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Molecular Shapes and the Pauli Force. An Outdated Fiction

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Abstract: Molecular-orbital calculations neglecting interelectronic Coulomb repulsions in the water molecule show that its shape is not determined by the Pauli exclusion principle. The water molecule is also used to test a recent definition of the Pauli force as the change in interatomic Coulomb force that results from orbital orthogonalization. Theoretical arguments are given against the dependence of the molecular shape on this electrostatic Pauli force, and the possibility of empirical correlation of the two is ruled out by calculation of discrepant indices of the Pauli force. The insufficiency of the Pauli principle to explain molecular shapes is further demonstrated by showing that Slater determinations of atomic orbitals are incapable of discriminating between observed and unobserved molecular shapes. The Pauli force appears to be a useless and even misleading fiction.

The "Pauli force" is a fictitious force invented to help a person to visualize the effect of the antisymmetry requirement of the Pauli exclusion principle on the spatial distribution of electrons.[1] In support of the fiction that the Pauli force keeps electrons of like spin separated in space, the wave function does vanish whenever two such electrons are assigned the same coordinates. Recent evidence, however, indicates that an electron's exclusive domain or "Fermi hole" is quite local[2] and generally does not have the expected effect either on the average interelectronic distance[3] or on the energy of repulsion[4] when states of different multiplicity are compared. The familiar explanation[1,5] of Hund's rule has been shown to be incorrect,[4] leaving no doubt that the concept of the Pauli force can be completely misleading. The time has come to investigate the validity of other applications of the Pauli force, and to reevaluate its usefulness as a fiction.

In this paper, we show that the Pauli force does not provide a valid explanation for molecular shapes, nor does the Pauli principle itself provide one. Using the water molecule as our test case, we first consider the Pauli force in the absence of the Coulomb force, and we then investigate the Pauli force defined as part of the Coulomb force. We conclude with some observations on Slater determinants of atomic orbitals.

The Pauli Force without the Coulomb Force. As justification for this section, we point out that the currently popular valence-shell electron-pair repulsion theory (VSEPR) assumes the existence of a Pauli force that has its own force law,[6a] that is more important than the Coulomb force in determining molecular shapes,[6b] and that can be used to deduce molecular shapes even when the Coulomb force is neglected.[6c] Other authors have also drawn a distinction between the Pauli force and the Coulomb force.[7] We have found that when the Coulomb force between electrons is neglected, molecular-orbital theory predicts a linear structure for the water molecule. Aside from the neglect of interelectronic Coulomb repulsions, we followed the procedure of Roothaan,[8] where each molecular orbital (MO) is written as a linear combination of atomic orbitals (LCAO). Our AO's were hydrogenic orbitals, with $Z = 8$ for oxygen. The O–H bond length was fixed at 1.8111 au[9] (1 au = 0.05292 nm), and calculations were made for bond angles of 90, 135, and 180°. The total energies obtained at these angles are −130.070, −130.161, and −130.184 hartrees, respectively. Of course, the MO's actually pertain to the H_2O^{9+} ion rather than H_2O, and will not be given here.[10]

The incorrect prediction of a linear structure for water is proof that molecular shapes generally cannot be explained without the Coulomb force between electrons, as has been suggested.[6c,7a] Furthermore, the differences in the total energies at the three angles were determined almost entirely by the differences in the Coulomb repulsion between the hydrogen nuclei.[11] No preference for any bond angle was attributable to the Pauli force or even to the Pauli principle, which was equally satisfied by the molecular wave functions at all three angles.

Since the Pauli force is completely ineffective in the absence of the Coulomb force, the only possible way for the Pauli principle to affect molecular shapes would be through the Coulomb force. This possibility is considered in the next section.

