \pi\,,\quad \alpha + \tfrac{3}{2}\pi\,, \qquad (21)$$

and the minimum for the values

$$\gamma_{\min} = \alpha + \pi/4\,,\quad \alpha + (3/4)\pi\,,\quad \alpha + (5/4)\pi\,,\quad \alpha + (7/4)\pi\,. \qquad (22)$$

The values of $D(u)$ at the extrema are

$$D_{\max}(u) = D(\varphi) + A_{12} + (A_{12}^2 + B_{12}^2)^{\frac{1}{2}}\,, \qquad (23)$$

$$D_{\min}(u) = D(\varphi) + A_{12} - (A_{12}^2 + B_{12}^2)^{\frac{1}{2}}\,. \qquad (24)$$

The localized orbitals λ_1, λ_2 are conveniently determined by the transformation

$$\begin{aligned} \lambda_1 &= \cos\alpha_0\varphi_1 + \sin\alpha_0\varphi_2\,,\\ \lambda_2 &= -\sin\alpha_0\varphi_1 + \cos\alpha_0\varphi_2\,, \end{aligned} \qquad (25)$$

where α_0 is that one of the four angles of Eq. (21), which lies between 0° and $\frac{1}{2}\pi$. (The other three angles merely correspond to changing the sign of λ_1 and/or λ_2.)

The calculation of $\cos\alpha_0$ and $\sin\alpha_0$ from the energy integrals (17), (18) is conveniently done as follows. First calculate $\cos 4\alpha_0$ and $\sin 4\alpha_0$ according to Eq. (19). Next find

$$x^2 = \tfrac{1}{2}\{1 \pm [1 - \tfrac{1}{2}(1 - \cos 4\alpha)]^{\frac{1}{2}}\}\,,$$

and

$$x = +(x^2)^{\frac{1}{2}}\,,\quad y = +[(1 - x^2)]^{\frac{1}{2}}\,,$$

which will yield two pairs (x_1,y_1) and (x_2,y_2). Then one has

$$\cos\alpha_0 = x_k\,,\quad \sin\alpha_0 = y_k\,,$$

where (x_k,y_k) is that pair which satisfies the further equation

$$4x_ky_k(x_k^2 - y_k^2) = \sin 4\alpha_0\,.$$

N-Dimensional Space

Our method of finding the maximum of $D(\varphi)$ for N orbitals $\varphi_1\cdots\varphi_N$ consists of successively maximizing D for appropriately chosen *pairs* of orbitals. Since D will increase each time, this iterative procedure will converge to the maximum of D in a similar manner as Jacobi's diagonalization procedure (by a succession of 2×2 diagonalizations) converges to the true eigenvalues.

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[13] The eigenvalues of the antisymmetric matrix F are purely imaginary, the eigenvectors complex. However, practical execution of the calculation indicated by Eqs. (12) and (13) is easily reduced to diagonalization of the symmetric matrix F^2, which has real eigenvectors and eigenvalues.

Each stage of our iteration method consists of the following two steps.

(1) Find that pair φ_i, φ_j (among all pairs of $\varphi_n \varphi_m$) which, upon 2×2 maximization of D will yield the *greatest* increase in D. Accoding to Eqs. (23), this is *that* pair $\varphi_i \varphi_j$ for which

$$D_{\max}(u_i u_j) - D(\varphi_i \varphi_j) = A_{ij} + (A_{ij}^2 + B_{ij}^2)^{\frac{1}{2}} \tag{26}$$

is largest, A_{ij} and B_{ij} being defined by Eqs. (17) and (18).

(2) Find the corresponding transformation (25), and thus two new orbitals φ_i', φ_j' which now replace the previous orbitals $\varphi_i \varphi_j$.

Writing the total sum in the form

$$D(\varphi) = \sum_{n \neq i,j} [\varphi_n^2 | \varphi_n^2] + [\varphi_i^2 | \varphi_i^2] + [\varphi_j^2 | \varphi_j^2] , \tag{27}$$

one recognizes that replacing φ_i, φ_j by φ_i', φ_j' will increase the last two terms, but leave the first $(N-2)$ terms unchanged.[14] Thus, each iteration consists of performing *that* 2×2 orthogonal transformation which guarantees the maximum increase in the *total* $D(\varphi)$. Convergence is achieved, when all $\frac{1}{2} N(N-1)$ quantities of Eq. (26) are smaller than the prescribed convergence criterion, e.g., the numerical accuracy of the calculation.

