A Principal of Linear Covariance for Quantum Mechanics and Its Consequences Taking one Beyond Symmetry *

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A Principle of Linear Covariance is stated which follows from the "superposition principle" of quantum mechanics. Accordingly, quantum mechanical equations should be written in linearly covariant form which makes them look the same under non-unitary as well as unitary transformations. The principle leads to a non-unitary classification of all molecules (and clusters and solids) into distinct equivalence classes giving hitherto unknown relations between isomeric molecules. One also gets kinetic and thermic selection rules for chemical reactions. All these are independent of, and far more general than any unitary or point group symmetrics. The invariants found for each class of molecules or clusters allow qualitative electronic deductions and are more generally applicable than symmetry based quantum numbers.

We state below a *principle of linear covariance* which follows from a most fundamental aspect of quantum mechanics, Q.M., that of the "superposition principle" [1]. The notion's below take one beyond the use of compact groups, e.g. in atomic physics, and way beyond point group symmetries for molecules (and clusters and solids). It leads, e.g., to a non-unitary classification of molecular electronic hamiltonians, thereby of molecules, showing seemingly different molecules to be transforms of one another in hidden abstract spaces. Thus one gets general and topological selection rules, both kinetic and thermic, for chemical reactions. The principle also allows, by covariant formulations, derivations of diverse approaches (such as valence-bond, molecular orbital, and localized orbital methods) with non-orthogonal (non-O.N.) as well as O.N. basis sets from the same covariant equations, some applications being also in the theory of finite many-particle systems. Some of these results are reported in a number of papers [2–6]. Before summarizing the principle of linear covariance below, I wish to congratulate George Sudarshan on the occasion of this symposium and to express my heartfelt thanks for the encouragement and stimulation [7] he provided me during my work in high-energy physics and non-compact groups [8], which opened up many horizons in other fields [9, 10] as well.

"Superposition principle" being at its foundation, quantum mechanical machinery is built on abstract linear algebra and linear operators. Q.M. procedures involve, in one form or another, transformations from one complete basis set to another in the Hilbert space. Real eigenvalues dictate for observables Hermitian operators whose eigenvectors form complete and *orthonormal* (O.N.) basis sets. The O.N. nature of bases is preserved under unitary transformations which also leave expectation values unchanged. This is one reason why O.N. bases have been focused on in most of the Q.M. of physics and chemistry, another reason being convenience in computations.

All such (O.N.) to (O.N.) transformations on a countably infinite dim. vector space $V_n (n \to \infty)$ constitute the unitary group $U(n)$. However, this is not the largest group implied by the "superposition principle". The group is that of *all* non-singular ($\det \neq 0$) transformations on *non-O.N.* as well as O.N. bases for V_n, i.e. GL (n, C) over the complex field C (or in many applications just over the real field R, thus $L(n, R)$). The emphasis on group theory, rather than topology, has led to the overlooking of major consequences and applications the other, i.e. non-unitary transformations, can lead to.

We state now the "principle of linear covariance" in three parts:

1) The abstract kets, bras, operators, and their relationships should be viewed as *invariants* under any transformations S non-O.N. as well as O.N. of bases ("coordinate frames") with $S \in L(n)$ and $|S| \neq 0$.

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2) In component from, any Q.M. equation should be in a linearly covariant ("*L-covariant*") form.

3) Regardless of which complete basis set is used, a Q.M. equation written in component, i.e. tensorial form should *look the same.*

Q.M. quantities are tensors of $L(n)$ with the metric tensor

$$\Delta_{kl} = \langle f_k | f_l \rangle \,, \tag{1}$$

where $\{|f_k\rangle\}$ are a complete in general non-O.N. basis set in V_n. The diagonal form of Δ_{kl} is δ_{kl} as $\Delta \to I$ the unity.

For arbitrary $S \in L(n)$, indices are raised by

$$a^i = \Delta^{ij} a_j \,. \tag{2}$$

Further

$$\Delta^{ij} \Delta_{jk} = \delta^i_k \,. \tag{3}$$

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

Thus e.g. the abstract (and L-invariant) equation for the eigenvalues λ of a one-electron model Hamiltonian h for a molecule, cluster, or solid,

$$(h - \lambda I) | \Psi \rangle = 0 \tag{4}$$

becomes e.g.

$$h_{\mu\nu} c^\nu - \lambda c_\mu = 0 \tag{5}$$

in L-covariant, component form.

Now, as one shifts to different non-O.N. frames the eigenvalues of $h_{\mu\nu}$ (or h^μ_ν or $h^{\mu\nu}$) will change with these **h** treated simply as matrices, although the eigenvalues of all abstract hence invariant h itself in (4) do not change. All matrices for the same abstract h, related to each other by

$$S\colon \; \{h_{\mu\nu}\} \longrightarrow \{h_{\mu'\nu'}\} \quad \textit{with } S \in L(n) \,, \tag{6}$$

stay on the same orbit and in one and only one equivalence class.

Isomeric molecules, or isomeric molecular assemblies, have also different $\{h_{\mu\nu}\}$'s and eigenvalues, different for another reason. They have different geometries in the 3-dim E_3, hence different Hilbert spaces, disjoint from those of other molecules. However, it has been possible to map all such spaces onto a "standardized" $\langle\!\langle V_n \rangle\!\rangle$ which contains now in it a number of distinct L-equivalence classes. Those moleules, that end up in the same class, are L-transforms of each other, a hitherto hidden relation between them.

In this way, the L-covariance leads to a "non-unitary classification" of molecular electronic structures once the *distinct* Hilbert space of each is mapped onto the said "standardized" vector space $\langle\!\langle V_n \rangle\!\rangle$, E_3-geometry independent, as are the distinct h's mapped onto a std dyad space $\langle\!\langle V_n \times V_n^+ \rangle\!\rangle$.

As isomeric sets of molecules react, rearrange into other molecules etc. in the 3-dim. Euclidean space E_3, their h's may remain within the same L-equivalence class in which case the molecules are said to be "structurally covariant" [5a], or with continuous geometry changes "deformationally covariant" [5b]. Then the reactions are "allowed". If the L-class changes, the reactions will have large energy changes and not be "allowed" (thus general reaction "selection rules" but *not* based on symmetry groups). As a bonus one finds that the fundamental invariants characterizing an L-class, and which remain unchanged during molecular changes of the "allowed" kind, are nothing but the energy level pattern indices, $n_+ =$ no. of "bonding molecular orbitals, MO's", $n =$ no. of antibonding, and $n_0 =$ no. on non-bonding MO's. These three numbers, along with their electron occupation numbers resulting from the Pauli Principle, allow one to deduce much of qualitative chemistry easily, especially since the L-transforms have been turned into pictorial rules for the manipulation of molecular structure type pictures/graphs right on the blackboard [6]. The L-invariants are more fundamental than quantum numbers, e.g. those arising from point group symmetries, as the former give more electronic information even where there is no symmetry.

It is intriguing how much qualitative chemistry can be deduced directly from Q.M. with the above principles and just looking at the periodic table. Perhaps Dirac would have liked this, who after all expected all chemistry to come out of Q.M., an expectation that had been recently chilled by the remarks of the renowned organic chemist Lord Todd who said "Q.M. has done little for the advancement of organic chemistry which has developed mainly from the idea of a tetrahedral carbon atom".

For a detailed understanding of the developments above we refer the reader to the more extensive papers [2–6, 11].

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