The Pauli Force as Part of the Coulomb Force. As shown by Salem,[12] the change in electron density, $\Delta\rho_{ab}$, that occurs when two filled nonorthogonal orbitals, ϕ_a and ϕ_b, are orthogonalized is

$$\Delta\rho_{ab} = -4S_{ab}\phi_a\phi_b + 2S_{ab}^2(\phi_a^2 + \phi_b^2) \qquad (1)$$

where S_{ab} is the overlap integral between ϕ_a and ϕ_b. Since the orthogonalized orbitals satisfy the Pauli principle, Bader and Preston[13] interpreted $\Delta\rho$ as the effect of the Pauli principle on the electron density. They defined "Pauli repulsions" as the changes in the Coulomb repulsions on the nuclei brought about by $\Delta\rho$. They concluded that the Pauli repulsions in water and ammonia were in the wrong direction to account for the observed deformations from tetrahedral symmetry. However, the Pauli repulsions due to $\Delta\rho$ represent only small changes in the Coulomb repulsions due to the complete electron density ρ. Any instability of the orthogonalized structure, and hence the form of any distortion, depends on ρ(orthogonalized), not on $\Delta\rho$. Furthermore, the Pauli principle itself does not require *any* distortion, for no distortion can improve on the perfect compliance to that principle already present in the orthogonalized structure. Therefore, the observed shape of a molecule is no more dependent on the Pauli force in connection with the Coulomb force than it is on the Pauli force without the Coulomb force. As we shall see, these electrostatic Pauli repulsions are also strongly dependent on a necessarily arbitrary choice of nonorthogonal orbitals.

We disagree with the proposed rule[13] that "one must start with an orbital set which is orthogonal because of some restraint" in order to determine the effect of the Pauli principle on the electron density. One may be guided in his choice of nonorthogonal orbitals by some orthogonal set, but the choice remains quite arbitrary. This point was evidenced when the same set of orbitals was chosen for the water molecule using either neon or methane as a reference.[13] We shall refer to that set of orbitals, viz., two nonorthogonal bonding orbitals and two orthogonal lone pairs, as set I. An alternative approach using methane as the reference is simply to drop the contributions of two of the hydrogen AO's and then renormalize, using orbital exponents for oxygen instead of carbon. The resulting orbitals, set II, then consist of two orthogonal bonding orbitals and two nonorthogonal lone pairs. This set contradicts the generalization[13] that lone pair orbitals centered on the same nucleus "will always be orthogonal by definition". The orbitals used in the present study are listed in Table I.

With more than two doubly occupied orbitals, the total change in electron density is given approximately by:[12]

$$\Delta\rho = \sum_{i<j} \Delta\rho_{ij} \tag{2}$$

Instead of plotting $\Delta\rho$ for sets I and II, we chose to compare values of Δq_{ab}, the increase in electronic charge in a region between the orbitals ϕ_{a} and ϕ_{b}. Within the accuracy of eq 2, we define

$$\Delta q_{\mathrm{ab}} = \sum_{i<j} \int_{R_{\mathrm{ab}}} \Delta\rho_{ij} \mathrm{d}\tau \tag{3}$$

where R_{ab} is a suitably chosen region between the major lobes of ϕ_{a} and ϕ_{b}. Two basic regions were selected for this report; both were square-based pyramids 1.60 au tall constructed of cubes 0.20 au on an edge. The angle at the (idealized) apex was 53° for one pyramid and 90° for the other. The (idealized) apex of either pyramid was located at the oxygen nucleus, with opposite sides of the pyramid facing the main lobes of the orbitals ϕ_{a} and ϕ_{b}. Wedge-shaped regions were also used, as well as a taller 53° pyramid, with results similar to those reported here.