APPROXIMATE LOCALIZED ORBITALS

It is sometimes desired to localize molecular orbitals, although the electron-repulsion integrals required for executing the procedure just described are not available. This may be the case if reasonably good approximations to the SCF orbitals have been found by semiempirical methods, or if SCF orbitals are taken from the literature. It should be noted that, according to Eq. (18), the *Coulomb and exchange integrals* between MO's, which are adequate for calculating the molecular energy, *are not sufficient for the localization procedure*. In many cases it would be of interest to find at least reasonably good approximations to the localized orbitals without being forced to calculate the electron-repulsion integrals which present difficulties in molecular problems.

Such an approximation to our "energy localized" orbitals can be obtained if, in the method developed here, one replaces the electron repulsion integrals $[\lambda_i \lambda_j | \lambda_k \lambda_l]$ by suitable other integrals $I(ij,kl)$ which are simpler to calculate but have a similar geometric behavior. For example, one can replace, in Eq. (5′), the operator (r_{12}^{-1}) by the delta function $\delta(\mathbf{r}_1 - \mathbf{r}_2)$. This yields the one-electron integrals

$$I(ij,kl) = \int dV \varphi_i(\mathbf{x}) \varphi_j(\mathbf{x}) \varphi_k(\mathbf{x}) \varphi_l(\mathbf{x}) , \tag{27′}$$

and the localized orbitals are then defined by maximizing

$$\sum_n \int dV \varphi_n^4(\mathbf{x}) ,$$

implying the minimization of

$$\sum_{m<n} \int dV [\varphi_n(\mathbf{x}) \varphi_m(\mathbf{x})]^2 .$$

If, on the other hand, one replaces (r_{12}^{-1}) by the function $-(\mathbf{r}_1 - \mathbf{r}_2)^2$, then the localization criterion will be somewhat comparable to that of S. F. Boys.[9]

EXAMPLES OF LOCALIZED ORBITALS

Localization between 1s and 2s Orbitals

As illustration, we apply the procedure to a case which has been unaccessible to previous approximate methods, namely, the construction of localized orbitals from the 1*s* Slater orbital and the 2*s* Slater orbital in oxygen.

These Slater orbitals are

$$(1s) = [(\zeta_1^3/\pi)]^{\frac{1}{2}} e^{-\zeta_1 r} , \qquad \zeta_1 = 7.7 ,$$
$$(2s) = [(\zeta_2^5/3\pi)]^{\frac{1}{2}} r e^{-\zeta_2 r} , \qquad \zeta_2 = 2.275 . \tag{28}$$

The conventional orthogonal orbitals are those obtained by Schmidt orthogonalization, viz.,

$$(1s^\circ) = (1s) ,$$
$$(2s^\circ) = [(2s) - S(1s)]/(1 - S^2)^{\frac{1}{2}} ,$$
$$(2s^\circ) = -0.24008(1s) + 1.02842(2s) . \tag{29}$$

They give rise to the exchange integral

$$[1s^\circ 2s^\circ | 1s^\circ 2s^\circ] = 0.0703(e^2/a) = 1.91 \text{ eV} . \tag{30}$$

If they are chosen as the basis orbitals (φ_1, φ_2) for the construction of an arbitrary orthogonal basis (u_1, u_2) according to Eq. (15), then the variation of the exchange integral with the transformation angle γ, as given by Eq. (20), becomes (in atomic units, e^2/a)

$$[u_1 u_2 | u_1 u_2] = 0.4539 - 0.4401 \cos 4(\gamma + 7^\circ 20.5') . \tag{31}$$

From this equation it follows that the localized or-

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[14] It is also easily seen that the sums

$$\sum_{n<m, n \neq i, m \neq j} [\varphi_n \varphi_m | \varphi_n \varphi_m]$$

and

$$\sum_{n \neq i,j} \{[\varphi_n \varphi_i | \varphi_n \varphi_i] + [\varphi_n \varphi_j | \varphi_n \varphi_j]\}$$

remain invariant. Hence, the change in the sum of *all* exchange integrals is equal to the change in $[\varphi_i \varphi_j | \varphi_i \varphi_j]$ alone.

