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On the Mathematical Formulation and Interpretation of LCAO MO Theory

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The mathematical basis of LCAO MO theory is studied, both within the Hartree-Fock approximation and in more exact formulations. The basic LCAO expansion for molecular orbitals $|\boldsymbol{\phi}\rangle$ in terms of atomic orbitals $|\boldsymbol{\chi}\rangle$ is conveniently written

$$|\boldsymbol{\phi}\rangle = |\boldsymbol{\chi}\rangle \boldsymbol{S}^{-1}\boldsymbol{B}$$

where $\boldsymbol{S}$ is the overlap matrix for atomic orbitals and $\boldsymbol{B}$ is the matrix of atomic orbital-molecular orbital overlaps. It is suggested that matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$, defined by

$$\boldsymbol{P} = \boldsymbol{B}\boldsymbol{B}^{\dagger}$$

and

$$\boldsymbol{Q} = \boldsymbol{B}\boldsymbol{n}\boldsymbol{B}^{\dagger},$$

where $\boldsymbol{n}$ is the matrix of molecular orbital occupation numbers, are appropriate to the interpretation of molecular calculations in terms of atomic orbital components, electronic populations and the degree of bonding. Implications for Hartree-Fock calculations are investigated.

Key words: LCAO MO theory, mathematical formulation of ~

1. Introduction

The main objective of this paper is to present a reformulation of linear combination of atomic orbitals molecular orbital (LCAO MO) theory when the atomic orbitals concerned are not orthogonal (that is, they have non-zero overlap integrals). We explore particularly the meaning of the coefficients in the LCAO expansion and of the associated "charge-and-bond-order matrix". Our results have consequences for finding the coefficients, for interpreting molecular calculations by means of the concepts of atoms in molecules and chemical bonds, and for defining quantities such as "atomic charge" and "bond order" suitable for correlation with experimental results.

Using Dirac's ket-bra notation [1], the LCAO expansion in its usual form [2] may be written

$$|\boldsymbol{\phi}\rangle = |\boldsymbol{\chi}\rangle \boldsymbol{C} \tag{1}$$

where $|\boldsymbol{\phi}\rangle$ is a $1 \times m_{\mathrm{MO}}$ row matrix of the m_{MO} occupied molecular orbitals $|i\rangle$, $|j\rangle$, etc., and $|\boldsymbol{\chi}\rangle$ is a $1 \times m_{\mathrm{AO}}$ row matrix of the atomic orbitals $|\mu\rangle$, $|\nu\rangle$, etc., chosen for the expansion. $\boldsymbol{C}$ is consequently an $m_{\mathrm{AO}} \times m_{\mathrm{MO}}$ rectangular matrix of coefficients of the expansion, and $m_{\mathrm{AO}} \geqq m_{\mathrm{MO}}$. The molecular orbitals are usually required to be orthonormal, whereupon we obtain the standard condition on $\boldsymbol{C}$:

$$\langle\boldsymbol{\phi}|\boldsymbol{\phi}\rangle = \boldsymbol{C}^{\dagger}\boldsymbol{S}\boldsymbol{C} = \boldsymbol{I}, \tag{2}$$

I being the unit matrix of order m_{MO} and S the matrix of overlap integrals over atomic orbitals:

$$S = \langle\chi|\chi\rangle\,, \tag{3}$$

having elements $S_{\mu\nu} = \langle\mu|\nu\rangle$.

In general given a suitable set of atomic orbitals $|\chi\rangle$ one needs to determine C and the occupation numbers of the resulting molecular orbitals. In calculations at the Hartree-Fock level, the problem is solved once C has been found, since the occupation numbers are fixed. The development that follows applies in general whenever an LCAO expansion is introduced, and we make some remarks specific to the Hartree-Fock case in Section 5.

