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Structural Equivalence in Molecules

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Localised and delocalised descriptions of molecular electronic structure may be shown to be entirely equivalent when the total wave function is expressed as a Slater determinant of one-electron wave functions [1], but the two descriptions appear to carry different implications concerning the equivalence of the valence electrons, as for example in methane [2], or ammonia [3], or water [3]. Consequently, it is necessary to define more closely the meaning of the term 'equivalence' in this context: two types of equivalence may be distinguished.

Permutational Equivalence

If any set of *m* objects within a molecule (atoms, orbitals, vectors, *etc.*) can be permuted amongst themselves by the symmetry elements of the molecule to form a single cycle of length *m* they are permutationally equivalent. The maximum cycle length in a finite point group is equal to the order of the group: in the linear point groups, the maxima cycle length is 1 for $C_{\infty v}$, and 2 for $D_{\infty h}$ (see Table I). Examples involving a high number of permutationally equivalent bonds to a common atom are found in $M(BH_4)_4$ (M = Zr, Hf), and the ions $M(NO_3)_6^{-2}$ (M = Ce, Th). In $M(BH_4)_4$, the metal forms twelve permutationally equivalent bonds to the hydrogen atoms of the triply chelating BH_4^- ligands; the overall symmetry is T for Zr [4] and T_d for Hf [5]. In $M(NO_3)_6^{-2}$, there are twelve permutationally equivalent M–O bonds, the overall symmetry being T_h [6–8]. In $(C_8H_8)_2M$ (M = Th, Pa, U, Np, Pu) of D_{8h} symmetry there are sixteen permutationally identical M–C distances [9], as there are also in $(C_8H_8)_2Ce^-$ of D_{8d} symmetry [10]. Perhaps the largest number of permutationally equivalent bonds in a rigid finite species, although not involving a common atom, is the 30 B–B distances in the icosahedral ion $B_{12}H_{12}^{-2}$ [11].

Representational Equivalence

If any set of objects, in symmetry adapted linear combinations, form a basis for an irreducible representation of the point group in question, they are representationally equivalent objects is equal to the dimension ($X_i(E)$) of the highest-dimensional symmetry class *i* of the group, or exceptionally, to *r* times this dimension if this symmetry class occurs *r* times in the reducible representation. Values of these maximum dimensions are given in the Table.

TABLE I. Structural Equivalence in Point Groups.

Group	Maximum permutational equivalence	Maximum representational equivalence
C_1	1	1
C_i, C_s, C_2	2	1
C_{2v}, C_{2h}, D_2	4	1
D_{2h}	8	1
S_n, C_n (n > 2)	n	2
C_{2v}, C_{nh}, D_n (n > 2)	2n	2
D_{nh} (n > 2), D_{nd}	4n	2
T	12	3
T_d, T_h, O	24	3
O_h	48	3
I	60	5
I_h	120	5
$C_{\infty v}$	1	2
$D_{\infty h}$	2	2

It follows therefore that for the finite groups, with the sole exception of C_1, the number of permutationally equivalent objects can always exceed the maximum number for representational equivalence, so that while a set of hybrid orbitals may be permutationally equivalent in a given point group they will generally not be representationally equivalent, and will transform as a sum of several irreducible representations.

The significance of representational equivalence becomes obvious when molecular integrals of type $\langle\phi_i|\chi|\phi_j\rangle$ are considered. Such integrals are identically zero if ϕ_i and ϕ_j belong to different symmetry classes, and if ϕ_i, ϕ_j belong to one symmetry class and ϕ_k and ϕ_l to another, only by remote chance will $\langle\phi_i|\chi|\phi_j\rangle$ and $\langle\phi_k|\chi|\phi_l\rangle$ have identical non-zero values: hence molecular orbitals of different symmetry types between a common pair of atoms almost invariably have different energies, as conclusively shown experimentally by photoelectron spectroscopy. In particular the four permutationally equivalent sp^3 hybrids in T_d give rise to two distinct sets of energy levels a_1 and t_2, the three permutationally equivalent sp^2 hybrids in D_{3h} give rise to energy levels $a_1' + e'$, and even the two permutationally equivalent sp hybrids in $D_{\infty h}$ give rise to two distinct energy levels Σ_g^+ and Σ_u^+: nor can four dsp^2 hybrids in D_{4h} or six d^2sp^3 hybrids in O_h give rise to single energy levels. No matter how many distinct electronic energy levels are generated in a particular point group by a set of hybrid orbitals, there is no question that the *bonds* concerned are all of the same length, dissociation energy, *etc.*, for it is the permutational equivalence of the bonds which initially defines the point group within which the hybrids are constructed.