bitals result for $\gamma = -7°20.5'$. Expressed in terms of the original Slater orbitals, they become

$$\text{Inner orbital} = is = \lambda_1 = 1.02248(1s) - 0.13142(2s),$$
$$\text{Outer orbital} = os = \lambda_2 = -0.110322(1s) + 1.01998(2s)\,. \quad (32)$$

Their exchange integral is

$$[is\; os|is\; os] = 0.0138(e^2/a) = 0.376\text{ eV}\,. \quad [(33)$$

so that localization has reduced the exchange integral by more than a factor 5.

It is of interest that those orthogonal orbitals which result from "symmetric orthogonalization," as proposed by Löwdin,[15] are very close to the localized orbitals. In terms of the original Slater orbitals, they are

$$(1s^L) = a(1s) + b(2s)\,,$$
$$(2s^L) = b(1s) + a(2s)\,,$$
$$2a = (1+S)^{-\frac{1}{2}} + (1-S)^{-\frac{1}{2}}\,,$$
$$2b = (1+S)^{-\frac{1}{2}} - (1-S)^{-\frac{1}{2}}\,.$$

Hence,

$$(1s^L) = 1.02129(1s) - 0.12088(2s)\,,$$
$$(2s^L) = -0.12088(1s) + 1.02129(2s)\,, \quad (34)$$

which corresponds to a value of $\gamma = -6°45'$ in terms of Eq. (31). Their exchange integral

$$[1s^L2s^L|1s^L2s^L] = 0.0141(e^2/a) = 0.384\text{ eV} \quad (35)$$

is only 0.008 eV larger than that of the localized orbitals. Since the Löwdin orbitals represent that set of orbitals which "differs least," in the sense defined by Carlson and Keller,[16] from the nonorthogonal Slater orbitals (28), it is remarkable that the latter have a considerably larger exchange integral, namely,

$$[1s2s|1s2s] = 0.1246(e^2/a) = 3.39\text{ eV}\,. \quad (36)$$

Finally, Eq. (31) shows that *minimal* localization (maximal delocalization) is reached for $\gamma = 37°39.5'$, at which point the exchange integral assumes the maximal value

$$[u_1u_2|u_1u_2]_{\max} = 0.8940(e^2/a) = 24.3\text{ eV}\,. \quad (37)$$

Discussion

(1) It can be seen that the low exchange integral for the localized orbitals (*is*), (*os*) comes about because the 1*s* orbital is somewhat contracted towards the nucleus and, more important, because the inner loop of the 2*s* orbital is concomitantly attenuated. In view of this observation, one is led to expect that, in case of *sp*, sp^2, or sp^3 hybridization, the exchange integral between different $(2s - 2p)$ hybrid orbitals will be further reduced if the (1*s*) orbital is also included in the localization process. For, in that case, the $(2s - 2p)$ hybrids would get some 1*s* admixture which would attenuate all of them in the region where they overlap each other.

(2) As mentioned before, the localized orbitals are those for which interorbital correlation is expected to be smallest. That it is possible to reduce the interorbital correlation to a small value is made likely by the results found by Allen and Shull in Be.[17] Their results suggest that Watson's very accurate configuration interation function can be closely reproduced from two separate pair functions. The relation to localized orbitals is being investigated at present.

These results have some bearing on the concept of "inner shells" in a many-electron atom, where a unitary transformation between the orbitals is arbitrary. There is no reason why Schmidt orthogonalization should define the various "shells." It seems to us that, within one symmetry, the *localized* orbitals correspond much more closely to the concept of inner and outer shells.

(3) This definition of inner shells finds further support in the observation that there seems to be evidence that the *localized* inner shell orbitals (*is*) of an atom may mix very little with the valence orbitals in the molecule. Thus, in an analysis of the H_2O calculation of Ellison and Shull, we were led to define certain "valence atomic orbitals"

$$(is^v) = 1.02265(1s) - 0.14809(2s) + 0.05(2p\sigma)\,,$$
$$(os^v) = -0.0469143(1s) + 0.843313(2s) + 0.5(2p\sigma)\,, \quad (38)$$

from the *molecular* wave function.[18] The inner valence orbital is^v, which is seen to be *very similar to the inner localized atomic orbital* (*is*) *of Eq.* (32), was found to mix very little into the valence *molecular* orbitals. This behavior is in strong contrast to that of the Schmidt-orthogonalized inner shell, i.e., the Slater 1*s* orbital. [The exchange integral between $1s^v$ and os^v is $0.0219(e^2/a) = 0.595$ eV.]

