A principle of linear covariance for quantum mechanics and the electronic structure theory of molecules and other atom clusters

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Quantum mechanical equations should look the same in any non-orthonormal or orthonormal basis frame when properly formulated so as to be fully covariant under the largest group indicated. Non-orthonormal frames are crucial especially for the quantum theory of chemistry. Various methods such as valence-bond, localized orbital, molecular orbital, etc. result from a single formulation using the principle of linear covariance which is stated, proved, and exemplified. Molecular quantities with the full inclusion of overlaps are derived with the same ease as without overlaps.

Key words: Linear covariance—atom clusters—electronic structure theory

1. Introduction

A fundamental aspect of quantum mechanics is the "superposition principle" [1]. Hence, the quantum mechanical machinery is built on abstract linear algebra and the theory of linear operators. Quantum mechanical procedures involve, in one form or another, transformations from one complete basis set to another in the Hilbert space (e.g. $\{|p'\rangle\} \rightarrow \{|q'\rangle\}$ or $\{|\psi_E\rangle\} \rightarrow \{|q'\rangle\}$, etc.). The requirement that eigenvalues of observables have to be real dictates Hermitian operators for the observables. Fortunately, the eigenvectors of Hermitian operators form complete basis sets which are also orthonormal (O.N.) (degenerate ones can be made O.N.).

The O.N. nature of basis sets are preserved under unitary transformations. Unitary transformations also leave expectation values and/or eigenvalues unchanged.

That O.N. basis sets have been used most often both in physics and in the quantum theory of chemistry rather than non-O.N. ones, may be tracable to the aforementioned key theorems on Hermitian and on unitary operators. However, where

basis sets are used for purely computational purposes by the variational principle, there is no *a priori* requirement that basis sets be O.N. The vectors of an arbitrary basis set are not in general the eigenvectors of an observable anyway.

Still, O.N. bases have been sought after for the convenience they afforded in the evaluation of e.g., N-eectron matrix elements between determinantal wave functions (w.f.) as in the Slater–Condon rules [2, 3]. The convenience continued in the theory of finite many-particle correlations [4].

The customary, algorithmic convenience of an O.N. basis is best displayed by the unity operator (I) trick:

With $\{|e_i\rangle\}$ the *complete* O.N. basis,

$$I = \sum_{i \geq 1}^{\infty} |e_i\rangle\langle e_i| \tag{1}$$

from $I^2 = I$ and

$$\langle e_i | e_j \rangle = \delta_{ij}. \tag{2}$$

To find the representation of an operator A on $\{|e_i\rangle\}$, the familiar trick is to insert an I, Eq. (1), whereever needed to get the matrix form of A:

$$IAI = \sum_{i,j} |e_i\rangle\langle e_i|A|ej\rangle\langle ej|, \tag{3}$$

hence

$$A = \{A_{ij}\}; \qquad A_{ij} = \langle e_i|A|e_j\rangle$$

(similarly to go from one O.N. basis to another, e.g., $\{|e_i\rangle\}$ to $\{|f_k\rangle\}$, $I^2 = I$ with one I in each basis in I^2).

However, orthogonal or unitary transformations are not the most general ones allowed fundamentally by the "superposition principle". Any linear transformation including those involving non-orthonormal vectors should do.

Considering a countably infinite dimensional linear vector space $V_n(n \to \infty)$, *the largest group of transformations implied by the "superposition principle" should be* not the orthogonal, nor the unitary groups, $O(n)$ or $U(n)$, but *the general linear group $GL(n, C)$ over the complex field C (or in many applications [5] just over the real field R, i.e., $L(n, R)$).*

The quantum mechanical machinery has *not* been based by and large, on the use of the most general linear transformations. There have been few occasions in atomic physics for using non-unitary transformations and non-O.N. bases. A striking case is in the prediction of accurate lifetimes, optical and other transition probabilities for many-electron atoms [6]. That development which went hand-in-hand with beam-foil spectroscopy [7] a decade ago, required matrix elements for the then new correlation effects [8] between sets of initial and final determinantal (det) w.f.'s where the orbitals in the bra dets are not orthogonal to those in the ket dets.

In the quantum theory of chemistry on the other hand, non-orthogonal bases are pervasive, and crucial [9].