2. Mathematical Aspects of the LCAO Expansion

Mathematically speaking, the set of occupied molecular orbitals $|\phi\rangle$ and the set of atomic orbitals $|\chi\rangle$ form subspaces of an abstract Hilbert space [3]. Any such subspace is conveniently and uniquely represented by a projection operator (or projector) P [4] having

$$P^2 = P\,, \qquad P^\dagger = P\,. \tag{4}$$

Thus one may define a projector P_{MO} on the occupied molecular orbitals;

$$P_{\mathrm{MO}} = \sum_{i=1}^{m_{\mathrm{MO}}} |i\rangle\langle i| = |\phi\rangle\langle\phi|\,, \tag{5}$$

($\langle\phi|$ being a column matrix of the molecular orbital bras $\langle i|$, $\langle j|, \ldots$), and a projector P_{AO} on the atomic orbitals:

$$\begin{aligned} P_{\mathrm{AO}} &= |\chi\rangle S^{-1}\langle\chi| \\ &= \sum_{\mu=1}^{m_{\mathrm{AO}}} \sum_{\nu=1}^{m_{\mathrm{AO}}} |\mu\rangle (S^{-1})_{\mu\nu}\langle\nu|\,. \end{aligned} \tag{6}$$

The mathematics of subspaces and projectors may now be applied to the situation.

By the standard projection theorem, each molecular orbital $|i\rangle$ has a unique component in the atomic orbital subspace (and conversely), and this component is $P_{\mathrm{AO}}|i\rangle$. If $|i\rangle$ belongs completely to the atomic orbital subspace, then

$$P_{\mathrm{AO}}|i\rangle \equiv |i\rangle \tag{7}$$

and the LCAO expansion for $|i\rangle$ is exact. If on the other hand the expansion is not exact, then we may employ a "best least-squares theorem" due to Löwdin [5] which states that $P_{\mathrm{AO}}|i\rangle$ is the best least-square approximation to $|i\rangle$ of any vector in the atomic orbital subspace.

In matrix notation, we have either

$$P_{\mathrm{AO}}|\phi\rangle = |\phi\rangle \tag{8}$$

for exact LCAO expansion of all molecular orbitals, or

$$P_{\mathrm{AO}}|\phi\rangle \approx |\phi\rangle \tag{9}$$

for the best least-square LCAO approximation to the molecular orbitals.

That is, exactly or approximately,

$$\begin{aligned} |\phi\rangle &= P_{\mathrm{AO}}|\phi\rangle \\ &= |\chi\rangle\, \boldsymbol{S}^{-1}\langle\chi|\phi\rangle \end{aligned} \tag{10}$$

or

$$|\phi\rangle = |\chi\rangle\, \boldsymbol{S}^{-1}\boldsymbol{B}\,.$$

Here $\boldsymbol{B}$ is a rectangular matrix ($m_{\mathrm{AO}} \times m_{\mathrm{MO}}$) whose elements are the overlap integrals between atomic orbitals and molecular orbitals:

$$\boldsymbol{B} = \langle\chi|\phi\rangle \quad \text{and} \quad B_{\mu i} = \langle\mu|i\rangle\,. \tag{11}$$

Equation (10) is an alternative and, we will argue, often more convenient form of the LCAO expansion. We see that the usual coefficient matrix C of Eq. (1) is reducible to

$$\boldsymbol{C} = \boldsymbol{S}^{-1}\boldsymbol{B} \tag{12}$$

and the standard condition, Eq. (2), may be converted to:

$$\boldsymbol{B}^{\dagger}\boldsymbol{S}^{-1}\boldsymbol{B} = \boldsymbol{I}\,. \tag{13}$$

Usually the matrix $\boldsymbol{C}$ is varied until those LCAO MO's are found that give the lowest energy. Since the overlap matrix $\boldsymbol{S}$ is known, we see that it is really only necessary to vary the matrix $\boldsymbol{B}$. In varying $\boldsymbol{B}$, we are actually varying the molecular orbitals in the scalar product, Eq. (11). Such a ready interpretation for the variation of $\boldsymbol{C}$ is difficult to find.