(4) While the foregoing conclusions have been made on the basis of the oxygen *Slater* orbitals, we believe that similar results will emerge when the *Hartree–Fock* orbitals are considered. This conjec-

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[15] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[16] B. C. Carlson and J. M. Keller, Phys. Rev. **105**, 102 (1957).

[17] T. L. Allen and H. Shull, J. Phys. Chem. **66**, 2281 (1962).

[18] C. Edmiston and K. Ruedenberg (to be published).

ture is based on a comparison of the electron interaction integrals in the two cases. One finds[19] (in atomic units, e^2/a)

	Hartree–Fock	Slater
$[1s1s\|1s1s]$	4.7421	4.8125
$[1s1s\|2s2s]$	1.1331	1.1334
$[2s2s\|2s2s]$	0.7974	0.8039
$[1s2s\|1s2s]$	0.0767	0.0703

In particular, the similarity in the value of the exchange integrals $[1s2s|1s2s]$ makes it likely, that localization of the Hartree–Fock orbitals would yield a lowering of the exchange integral similar to that found for the Slater orbitals.

Localization Between 2*s*, 2*px*, 2*py* Orbitals

From condition (9) it is clear that localization of the atomic orbitals $(2s)$, $(2px)$, $(2py)$ will lead to the trigonal hybrids t_1, t_2, t_3,

$$t_k = (\tfrac{1}{3})^{\frac{1}{2}}(2s) + (\tfrac{2}{3})^{\frac{1}{2}} p_k \,,$$

where p_1, p_2, p_3 are three $(2p)$ orbitals yielding pairwise the inner product

$$\int dV p_j(\mathbf{x}) p_k(\mathbf{x}) = -\tfrac{1}{2} \,, \quad (j \neq k) \,,$$

for example

$$p_1 = (2px) \,, \quad p_2 = -\tfrac{1}{2}\,(2px) + \tfrac{1}{2}\sqrt{3}(2py) \,,$$
$$p_3 = -\tfrac{1}{2}\,(2px) - \tfrac{1}{2}\sqrt{3}(2py) \,.$$

The orbital triple $(2s)$, $(2px)$, $(2py)$ presents therefore a convenient case with known solutions, where our iteration procedure can be tested.

A machine program was applied to the Slater orbitals of oxygen and the results are exhibited in Table I. The following observations are of interest:

(1) Although the increasing error in the invariant total exchange energy X indicates that, after about fifteen iterations, the calculation is becoming unreliable in the sixth decimal, the individual integrals as well as the localized orbitals themselves nevertheless improve consistently up to the thirty-first iteration;

(2) The improvement in $D(\lambda)$ due to the last pair transformation is always smaller than the total defect in $D(\lambda)$;

(3) The total defect in $D(\lambda)$ is always considerably smaller than the maximal absolute deviations in the individual integrals;

(4) The deviations in the individual integrals are always smaller in absolute value than the maximal deviation in the localization criterion B_{12}.

The last observation is particularly gratifying, if it can be assumed to hold generally true. For, in problems where the answer is unknown, the quantities B_{ij} are the only ones which can be calculated to test the

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[19] The SCF values are taken from J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I, pp. 357–358.

TABLE I. Construction of Trigonal Hybrids by Maximization of Total Orbital Self-Energy