The integrals in eq 3 were evaluated by numerical integration, using 204 points in each 53° pyramid and 680 points in each 90° pyramid. Except when nullified by orthogonality, the integral of each $\Delta\rho_{\mathrm{ab}}$ was largest (in absolute value) over R_{ab}, where it was the dominant term in Δq_{ab}. These integrals of $\Delta\rho_{\mathrm{ab}}$ and Δq_{ab} are both changes in the charge of R_{ab}, but the former results from orthogonalization of only ϕ_{a} and ϕ_{b}, and the latter from orthogonalization of all pairs of orbitals. Whether the $\Delta\rho_{\mathrm{ab}}$ integral or Δq_{ab} should be used to seek correlation with the hypothetical Pauli force of VSEPR[6] is an open question. The $\Delta\rho_{\mathrm{ab}}$ integral depends only on ϕ_{a} and ϕ_{b}, as the Pauli force is supposed to do, but Δq_{ab} has the advantage of being the total change in the charge of R_{ab}. Therefore, let us consider both possibilities, and examine the $\Delta\rho_{\mathrm{ab}}$ integrals in Table II and the Δq_{ab} values in Table III.

Table I. Orbitals Used in this Study[a]

Set I. Nonorthogonal Bonding Orbitals

$$\phi_{\mathrm{b}_1} = 0.5669(\frac{1}{2}\mathrm{s} + \frac{\sqrt{2}}{2}\mathrm{p}_x + \frac{1}{2}\mathrm{p}_z + \mathrm{h}_1)$$

$$\phi_{\mathrm{b}_2} = 0.5669(\frac{1}{2}\mathrm{s} - \frac{\sqrt{2}}{2}\mathrm{p}_x + \frac{1}{2}\mathrm{p}_z + \mathrm{h}_2)$$

$$\phi_{\mathrm{l}_1} = \frac{1}{2}\mathrm{s} + \frac{\sqrt{2}}{2}\mathrm{p}_y - \frac{1}{2}\mathrm{p}_z$$

$$\phi_{\mathrm{l}_2} = \frac{1}{2}\mathrm{s} - \frac{\sqrt{2}}{2}\mathrm{p}_y - \frac{1}{2}\mathrm{p}_z$$

Set II. Nonorthogonal Lone Pairs

$$\phi_{\mathrm{b}_1}' = 1.0177\phi_{\mathrm{b}_1} - 0.1100\phi_{\mathrm{b}_2}$$

$$\phi_{\mathrm{b}_2}' = -0.1100\phi_{\mathrm{b}_1} + 1.0177\phi_{\mathrm{b}_2}$$

$$\phi_{\mathrm{l}_1}' = 0.9942\phi_{\mathrm{l}_1} - 0.1075\phi_{\mathrm{l}_2}$$

$$\phi_{\mathrm{l}_2}' = -0.1075\phi_{\mathrm{l}_1} + 0.9942\phi_{\mathrm{l}_2}$$

[a] The hydrogen 1s orbitals, h_1 and h_2, and the oxygen 2s and 2p orbitals are all Slater functions. The O–H bonds of length 1.8111 au[9] were assigned the tetrahedral angle 109.47°.

Table II. Integrals of $\Delta\rho_{\mathrm{ab}}$ Over R_{ab} (units of e)

Orbital set	Angle of R_{ab}, deg	$\Delta\rho_{\mathrm{b_1b_2}}$	$\Delta\rho_{\mathrm{b_1l_1}}$	$\Delta\rho_{\mathrm{l_1l_2}}$
I	53	−0.037	−0.021	0.000
I	90	−0.079	−0.046	0.000
II	53	0.000	−0.018	+0.065
II	90	0.000	−0.039	+0.143

Table III. Values of Δq_{ab} (units of e)

Orbital set	Angle of R_{ab}, deg	$\Delta q_{\mathrm{b_1b_2}}$	$\Delta q_{\mathrm{b_1l_1}}$	$\Delta q_{\mathrm{l_1l_2}}$
I	53	−0.009	−0.002	+0.013
I	90	−0.018	−0.002	+0.028
II	53	+0.019	−0.023	+0.072
II	90	+0.025	−0.045	+0.153