The matrix $\boldsymbol{B}$ has an additional advantage in that it (and not $\boldsymbol{C}$) is analogous to the matrix of coefficients $\boldsymbol{C}^{\lambda}$ in the expansion of molecular orbitals in terms of some set $|\lambda\rangle$ of orthogonal atomic orbitals (OAO's). The LCOAO expansion is

$$|\phi\rangle = |\lambda\rangle\, \boldsymbol{C}^{\lambda} \tag{14}$$

and $\boldsymbol{C}^{\lambda}$ is now the matrix of OAO-MO overlap integrals:

$$\boldsymbol{C}^{\lambda} = \langle\lambda|\phi\rangle\,. \tag{15}$$

In the past a number of problems have arisen when attempts have been made to transfer concepts and quantities formulated in theories where atomic orbitals have been assumed orthogonal and overlap neglected (for example, Hückel, Pariser-Parr-Pople, and CNDO methods) to theories where overlap has been included (for example, *ab initio* Hartree-Fock methods). We will show in the next sections how some of these problems may be avoided if the results of this section are used.

3. Interpretation of LCAO Calculations

When orthogonal atomic orbitals have been used or overlap has been neglected, the interpretation of LCAO calculations has usually been based on the "charge-and-bond-order matrix" $\boldsymbol{Q}^{\lambda}$, first defined by Coulson [6]. In general we may write:

$$\boldsymbol{Q}^{\lambda} = \boldsymbol{C}^{\lambda}\boldsymbol{n}(\boldsymbol{C}^{\lambda})^{\dagger} \tag{16}$$

where $\boldsymbol{n}$ is a matrix (usually diagonal) of molecular orbital occupation numbers. A similar matrix $\boldsymbol{R}$ may be defined for nonorthogonal orbitals,

$$\boldsymbol{R} = \boldsymbol{C}\boldsymbol{n}\boldsymbol{C}^{\dagger} \tag{17}$$

but it is not clear that $\boldsymbol{R}$ plays a corresponding role in interpretation to $\boldsymbol{Q}^{\lambda}$. Several authors [7–15] have studied this problem, and the procedure commonly used is Mulliken's population analysis [11] which depends upon the matrix product $\boldsymbol{RS}$.

The reasoning of Section 2 leads to the suggestion that there are two matrices which ought to be important in interpretation. The first is a projection matrix $\boldsymbol{P}$, given in general by

$$\boldsymbol{P} = \langle \chi | P_{\mathrm{MO}} | \chi \rangle . \tag{18}$$

The diagonal elements of $\boldsymbol{P}$, given by

$$P_{\mu\mu} = \langle \mu | P_{\mathrm{MO}} | \mu \rangle \tag{19}$$

measure the magnitudes of the components of atomic orbitals $|\mu\rangle$ in the molecular orbital subspace, and hence give an indication of the importance of the orbital in describing the molecule. LCAO expansion gives

$$\boldsymbol{P} = \boldsymbol{B}\boldsymbol{B}^{\dagger} \tag{20}$$

and multiplication of Eq. (13) on the left by $\boldsymbol{B}$ and on the right by $\boldsymbol{B}^{\dagger}$ gives a condition on $\boldsymbol{P}$:

$$\boldsymbol{P}\boldsymbol{S}^{-1}\boldsymbol{P} = \boldsymbol{P} . \tag{21}$$

The second matrix, which on the arguments presented herein properly deserves the name "charge-and-bond-order matrix" for nonorthogonal atomic orbitals, is the matrix $\boldsymbol{Q}$, given in general by:

$$\boldsymbol{Q} = N \langle \chi | \varrho | \chi \rangle \tag{22}$$

where N is the number of electrons in the molecule and ϱ is the molecular one-electron density operator ([3] and Refs. quoted therein) given by

$$\varrho = |\phi\rangle\, \boldsymbol{\lambda} \langle \phi | , \tag{23}$$

$\boldsymbol{\lambda}$ being the (diagonal) matrix of molecular orbital probabilities of occupation, with $N\boldsymbol{\lambda} = \boldsymbol{n}$.