Number of Iterations	$n = \infty$	$n = 0$	$n = 3$	$n = 8$	$n = 13$	$n = 18$	$n = 24$	$n = 31$
	Exact Value	Deviations from Exact Value after n Pair Transformations						
$[\lambda_1\lambda_2\|\lambda_1\lambda_2]$[a]	0.062323	0.112615	0.001792	0.000227	0.000055	0.000014	0.000014	0.000003
$[\lambda_1\lambda_3\|\lambda_1\lambda_3]$	0.062323	0.112615	0.001792	0.000227	−0.000110	−0.000027	−0.000007	−0.000007
$[\lambda_2\lambda_3\|\lambda_2\lambda_3]$	0.062323	−0.014335	0.009597	−0.000442	0.000055	0.000014	−0.000007	0.000003
$[\lambda_1\lambda_1\|\lambda_1\lambda_1]$	1.002199	−0.198288	0.003152	−0.000665	0.000080	0.000020	−0.000011	0.000004
$[\lambda_2\lambda_2\|\lambda_2\lambda_2]$	1.002199	−0.111750	−0.014757	0.000319	−0.000163	−0.000041	−0.000011	−0.000011
$[\lambda_3\lambda_3\|\lambda_3\lambda_3]$	1.002199	−0.111750	−0.014757	0.000319	0.000080	0.000020	0.000020	0.000004
B_{12}[b]	0	0	−0.055922	0.001641	−0.000411	0.000103	0.000000	0.000026
B_{13}	0	0	−0.055922	0.001641	−0.000000	0.000000	0.000051	0.000000
B_{23}	0	0	0.000000	0.000000	0.000411	0.000103	0.000051	−0.000026
$D(\lambda)$[c]	3.006597	−0.421789	−0.026362	−0.000027	−0.000003	−0.000002	−0.000003	−0.000003
X[d]	3.380538	0	0	0.000001	0.000002	0.000002	0.000003	0.000004
$(\lambda_1\|2s)$[e]	0.57735	0.42265	0.12976	−0.00453	+0.00056	0.00014	−0.00007	0.00004
$(\lambda_2\|2s)$	0.57735	−0.57735	0.27735	0.00225	−0.00113	−0.00028	−0.00007	−0.00007
$(\lambda_3\|2s)$	0.57735	−0.57735	0.27735	0.00225	0.00056	0.00014	0.00014	0.00004
			Improvement in $D(\lambda)$ due to Last Pair Transformation[f]					
$\Delta^n D(\lambda)$	——	——	0.03954271	0.00000965	0.00000060	0.00000003	0.00000001	0.00000000

[a] $[\lambda_n\lambda_m|\lambda_n\lambda_m]$ defined by Eq. (5′), energy unit: (e^2/a).

[b] B_{ij}, given by Eq. (18), should vanish according to localization criterion (9).

[c] $D(\lambda)$, given by Eq. (6), is to be maximized.

[d] X, given by Eq. (4), should remain invariant.

[e] Overlap integrals indicating the amount of s-character in the trigonal hybrids and, hence, characterizing the basis transformation.

[f] Test parameter determining the interruption of the iterative cycle.

quality of the localization. It is encouraging that they seem to provide an upper bound for the deviations of the individual energy integrals. It is questionable whether the number of iterations found necessary here is typical. Our particular case possibly shows a slower-than-average convergence, since the indeterminacy in the p orbitals may favor evasive oscillations from iteration to iteration.

Localized Molecular Orbitals

Examples for energy localized orbitals in molecules will be given elsewhere.

SELF-CONSISTENT-FIELD EQUATION FOR LOCALIZED ORBITALS

In the preceding sections we have constructed the localized SCF orbitals from the Hartree–Fock SCF orbitals which were assumed to have been determined previously by solving the Hartree–Fock equations

$$\mathfrak{F}(\rho)\varphi_n = \epsilon_n\varphi_n\,, \tag{39}$$

where $\mathfrak{F}(\rho)$ is the Hartree–Fock operator which, itself, is a function of the density matrix ρ of Eq. (5). It is natural to ask whether there exists an equation whose solution yields the localized SCF orbitals directly without the intermediate of the Hartree–Fock orbitals. Such "localized SCF equations" can be found as follows.