A hybridisation scheme which uses *n* different types (defined by the *l* quantum number) of atomic orbital will rise to at least *n* distinct energy levels for bonding electrons: only simple atomic orbitals of definite quantum number *l* can give non-accidentally degenerate energies. If proper symmetry adapted combinations are made of the hybrid orbitals on an atom, as they always should be when the basis orbitals span several symmetry classes, the resultant symmetry adapted orbitals are simply the atomic orbitals back again.

The foregoing discussion in terms of molecular point groups applies to atoms in molecules, and it is interesting to consider the problem of hybrid equivalence without the symmetry constraints applied by the presence of peripheral atoms, such as in CH_4. For the corresponding isolated atom or ion, C^{-4} or Ne, having both the rotation and inversion symmetry of a sphere, the appropriate point group is $R^{\pm}(3)$ [12]. The angular parts Y of the wave functions of the hydrogenic atom

$$\psi = R_{n,l}(r)Y_{l,m}(\theta,\phi)$$

transform for each value of the quantum number *l*, as the representations $D^{(l)}$ of the group $R^{\pm}(3)$: each representation $D^{(l)}$ is of dimension $(2l + 1)$, so that even in the isolated atom no set of, say, 2 or 4 or 6 permutationally equivalent hybrid orbitals can be representationally equivalent: such equivalence is restricted to functions having a common value of *l*, *i.e.* pure atomic orbitals: all atomic spectra have been interpreted on this basis [13], and the photoelectron spectra of atoms also confirm this restriction [14].

The correspondance of the angular functions $Y(\theta,\phi)$ with the $D^{(l)}$ of dimension $(2l + 1)$ is a consequence of building spherical symmetry into the hydrogenic atom solution of Schrödinger equation

$$\Delta^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

by writing $V = -Ze^2/r$: assuming that the permittivity of the neighbouring space is isotropic, this central potential imposes $R^{\pm}(3)$ symmetry on the solutions to the equation. If the permittivity were anisotropic, then the symmetry imposed on the solutions would be lowered to $D_{\infty h}(\epsilon_x \equiv \epsilon_y \not\equiv \epsilon_z)$ or D_{2h} $(\epsilon_x \not\equiv \epsilon_y \not\equiv \epsilon_z)$. Once the spherically symmetric potential has been introduced, all the solutions of this wave equation must conform to $R^{\pm}(3)$. Most of the properties of the angular functions $Y(\theta,\phi)$ are contained implicitly in the character table for $R^{\pm}(3)$, which can be worked out without any reference to any aspect of quantum mechanics. Consequently using only this character table and straightforward descent of symmetry techniques, all the angular properties of the $Y(\theta,\phi)$ functions can be obtained without the need to solve the wave equation. When applying the transformations of molecular point groups to atomic orbitals, one is not applying symmetry to quantum mechanical functions previously innocent of symmetry but merely lowering the symmetry from $R^{\pm}(3)$ to that of some other group, by the usual methods for descent of symmetry, since all molecular point groups are sub-groups of $R^{\pm}(3)$.

The interchangeability of the localised and delocalised descriptions, at the level of the Slater determinant, will always occur, regardless of what basis orbitals are chosen: only subsequently, when the integrals $\langle\phi_i|H|\phi_j\rangle$ are evaluated does the symmetry impose itself, and it does so *via* the symmetry intrinsic to the angular parts $Y(\theta,\phi)$ of the basis atomic orbitals. The properties of the $Y(\theta,\phi)$ functions in the context of the point group for a particular molecule are sufficient to block-diagonalise the energy matrix, with separate blocks for each symmetry class. Regardless of what scheme of hybridisation is imposed on a molecular system, its electronic energy levels are determined by the values of the quantum number *l* of the atomic orbitals used by the central atom, and for each value of l, by the way in which the $(2l + 1)$-fold degeneracy in $R^{\pm}(3)$ correlates with the point group in question.

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