$\boldsymbol{Q}$ thus contains the expectation values of the atomic orbitals with respect to the molecular one-density ϱ. LCAO expansion gives

$$\boldsymbol{Q} = \boldsymbol{B}\boldsymbol{n}\boldsymbol{B}^{\dagger} \tag{24}$$

and also

$$\boldsymbol{Q} = \boldsymbol{S}\boldsymbol{R}\boldsymbol{S} . \tag{25}$$

The condition on the one-density operator that

$$\mathrm{Tr}\,\varrho = 1 \tag{26}$$

where "Tr" here means the operator trace of ϱ – the sum of elements $\langle i | \varrho | i \rangle$ with respect to some complete orthonormal set $\{|i\rangle\}$ – leads by substitution in Eq. (23) to the following condition on $\boldsymbol{Q}$:

$$\mathrm{Tr}\,\boldsymbol{Q}\boldsymbol{S}^{-1} = \mathrm{Tr}\,\boldsymbol{S}^{-1}\boldsymbol{Q} = N . \tag{27}$$

Here we have used the matrix trace, being the sum of the diagonal elements of the matrix concerned.

The argument that $\boldsymbol{Q}$ is a more appropriate quantity than $\boldsymbol{R}$ for interpretation rests on the analogy of $\boldsymbol{Q}$ and $\boldsymbol{Q}^{\lambda}$, each depending in the same way on the respective AO-MO overlap matrices $\boldsymbol{B}$ and $\boldsymbol{C}^{\lambda}$, and on a new and general definition of occupation number and charge proposed recently [16]. The definition depends on the proposition that if P is the projector on some subspace of the molecular one-electron Hilbert space and ϱ is the molecular one-density operator, then the occupation number n of that subspace is

$$n = N \operatorname{Tr} \varrho P . \tag{28}$$

The diagonal elements of $\boldsymbol{Q}^{\lambda}$ have traditionally been regarded as OAO occupation numbers, and this is in accord with the definition, Eq. (28). Thus if $|\lambda_{\mu}\rangle$ is a particular OAO, then its projector is

$$P_{\mu}^{\lambda} = |\lambda_{\mu}\rangle \langle \lambda_{\mu}| \tag{29}$$

and substitution in Eq. (28) yields the occupation number n_{μ}^{λ} of this orbital,

$$n_{\mu}^{\lambda} = Q_{\mu\mu}^{\lambda} . \tag{30}$$

We find in a similar way that the occupation number n_{μ} of an AO $|\mu\rangle$ is given by

$$n_{\mu} = Q_{\mu\mu} \tag{31}$$

and that atomic occupation numbers $n_A, n_B, \ldots$ for the various atoms in the molecule also depend on $\boldsymbol{Q}$ (assuming that the set of atomic orbitals on each atom is orthonormal):

$$n_A = \sum_{\mu \in A} Q_{\mu\mu} . \tag{32}$$

Thus $\boldsymbol{Q}$ for AO's may be used in the same way as $\boldsymbol{Q}^{\lambda}$ for the OAO's in defining AO occupation numbers and atomic charges, and the analogy between them is complete.

4. Remarks on the Concept of Bond Order

A number of quantities have been proposed as a measure of the degree of bonding between any two atoms in a molecule [6–17]. The present work suggests several new possibilities, each having a special significance.

The shared electron density occupation number s_{AB}, defined for two atoms A and B in the molecule, is one such measure [16]. It is given by

$$s_{AB} = n_A + n_B - n_{AB} \tag{33}$$

where n_A, n_B, and n_{AB} are occupation numbers for atom A, atom B, and the total subspace of A and B, respectively, each defined as in Eq. (28). s_{AB} measures the amount of electron sharing between the two atoms, and may range from zero when there is no sharing to a maximum of n_{AB} when all electron density assigned to either of the atoms is also shared between them.

Equation (33) is a general definition, and we may now show the dependence of s_{AB} on $\boldsymbol{Q}$ in the LCAO case. The result is:

$$\begin{aligned} s_{AB} &= \operatorname{Tr}(\boldsymbol{Q}_A + \boldsymbol{Q}_B - \boldsymbol{Q}_{AB} \boldsymbol{S}_{AB}^{-1}) \\ &= \sum_{\mu} Q_{\mu\mu} - \sum_{\mu} \sum_{\nu} Q_{\mu\nu} (S_{AB}^{-1})_{\nu\mu} \end{aligned} \tag{34}$$