Take e.g. the valence-bond [10, 11] method (VB). The atomic orbitals (AO) centered on neighboring nuclei are certainly not orthogonal. Such overlaps, $\Delta_{\mu\nu} = \langle e_\mu | e_\nu \rangle$ are often close to a half. If they are neglected, no chemical binding results! Yet in qualitative quantum chemistry they were often assumed to be zero (to mimic an O.N. set again). Equations and computations including all the overlaps looked unwieldy.

That is one reason why molecular orbitals (MO) got to be preferred in the late fifties over the VB method. The MO looses the chemist's intuitive structural picture of isolated bonds and lone pairs as in the "ball and stick models" of molecules. But MO's are O.N., being the eigenvectors of an effective one electron hamiltonian. In actual calculations of MO's too it turned out, the $AO - AO'$ overlaps $\Delta_{\mu\nu}$ could not be neglected, though in the initial semiempirical MO methods such as the Hückel [12, 13] one they were. Since the semi-empirical methods nevertheless worked better, it appeared the non-O.N. AO's could be first transformed into orthogonalized AO's (OAO's) [9]. Then the meaning of the parameters changed, but the formalism could still be based on an O.N. set.

Many of the basic difficulties that still plaque the quantum theory of molecules and reactions appear to be due to the seeming dichotomy between the chemist's structural picture, alright in the VB but then at the expense of the non-orthogonality problems, and the MO, delocalized orbitals (O.N. basis) method which is more like the band theory of metals. Adding to the complication is the difficulty of treating electronic excitation in the VB method. MO's are easier in this, but they too get into serious difficulty due to the non-O.N. AO's in e.g. the vacuum ultraviolet spectra of molecules (cf. the notion of "pre-Rydberg" excited states, introduced by this writer, in connection also with the non-O.N. problem) [14].

Lennard-Jones [15] (L.-J.) and subsequent workers [16] attempted to recover the chemical structural picture from the MO's. In special, symmetric cases like the methane molecule, CH_4, L.J. transformed (unitary) the MO set into still O.N., localized orbitals, the LO set, which looked like bonds without affecting the values of the observables. But where the molecule lacked a high point group symmetry, e.g., even in propane, C_3H_8, the L.-J. transform did not apply. It could only be extended by introducing some *ad hoc* and rather arbitrary localization criteria [16] (a very recent development by Luken [17] appears so far to have the easiest to use, yet physically meaningful criterion).

The VB and MO formalisms look very different though it is known that if they are both extended they should yield the same result [11]. The VB and MO's are treated in chemistry as if they were different fields of study.

One more and now major difficulty for chemistry is that, in both VB and the MO, each geometry of each atom cluster, and each molecule is treated as a separate problem. It has been awkward or impossible (in part due to the non-O.N. bases) to relate different molecules, isomers, different geometries to each other

(cf. Ref. in [5]) especially when the species lacked extensive point group symmetries [18–20].

In short, it appears a general formulation is needed which can relate different molecules to each other directly, as well as give all at once both the VB and the MO (and LO, OAO, *etc.*) pictures dealing head-on with the non-unitary transformations involved.

The present paper introduces a covariance principle, that· of *linear covariance* which follows from the fundamental linearity of quantum mechanics. The author developed it initially both for the chemical problems and for the wider context of the general mathematical machinery of quantum theory. The principle also leads to a deeper understanding of the origin of higher symmetries in the Hilbert space and their relation to those in the 3-*dim.* Euclidean space.

2. Principle of linear covariance

We state the principle in three interrelated parts:

i) The abstract kets, bras, operators, and relations involving them are to be viewed as invariants under any linear transformation of bases ("coordinate frames") $S \subseteq L(n)$ on V_n where S is non-singular ($|S| \neq 0$). The abstract objects are unaffected by arbitrary changes of bases for their representation, whether the bases are non-O.N. or O.N. so long as they are complete. Starting with one complete basis set, the non-singularity of S ensures that the new set is also complete (cf. Ref. [14], p. 379 for cases in the MO's of molecular states where conventional theories lost the singularity of S causing the "Δ-catastrophe" [14]).

ii) In component form, any quantum mechanical equation should be linearly covariant.

iii) Regardless of which basis set (complete) is used out of the infinite number of sets possible, O.N. or non-O.N., quantum mechanical equations written out in component, i.e. tensorial form should *look the same.*

The (*iii*) implies for example that, if properly formulated, i.e., in covariant form, quantum chemical equations will look the same whether they refer to VB, or MO, LO, OAO or any other description (each treated in the past as a distinct method) of the same physical problem. Any corrections needed to the conventional forms of each such method, will now be deducible by looking at what is missing from the conventional (non-convariant, intuitive, *etc.*) equation as compared to the covariant equations.