An arbitrary real orthonormal basis set $\psi_1\cdots\psi_N$, in the self-consistent-field space satisfies the *general* SCF equations

$$\mathfrak{F}(\rho)\psi_j = \textstyle\sum_k \gamma_{jk}\psi_k\,, \quad \gamma_{jk} = \gamma_{kj}\,, \tag{40}$$

(the density matrix ρ is assumed invariant with respect to the choice of basis). Arbitrary fixation of the off-diagonal Lagrangian multipliers γ_{jk} determines a specific basis set. The Hartree–Fock orbitals result from the choice $\gamma_{jk} = 0 (j \neq k)$, whereas our localized orbitals result by adding the conditions of Eq. (9), which are just sufficient to fix the off-diagonal γ_{jk}. Now, Gilbert[20] has pointed out that the fixation of the $\gamma_{jk} (j \neq k)$, and hence of a particular basis set ψ, is equivalent to replacing Eq. (40) by a pseudo-eigenvalue equation

$$\{\mathfrak{F}(\rho) + \mathfrak{G}\}\psi_n = \epsilon_n'\psi_n\,,$$

where $\mathfrak{G}$ is a suitably defined operator. It should, therefore, be possible to determine this operator in such a way that the localized SCF orbitals will result as solutions.

Thus, according to Gilbert, it is to be expected that there exists an equation

$$\{\mathfrak{F}(\rho) + \mathfrak{L}(\lambda_1\lambda_2\cdots\lambda_N)\}\lambda_n(\mathbf{x}) = \eta_n\lambda_n(\mathbf{x}) \tag{41}$$

with the following property: If the orbitals λ_n satisfy this equation, then they satisfy Eq. (40) as well as the localization condition (9). Equations which yield this result we can indeed find. A possible choice for $\mathfrak{L}$ is the integral operator

$$\mathfrak{L}f(\mathbf{x}) = \int dV' L(\mathbf{x},\mathbf{x}')f(\mathbf{x}')\,, \tag{42}$$

$$L(\mathbf{x},\mathbf{x}') = \sum_{m\neq n} \lambda_n(\mathbf{x})\lambda_m(\mathbf{x}')L_{nm}\,, \tag{43}$$

the matrix L_{nm} being defined by

$$L_{nm} = \Lambda\{[\lambda_n^2 - \lambda_m^2|\lambda_n\lambda_m]\} - (\lambda_n|\mathfrak{F}|\lambda_m)\,, \tag{43$'$}$$

where $\Lambda\{t\}$ can be any real symmetric function of t which vanishes for $t = 0$ and only for $t = 0$. The simplest choice is

$$L_{nm} = [\lambda_n^2 - \lambda_m^2|\lambda_n\lambda_m]^2 - (\lambda_n|\mathfrak{F}|\lambda_m)\,. \tag{44}$$

In order to prove the contention, suppose that $\lambda_1\lambda_2\cdots\lambda_N$ are solutions of Eq. (41). Since both $\mathfrak{L}$ as well as $\mathfrak{F}$ are Hermitian operators, different functions λ_n, λ_m are mutually orthogonal and, hence,

$$(\lambda_n|\mathfrak{F} + \mathfrak{L}|\lambda_m) = 0 \text{ for } (n \neq m)\,.$$

Inserting here the definition for $\mathfrak{L}$, one obtains immediately condition (9). It follows then furthermore that

$$(\mathfrak{F} + \mathfrak{L})\lambda_n = \mathfrak{F}\lambda_n - \sum\nolimits_{m \atop (m\neq n)} (\lambda_n|\mathfrak{F}|\lambda_m)\lambda_m$$

so that Eq. (41) becomes identical with the general SCF Eq. (40), with $\gamma_{jk} = (\lambda_j|\mathfrak{F}|\lambda_k)$ for $j \neq k$.

The solutions of Eq. (41) have to be found by the iterative process

$$\mathfrak{R}^{(\nu)}\lambda_n^{(\nu+1)}(\mathbf{x}) = \eta_n^{(\nu+1)}\lambda_n^{(\nu+1)}(\mathbf{x})\,,$$

where

$$\mathfrak{R}^{(\nu)} = \mathfrak{F}\{\rho^{(\nu)}\} - \mathfrak{L}\{\lambda_1^{(\nu)}\cdots\lambda_N^{(\nu)}\}\,.$$

Examination of this process shows the omission of the diagonal elements $(\lambda_n|\mathfrak{F}|\lambda_n)$ in the definition of $\mathfrak{L}$, Eq. (43′), to be an essential necessity for obtaining convergence towards the localized orbitals. Because of this omission, the sum of the terms containing $\mathfrak{F}$ in $\mathfrak{L}$ is *not* identical with the projection $\rho\mathfrak{F}\rho$.