with $|\mu\rangle \in A$ or B, $|\nu\rangle \in A$ or B. Here $\boldsymbol{Q}_A$ is the submatrix of $\boldsymbol{Q}$ having elements $Q_{\mu\nu}$ with $|\mu\rangle \in A$ and $|\nu\rangle \in A$, $\boldsymbol{Q}_B$ is a similar submatrix referring to atom B, and $\boldsymbol{Q}_{AB}$ and $\boldsymbol{S}_{AB}$ are submatrices of $\boldsymbol{Q}$ and $\boldsymbol{S}$ respectively with elements $Q_{\mu\nu}$ and $S_{\mu\nu}$, $|\mu\rangle \in A$ or B, $|\nu\rangle \in A$ or B.

s_{AB} is thus easily found once the $\boldsymbol{Q}$ matrix is known.

While it seems that s_{AB} is the most satisfactory measure of the degree of bonding (for reasons advanced in [16]), it is worthwhile investigating the use of off-diagonal elements of the $\boldsymbol{P}$ or $\boldsymbol{Q}$ matrix directly, by analogy with Coulson's use of the off-diagonal elements of $\boldsymbol{Q}^\lambda$ as "bond orders" in OAO theory. Considering $\boldsymbol{P}$ first, we have:

$$\begin{aligned} P_{\mu\nu} &= \langle\mu|P_{\text{MO}}|\nu\rangle \\ &= \langle\mu|P_{\text{MO}}\cdot P_{\text{MO}}|\nu\rangle \end{aligned} \tag{35}$$

and $P_{\mu\nu}$ measures the overlap of the components in the molecular orbital subspace of atomic orbitals $|\mu\rangle$ and $|\nu\rangle$. We might expect that the larger the absolute magnitude of this quantity the greater is the order of the bond. The absolute magnitude of $P_{\mu\nu}$ is subject to a limit imposed by the Schwarz inequality [4]:

$$|P_{\mu\nu}| \leqq (\langle\mu|P_{\text{MO}}|\mu\rangle\,\langle\nu|P_{\text{MO}}|\nu\rangle)^{\frac{1}{2}} \leqq 1\,. \tag{36}$$

Similarly we may consider the off-diagonal elements of $\boldsymbol{Q}$, giving the magnitudes relative to the molecular density,

$$Q_{\mu\nu} = N\langle\mu|\varrho|\nu\rangle\,. \tag{37}$$

Again we expect that the larger the absolute magnitude of this quantity the greater the contribution to bonding, and again there is a limit due to the Schwarz inequality:

$$\begin{aligned} |Q_{\mu\nu}| &= N\,|\langle\mu|\varrho^{\frac{1}{2}}\cdot\varrho^{\frac{1}{2}}|\nu\rangle| \\ &\leqq (Q_{\mu\mu}Q_{\nu\nu})^{\frac{1}{2}} = (n_\mu n_\nu)^{\frac{1}{2}}\,. \end{aligned} \tag{38}$$

In either case one could use a simple sum, $\sum\limits_{\mu\in A}\sum\limits_{\nu\in B}|P_{\mu\nu}|$ or $\sum\limits_{\mu\in A}\sum\limits_{\nu\in B}|Q_{\mu\nu}|$, as an index of the total "bond order" between any two atoms.

Finally our formulation permits a generalization of Wiberg's "bond index" [17], which was originally defined within Hartree-Fock theory and the LCOAO expansion, and has proven useful in a number of studies [17, 18]. The bond index for atoms A and B is the sum of the squares of the bond orders, $\sum\limits_{\mu\in A}\sum\limits_{\nu\in B}(Q^\lambda_{\mu\nu})^2$. Obviously the analogous quantity in the general theory is

$$\begin{aligned} \sum_{\mu\in A}\sum_{\nu\in B} Q^2_{\mu\nu} &= \sum_{\mu\in A}\sum_{\nu\in B} N^2\langle\mu|\varrho|\nu\rangle\,\langle\nu|\varrho|\mu\rangle \\ &= \sum_{\mu\in A} N^2\langle\mu|\varrho P_B\varrho|\mu\rangle \\ &= N^2\,\mathrm{Tr}\,P_A\,\varrho\,P_B\,\varrho\,. \end{aligned} \tag{39}$$