The principles stated above are amplified, proved, and exemplified below.

3. The metric tensor, covariant and contravariant components

If we start from an O.N. basis set $\{|e_i\rangle\}$ for V_n, the "overlap matrix"

$$\{\langle e_i|e_j\rangle = \delta_{ij}\} \tag{4}$$

remains invariant under any orthogonal (or unitary) transformation as does the "closure" relation, Eq. (1).

With a complete, but non-O.N. basis $\{|f_k\rangle\}$, Eqs. (1) and (4) no longer hold. We have the non-diagonal Δ:

$$\langle f_k|f_l\rangle = \Delta_{kl}. \tag{5}$$

The Δ is the metric tensor under $L(n)$ whose diagonal form is I, the latter acting as the metric for the Cartesian tensors under $O(n)$ (analogously $U(n)$ if field $= C$).

For arbitrary $S \in L(n)$, contravariant components $\{a^i\}$ are obtained from the covariant ones $\{a_i\}$ by

$$a^i = \Delta^{ij}a_j \tag{6a}$$

(repeated indices summation convention applies if one up, one down).

Only in O.N. frames

$$[a^i = \delta^{ij}a_j = \delta_{ij}a^j = a_i]_{0(n)}.$$

Generally with any non-O.N. or O.N. frame, we have

$$\Delta^{ij}\Delta_{jk} = \delta^i_k. \tag{6b}$$

Thus if $\Delta \equiv \{\Delta^{ij}\}$, then $(\Delta^{-1})^+ = \{\Delta_{ij}\}$ (where $(+)$ is adjoint").

General $L(n)$ tensor components are raised and lowered by Δ as in Eq. (6a) and

$$a_j = \Delta_{jk}a^k. \tag{6c}$$

4. The "Unity Trick" extended to non-O.N. frames

Eq. (1) becomes applicable to arbitrary $L(n)$ frames as the $L(n)$ invariant

$$I = |f^i\rangle\langle f_i| = |f_k\rangle\langle f^k|. \tag{7}$$

Thus, abstract objects can be described in any $L(n)$ frame using Eq. (7). E.g.

$$|\Psi\rangle = I|\Psi\rangle = |f^i\rangle\langle f_i|\Psi\rangle$$
$$|\Psi\rangle = |f^i\rangle c_i = |f_k\rangle c^k. \tag{8}$$

This form is the same in any O.N. or non-O.N. frame, showing also that indeed the abstract object $|\Psi\rangle$ is invariant regardless of the $L(n)$ frame used for its description.

Similarly for an abstract (hence $L(n)$ frame independent) operator like H,

$$H = IHI = |f_i\rangle\langle f^i|H|f^k\rangle\langle f_k|$$
$$H = H^{ik}|f_i\rangle\langle f_k| \tag{9}$$

or alternately

$$H = H_{ik}|f^i\rangle\langle f^k|$$

or

$$H^i_{\cdot k}|f_i\rangle\langle f^k|$$

yielding the contravariant $\{H^{ik}\}$, the covariant $\{H_{ik}\}$, or the mixed tensor $\{H^i_{\cdot k}\}$ forms of H.

5. Examples of $L(n)$-frame independent abstract operator relations and their invariant, covariant, and contravariant forms.

5.1. Effective one-electron energy eigenvectors for a molecule

The abstract form of the characteristic equation from which the MO energy levels $\{\lambda_i\}$ and the MO's $\{|\Psi_i\rangle\}$ (e.g. Hückel ones) [12] are obtained is

$$(h - \lambda I)|\Psi\rangle = 0. \tag{10}$$

This is the physical statement independent of any $L(n)$-frame.

Normally the one electron (e^-) Hilbert space is projected onto the "valency vector space" [5] of dim = [no. of atoms of each kind × no. of valence shell AO's of that atom]. We can therefore take the V_n to be the valency vector space now.