Thus, Eq. (41) replaces both Eq. (40) and Eq. (9) and, in contrast to the Hartree–Fock SCF equation,

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[20] T. L. Gilbert in *Molecular Orbitals in Chemistry, Physics and Biology. A Tribute to R. S. Mulliken*, edited by B. Pullmann and P. O. Löwdin (to be published). The authors are grateful to Dr. Gilbert for making available a preprint of this interesting work, and for a stimulating discussion.

it can be considered as an SCF equation for orthogonal energy localized orbitals. Whether, in practice, it is easier to solve directly for Eq. (41), instead of first solving for Eq. (39) and then applying the transformations described in the preceding sections, is questionable. It must also be borne in mind that Eq. (41) represents not only an equation for the SCF orbitals of maximal localization, but that it holds for the SCF orbitals of minimal localization as well.

COMPLEX LOCALIZED ORBITALS

Up to now all orbitals were assumed to be real, as is usually the case in molecules. Moreover the definition (42,ff) of the operator $\mathfrak{L}$ was purposely chosen such as to keep all quantities real.

If one abandons the convenience of reality, then the localization condition (9) becomes

$$[\varphi_n^*\varphi_n - \varphi_m^*\varphi_m|\varphi_n^*\varphi_m] = [\varphi_n^*\varphi_n - \varphi_m^*\varphi_m|\varphi_n\varphi_m^*] = 0\,, \quad (45)$$

and the transformation to localized orbitals is in general unitary. The kernel $L(\mathbf{x},\mathbf{x}')$ of the localization operator $\mathfrak{L}$ of Eq. (42) is now to be defined by

$$L(\mathbf{x},\mathbf{x}') = \sum_{n\neq m} \lambda_n(\mathbf{x})\lambda_m^*(\mathbf{x}')L_{nm}\,, \quad (46)$$

with

$$L_{nm} = \Lambda\{[\lambda_n^*\lambda_n - \lambda_m^*\lambda_m|\lambda_n^*\lambda_m]\} - (\lambda_n|\mathfrak{F}|\lambda_m)\,, \quad (46')$$

where $\Lambda\{z\}$ is now any complex function of the complex variable z, satisfying

$$\Lambda^*\{z\} = \Lambda\{-z^*\}\,,$$
$$\Lambda\{z\} = 0 \text{ only for } z = 0\,.$$

This guarantees that L_{nm} is a Hermitian matrix and, hence, $\mathfrak{L}$ a hermitian operator. The simplest choice is

$$L_{nm} = i[\lambda_n^*\lambda_n - \lambda_m^*\lambda_m|\lambda_n^*\lambda_m] - (\lambda_n|\mathfrak{F}|\lambda_m)\,. \quad (47)$$

It may be noted that the integral operator with the kernel

$$\lambda(\mathbf{x},\mathbf{x}') = i \sum_{n,m} \lambda_n(\mathbf{x})\lambda_n^*(\mathbf{x}')[\lambda_n^*\lambda_n - \lambda_m^*\lambda_m|\lambda_n^*\lambda_m]$$

is the projection, on the space subtended by λ_1, $\lambda_2 \cdots \lambda_N$, of the integral operator with the kernel

$$\tilde{\lambda}(\mathbf{x},\mathbf{x}') = i \sum_n \lambda_n(\mathbf{x})\lambda_n^*(\mathbf{x}')\{U_n(\mathbf{x}') - U_n(\mathbf{x})\}\,,$$

where

$$U_n(x) = \int dV''\lambda_n^*(\mathbf{x}'')\lambda_n(\mathbf{x}'')/|\mathbf{x} - \mathbf{x}''|\,.$$

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Pair Correlation Energies*

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I. INTRODUCTION

REALIZATION of a practical and easy-to-interpret theoretical formalism for electron-correlation effects is today the most actively pursued goal in the quantum mechanical description of atoms and molecules. The present article is an attempt to abstract from existing numerical data a set of empirical rules which can act as a guide to theoretical formulations of electron correlation.[1]

The correlation energy E_{corr} of an atomic or molecular system may be defined as the difference between the exact nonrelativistic energy and the Hartree–Fock energy for this system.[2] The nonrelativistic experimental energy can be obtained

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[1] For other work on this problem see E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

[2] P. O. Löwdin, *Advances in Chemical Phys.*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. II, p. 207.