This general bond index thus depends on the projectors P_A and P_B for the two atoms and on the molecular one-density operator. From the theoretical point of view, however, there does not seem to be any advantage in using this quantity

Table 1. Comparison of indices of bonding in diatomic molecules[a]

Molecule	Shared density occuption number s_{AB}[b] [Eq. (60)]	Bond order sum	Bond index [Eq. (65)]
Li_2	1.74	3.93	3.51
Be_2	1.68	4.19	4.11
C_2	2.94	6.79	7.58
N_2	2.71	6.74	6.65
F_2	0.45	2.34	1.60
LiH	1.41	2.57	2.89
BH	1.46	2.63	3.11
NH	1.12	2.01	2.34
HF	0.91	2.24	2.30
CO	2.41	6.35	5.94
LiF	0.97	4.08	2.82
BF	1.59	5.10	3.95

[a] STO calculations by B. J. Ransil, Rev. mod. Phys. 32, 239 (1960).
[b] Values taken from Ref. [19].

over the simple sum $\sum_{\mu\in A}\sum_{\nu\in B}|Q_{\mu\nu}|$ proposed above, provided that absolute values are used in the sum.

This prediction is borne out in Table 1, where calculated values for diatomic molecules are listed. Note especially the similarity between actual values of the bond order sum and the bond index. These values are two or three times the values of s_{AB}. There is some difference in the order of the values; for example, F_2 has the smallest s_{AB} and bond index but NH has the smallest bond order sum. Broadly speaking, however, the order is the same, rearrangements occurring for fluorine-containing molecules (where special reasons prevail [16]) or where values are close together. For example all three quantities give lowest values to the group F_2, HF and NH, and highest values to the group CO, N_2, C_2.

5. Hartree-Fock LCAO Equations

In the previous sections two general matrices were introduced, namely, the projection matrix $\boldsymbol{P}$ and the "charge-and-bond-order matrix" $\boldsymbol{Q}$. We now specialize to the Hartree-Fock approximation where all MO occupation numbers n_i are constant at unity (assuming molecular spin orbitals) and $\boldsymbol{P}$ and $\boldsymbol{Q}$ therefore become identical.

Previously the problem has been to find the coefficients $\boldsymbol{C}$ by an SCF procedure, or alternatively to find $\boldsymbol{R}$ by other minimization techniques. The problem now is to find $\boldsymbol{B}$ or $\boldsymbol{Q}$.

We make the following points:

(a) The Fock Hamiltonian operator F and the Hartree-Fock electronic energy E have the same form in terms of $\boldsymbol{Q}$ as they did in terms of $\boldsymbol{R}$, provided that other matrices concerned are transformed using $\boldsymbol{S}^{-1}$.

That is,

$$F = H + \mathrm{Tr}\,\boldsymbol{Q}(\boldsymbol{J}' - \tfrac{1}{2}\boldsymbol{K}') \tag{40}$$

and

$$E = \tfrac{1}{2}\,\mathrm{Tr}\,\boldsymbol{Q}(\boldsymbol{H}' + \boldsymbol{F}') \tag{41}$$

where

$$\boldsymbol{A}' = \boldsymbol{S}^{-1}\boldsymbol{A}\boldsymbol{S}^{-1}, \quad \boldsymbol{A} = \boldsymbol{J}, \boldsymbol{K}, \boldsymbol{H} \text{ or } \boldsymbol{F}. \tag{42}$$

Here $\boldsymbol{H}$ and $\boldsymbol{F}$ are the usual core Hamiltonian and total Hamiltonian matrices over AO's and the elements of $\boldsymbol{J}$ and $\boldsymbol{K}$ are the Coulomb and exchange repulsion operators $J_{\lambda\sigma}$ and $K_{\lambda\sigma}$ over AO's.