For an O.N. frame, e.g., the valency shell MO set, $\{|\Psi_i\rangle\}$, using $I = \sum_{i\geq 1}^{n} |\Psi_i\rangle\langle\Psi_i|$ on Eq. (10), (and in this case $|\Psi_i\rangle = |\Psi^i\rangle$), we get

$$|\Psi_i\rangle\langle\Psi_i|h|\Psi_j\rangle\langle\psi_j|\psi\rangle - \lambda|\Psi_i\rangle\langle\Psi_i|\Psi\rangle = 0. \tag{11a}$$

If $|\Psi\rangle$ is one of the eigenvectors $|\Psi_k\rangle$ with $\lambda = \lambda^{(k)}$ then

$$h_{ij}\delta_{jk} - \lambda^{(k)}\delta_{jk} = 0; \; h_{ik} = \lambda^{(k)}\delta_{ik} \tag{11b}$$

showing h_{ij} is diagonal in this frame.

For the non-O.N. valency AO's frame $\{|e_\mu\rangle\}$, we have $I = |e^\mu\rangle\langle e_\mu|$ and $|e^\mu\rangle = \Delta^{\mu\nu}e_\nu\rangle$. On Eq. (10), the I's give

$$|e^\mu\rangle\langle e_\mu|h|e_\nu\rangle\langle e^\nu|\Psi\rangle - \lambda|e^\mu\rangle\langle e_\mu|\Psi\rangle = 0 \tag{12a}$$

or since the basis vectors $|e^\mu\rangle$ are linearly independent $(|\Delta| \neq 0)$,

$$h_{\mu\nu}c^\nu - \lambda c_\mu = 0 \tag{12b}$$

where e.g. $c_\mu \equiv \langle e_\mu|\Psi\rangle$.

Eq (12b) is a *covariant form of Eq.* (10) *and will look the same in any $L(n)$-frame.*

If we identify $h_{\mu\nu}$, the covariant components of h in the non-O.N. AO frame with the AO-basis hamiltonian matrix h from which the usual $2D$ or $3D$ Hückel calculations are made ($h_{ii} \equiv \alpha_i$, $h_{ij} \equiv \beta_{ij} \equiv \beta_{ij}$) [11, 12, 21, 22], then c_μ are the usual LCAO MO (linear combinations of AO's MO) coefficients.

The explicit non-O.N. AO matrix form of Eq. (12b) is obtained for actual calculations by $c^{\nu\rho} = \Delta \; c_\rho$ where now $\{\Delta^{\nu\rho}\} \Rightarrow (\Delta^{-1})^+$

$$h\Delta^{-1}c - \lambda c = 0. \tag{12c}$$

If we interpret Eq. (12b) for the O.N., OAO-frame, $\Delta_{\mu\nu} = \delta_{\mu\nu} = \delta^{\mu\nu} = \delta^\mu_\nu$, then we get the explicit matrix form

$$h'c' - \lambda c' = 0 \tag{13}$$

where now the elements of h' are calculated with the OAO's and the c' are the LCOAO MO coefficients. Eq. (13) formally *looks like* the conventional $2D$ Hückel method [12] where the overlaps were neglected (cf. also. [9]).

One may note that h (non-O.N. AO basis), and the h' (O.N. OAO's) by itself, do not have the same eigenvalues. The h and h' are related by

$$h'_{\mu\nu} = S^{\cdot\rho}_\mu h_{\rho\tau} S^\tau_{\cdot\nu} \tag{14a}$$

where $S \in L(n)$ is a non-unitary transformation. (From Eq. (7), $\dot{S}^\rho_\mu = \langle f_\mu | e^\rho \rangle$ where $f \equiv$ OAO and $e \equiv$ AO).

While unitary or orthogonal transformations of the basis frames preserve the eigenvalues of h, the non-unitary ones out of the general $L(n)$ do not. The "energy level pattern indices" ("LPI") of h are *however preserved*. The LPI are the three numbers $\{n_0, n_+, n_-\}$ where $n_0 =$ no. of zero eigenvalues (e.v.), and n_+ and n_- the nos. of positive and negative eigenvalues of h relative to the reference zero of energy chosen for h and λ initially. *The LPI therefore are the more fundamental electronic invariants of a molecule as indicated by the above principle of linear covariance.*

The actual energy eigenvalues are given not by h (AO basis) by itself (compare Eq. (12c)), but by h' (OAO basis) since the OAO-frame and the MO-frame are related by a unitary (or orthogonal) transformation (but not the $\{AO\} \to \{MO\}$).

5.2. Total electronic (2D or 3D Hückel) energy of a molecule (or cluster) and the electron density

The sum of the occupied MO orbital energies (which in the $2D$ or $3D$ Hückel method is taken as the total electronic energy) [23] is

$$E_{(HMO)} = \text{Tr } \rho h \tag{15}$$

with ρ the one electron density operator [1]. This abstract form and of course the value of E are $L(n)$-frame invariant.

Specializing to the O.N. MO-frame with $I = \sum_i |\Psi_i\rangle\langle\Psi_i|$ on the valency vector space V_n,

$$E_{(HMO)} = \rho_{ij} h^{ji} = \rho_{ij} h_{ji(MO\,frame)}. \tag{16a}$$

By Eq. (11b) and from [1] $\rho = \sum_i^n \rho^{(i)} |\psi_i\rangle\langle\psi_i|$ with $\rho^{(i)} \in \{0, 1, 2\}$, the number of electrons occupying the MO, (i),

$$E_{(HMO)} = \sum_{i \geq 1}^n \rho^{(i)} \lambda^{(i)}. \tag{16b}$$

The expressions for E and ρ in other frames (non-O.N. AO, O.N. OAO, O.N. LO, non-O.N. LO, *etc.*) have been derived in the past, each time as a special formalism, having been especially cumbersome with inclusion of overlaps (non-O.N. AO's) [11, 22] The principle of linear covariance gives an immediate derivation of all these versions.

Using $I = |e^{\mu}\rangle\langle e_{\mu}|$ for any arbitrary, general $L(n)$-frame in Eq. (15) one gets the frame-invariant

$$E_{(HMO)} = \mathrm{Tr}|e^{\mu}\rangle\langle e_{\mu}|\rho|e_{\nu}\rangle\langle e^{\nu}|h|e^{\tau}\rangle\langle e_{\tau}| = \rho_{\mu\nu}h^{\nu\tau}\delta^{\mu}_{\tau} \tag{17a}$$

(used $\mathrm{Tr}|\rangle\langle| = \langle|\rangle$), or

$$E_{(HMO)} = \rho_{\mu\nu}h^{\nu\mu} = \rho^{\mu\nu}h_{\nu\mu} = \rho^{\mu}_{.\nu}h^{\nu}_{.\mu}. \tag{17b}$$

This same $L(n)$ invariant or covariant form can now be interpreted for the different bases: *i*) The MO frame recovers Eq. (16b), *ii*) for the O.N. OAO basis, $\{h_{\nu\mu}\} \Rightarrow h$ in the α, β-semi-empirical Hückel form with the overlaps formally ignored but now implicit in the values of the matrix elements. The $\rho^{\mu\nu}(OAO) = \rho_{\mu\nu}(OAO)$, and $\rho_{\mu\nu}(OAO) = P_{\mu\nu} =$ the usual "charge-bond order matrix" of MO-theory [11] (*cf.* also below); *iii*) for the non-O.N. AO basis, $E_{(HMO)} = (\rho^{\mu\nu}h_{\nu\mu})_{AO}$ with

$$\{h_{\nu\mu}\} \to \{h\}_{AO} = (\alpha, \beta\text{-matrix but different } values \text{ of the elements than with} \\ OAO's),$$

and

$$\rho^{\mu\nu} = \Delta^{\mu\tau}\rho_{\tau\sigma}\Delta^{\sigma\nu})(\text{non. O.N. AO's}). \tag{18}$$

The $\rho^{(AO)}_{\tau\sigma}$ still looks like the "charge-bond order matrix" $P_{\tau\sigma}$ but the values of its elements are not the same as the (OAO)-one. Only $\rho^{\mu\nu}$, Eq. (18) with the Δ's in it would give the correct $E_{(HMO)}$ in $\rho^{\mu\nu}h_{\nu\mu}(AO)$, not $\rho_{\mu\nu}h_{\nu\mu}(AO)$.

The covariant formulation also gives the explicit expressions for the actual calculation of charge-bond order matrix elements in each frame as shown below.

Let $S \in L(n)$ be the transform from the MO-frame $\{|\psi_i\rangle\}$ to the OAO-frame $\{|e_{\mu}\rangle\}$. The S defined by

$$|e_{\mu}\rangle = S^{.i}_{\mu}|\psi_i\rangle \tag{19a}$$

is obtained from $|e_{\mu}\rangle = I|e_{\mu}\rangle = |\psi_i\rangle\langle\psi^i|e_{\mu}\rangle$, as

$$S^{.i}_{\mu} = \langle\psi^i|e_{\mu}\rangle. \tag{19b}$$

Similarly $|\psi_k\rangle = |e_{\mu}\rangle S^{\mu}_{.k}$, and

$$S^{\mu}_{.k} = \langle e^{\mu}|\psi_k\rangle \tag{20a}$$

but there are the LC OAO MO coefficients,

$$\langle e^{\mu}|\psi_k\rangle = c^{\mu}_{.k}. \tag{20b}$$

Since S is from O.N. to O.N. (and often involving only the real field),

$$S \in O(n) \subset U(n) \subset L(n). \tag{21}$$

Now we transform the density ρ from the MO frame where it is known (Eq. (16)) to the new OAO frame using S.