(b) Variation of the energy in its usual form with variation in $\boldsymbol{R}$ leads to the results,

$$\delta E = 2\,\mathrm{Tr}\,\boldsymbol{F}\,\delta\boldsymbol{R}. \tag{43}$$

An analogous derivation based on Eq. (42) gives

$$\delta E = 2\,\mathrm{Tr}\,\boldsymbol{F}'\,\delta\boldsymbol{Q}. \tag{44}$$

Equation (44) may be used in a similar way to Eq. (43) to derive optimization formulae such as the SCF equations of Roothaan [2] and others, McWeeny's method of steepest descent [19], or Fletcher's method [20]. $\boldsymbol{Q}$ or $\boldsymbol{B}$ may be found directly by McWeeny's or Fletcher's method, but the new formalism offers no extra advantages for the direct solution of the SCF equations. One still needs to orthogonalize the atomic orbitals, say by symmetric orthogonalization [8], solve for $\boldsymbol{C}^{\lambda}$ and $\boldsymbol{Q}^{\lambda}$ over the OAO's, and back transform:

$$\boldsymbol{B} = \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{C}^{\lambda} \tag{45}$$

$$\boldsymbol{Q} = \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{Q}^{\lambda}\boldsymbol{S}^{\frac{1}{2}}. \tag{46}$$

Note that the relation between $\boldsymbol{Q}$ and $\boldsymbol{Q}^{\lambda}$ is the same as the relation between any other matrices in the two bases, for example $\boldsymbol{F}$ and $\boldsymbol{F}^{\lambda}$, $\boldsymbol{H}$ and $\boldsymbol{H}^{\lambda}$, etc.

(c) Rapidity of convergence of the SCF procedure depends in part on the initial guess of $\boldsymbol{R}$ or $\boldsymbol{Q}$ before orthogonalizing and the present work is suggestive in this regard. We would expect the superposition of individual atom electron densities to be a good starting point. Because of the close relation between projectors and density operators in Hartree-Fock theory, superposition of atomic densities yields the initial molecular density ϱ_0:

$$\varrho_0 = (|\chi\rangle\, S^{-1} \langle\chi|)/N \tag{47}$$

showing that a good initial choice of $\boldsymbol{R}$ or $\boldsymbol{Q}$ would be:

$$\boldsymbol{R}_0 = \boldsymbol{S}^{-1} \quad \text{or} \quad \boldsymbol{Q}_0 = \boldsymbol{S}. \tag{48}$$

6. Conclusions

There is some value in reformulating the LCAO expansion in terms of the atomic orbital-molecular orbital overlap matrix $\boldsymbol{B}$ rather than the matrix of coefficients $\boldsymbol{C}$. This reformulation emphasizes the connection between LCAO theory and the mathematics of Hilbert space and projection operators, and enables the introduction of the projection matrix $\boldsymbol{P}$ and the new "charge-and-bond-order matrix" $\boldsymbol{Q}$.

Because it contains the magnitudes of the components of atomic orbitals in the occupied molecular orbital subspace, the matrix $\boldsymbol{P}$ measures the importance of the various atomic orbitals to the description of the molecular structure. The elements of the matrix $\boldsymbol{Q}$ include the expectation values of atomic orbitals relative to the molecular one-electron density, and are regarded as atomic orbital occupation numbers. It is suggested that $\boldsymbol{P}$ and $\boldsymbol{Q}$ are therefore important for the interpretation of LCAO calculations. We have also argued that $\boldsymbol{B}$ and $\boldsymbol{Q}$ (rather than $\boldsymbol{C}$ and $\boldsymbol{R}$ as traditionally assumed) are analogous to the matrices $\boldsymbol{C}^{\lambda}$ and $\boldsymbol{Q}^{\lambda}$ respectively, which have been central to the interpretation of orthogonal atomic orbital or overlap-neglected calculations.

Several new possibilities for measuring the degree of bonding between any two atoms have emerged from these considerations. The most promising appears to be the shared density occupation number, given by Eq. (34) in its LCAO form.

The basic equations of the reformulation are the LCAO Eq. (10); the condition on B, Eq. (13), the general and LCAO definitions of $\boldsymbol{P}$ and $\boldsymbol{Q}$, Eqs. (18), (20), (22), (24) and the conditions on $\boldsymbol{Q}$, Eq. (27).

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