$$S : \{\rho_{ij}\}_{(MO)} \rightarrow \{\rho_{\mu\nu}\}_{(OAO)}$$

$$\rho_{\mu\nu} = S_{\mu}^{\cdot i} \rho_{ij} S_{\cdot\nu}^{j}. \tag{22a}$$

Being

$$O.N. \rightarrow (O.N.)', \ S_{\mu}^{\cdot i} = S_{\cdot i}^{\mu}. \tag{22b}$$

Hence,

$$\rho_{\mu\nu}(OAO) = c_{\mu i} \rho_{ij} c_{j\nu}. \tag{23a}$$

The (OAO) charge-bond order matrix $\{P_{\mu\nu}\} \equiv \boldsymbol{P}$ explicitly results (using also Eq. 16b):

$$P_{\mu\nu}^{(OAO)} = \sum_{i,j \geq 1}^{n} (\rho^{(i)} \delta_{ij}) c_{\mu i} c_{\nu j}^{+}$$

$$\tag{23b}$$

$$P_{\mu\nu}^{(OAO)} = \sum_{i \geq 1}^{n} \rho^{(i)} c_{\mu i} c_{\nu i}^{+}$$

the customary expression [11] for $\boldsymbol{P}$ with AO overlaps ignored, or better yet with AO's interpreted as OAO's.

The covariance principle yields also the non-O.N. AO basis $\{|f_{\mu}\rangle\}$ form of ρ just as well. Eq. (22a) looks the same, but (22b) is no longer true.

$$\rho_{\mu\nu}' \qquad = S_{\mu}^{\prime \cdot i} \rho_{ij} S_{\cdot\nu}^{\prime j}$$

$$\tag{24a}$$

$$AO_{(Non-O.N.)} \qquad (MO)$$

$$S_{\mu}^{\prime \cdot i} = \langle f_{\mu} | \Psi^{i} \rangle \equiv c_{\mu}^{\prime \cdot i} \neq c_{\cdot i}^{\prime \mu} \tag{24b}$$

where only the latter, $c_{\cdot i}^{\prime \mu}$ are the standard LCAO MO coefficients.

But

$$c_{\mu}^{\prime \cdot i} = \Delta_{\mu\tau} c_{\cdot i}^{\prime \tau} = \Delta_{\mu\tau} c_{\cdot k}^{\prime \tau} \Delta^{ki} = \Delta_{\mu\tau} c_{\cdot k}^{\prime \tau} \delta^{ki} = \Delta_{\mu\tau} c_{\cdot i}^{\prime \tau} \tag{25}$$

with $\{\Delta_{\mu\tau}\} \Rightarrow \Delta$, the std AO overlap matrix. Therefore from Eqs. (25) and (24a) we obtain

$$P_{\mu\nu}' \qquad = \Delta_{\mu\tau} \underbrace{\left(\sum_{i \geq 1}^{n} \rho^{(i)} c^{\tau i} c^{+\gamma i} \right)}_{\equiv \boldsymbol{P}^{0}} \Delta_{\gamma\nu}$$

$$(AO\text{-frame}; \text{non-O.N.})$$

$$\{\boldsymbol{P}_{\mu\nu}'\} = \Delta \boldsymbol{P}^{0} \Delta. \tag{26}$$

The one-electron density matrix ("charge-bond order") is calculated, by first calculating the $\boldsymbol{P}^{0}$ in terms of the LCAO MO coefficients *as if* the AO overlaps were neglected. Then Eq. (26) using the overlap matrix converts $\boldsymbol{P}^{0}$ into the proper one $\boldsymbol{P}'$ for the non-O.N. AO's.

Such derivations which otherwise are cumbersone in quantum chemistry thus readily follow from the covariance principle.

Other examples and applications (e.g. in the many-electron theory great ease is afforded by the covariance principle) [23] for a fixed molecular geometry, as well as in relating different molecules, geometries and symmetries to each other [5] will also be reported.

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