If we let the integrand stand for the absolute value of its integral, Table II for set I shows $\Delta\rho_{\mathrm{b_1b_2}} > \Delta\rho_{\mathrm{b_1l_1}} > \Delta\rho_{\mathrm{l_1l_2}} = 0$, confirming the order found by Bader and Preston.[13] This order is just the opposite of that proposed in VSEPR.[6] The order for set II is $\Delta\rho_{\mathrm{l_1l_2}} > \Delta\rho_{\mathrm{b_1l_1}} > \Delta\rho_{\mathrm{b_1b_2}} = 0$, but this order is no support to VSEPR, resting as it does on an arbitrary choice of orbitals. A third set, $\phi_{\mathrm{b_1}}$ and $\phi_{\mathrm{b_2}}$ from set I plus $\phi_{\mathrm{l_1}}'$ and $\phi_{\mathrm{l_2}}'$ from set II, would give $\Delta\rho_{\mathrm{l_1l_2}} > \Delta\rho_{\mathrm{b_1b_2}} > \Delta\rho_{\mathrm{b_1l_1}}$, and the remaining orbitals from sets I and II would give $\Delta\rho_{\mathrm{b_1l_1}} > \Delta\rho_{\mathrm{b_1b_2}} = \Delta\rho_{\mathrm{l_1l_2}} = 0$. The results are no less arbitrary when values of Δq_{ab} are compared. Again using absolute values, Table III gives $\Delta q_{\mathrm{l_1l_2}} > \Delta q_{\mathrm{b_1b_2}} > \Delta q_{\mathrm{b_1l_1}}$ for set I, and $\Delta q_{\mathrm{l_1l_2}} > \Delta q_{\mathrm{b_1l_1}} > \Delta q_{\mathrm{b_1b_2}}$ for set II. The mixed sets just described would give still different orders.

These divergent results tend to overemphasize the differences between the various sets of orbitals. Within the accuracy of eq 2, all of the above sets of orbitals yield the same ρ (orthogonalized), and hence they all must lead to the same distortion, whatever that may be. The integrals of $\Delta\rho_{\mathrm{ab}}$ and the values of Δq_{ab} are obviously useless for predicting that distortion, as much from a practical standpoint as from a theoretical one.

Slater Determinants of Atomic Orbitals. Of the many attempts to use the Pauli principle to explain molecular shapes, perhaps the earliest and most often used approach has been to write a Slater determinant of selected orbitals on the central atom (all with the same spin), and then to determine the relative locations of the electrons which maximize the square of the determinant.[14] The problem with this approach is that the configuration which results depends on which orbitals are included in the determinant, just as the configuration of hybrid orbitals depends on which orbitals are hybridized. By means of group theory, appropriate orbitals can be chosen to generate *any* imagined symmetry for a given molecule.[15] As far as the Pauli principle is concerned, determinants giving unobserved configurations are as valid as the one giving the observed configuration. A classic example is the option of the d orbital in dsp^3, where the configuration is trigonal bipyramidal with d_{z^2} but square pyramidal with $d_{x^2-y^2}$. Attempts to justify the preference for d_{z^2} in terms of probability[14b] or Pauli forces[6c] are clearly incorrect.

Conclusion. For every conceivable shape of any molecule, a wave function can be written in compliance to the Pauli principle. From the infinity of such functions, the one representing the correct shape is not determined by the Pauli principle, which is equally satisfied by all of them. The Pauli principle is a necessary but not sufficient condition to the understanding of molecular shapes. The Pauli force is a misleading fiction that is as unjustified for explaining molecular shapes as it is for explaining Hund's rule.

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Supplementary Material Available. Tables IV–VI containing MO coefficients and energies for H_2O^{9+} will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6340.

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Molecular Structure of Gaseous Hexachlorobutadiene

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Abstract: The molecular structure of hexachlorobutadiene has been investigated by electron diffraction from the vapor. The molecule is not coplanar anti as is butadiene itself at normal temperatures, but instead has a gauche conformation approximately midway between syn and anti corresponding to a rotation around the conjugated single bond. Assuming symmetry C_2, symmetric $C{=}CCl_2$ groups, and equal C–Cl bonds the important distance, r_a, and angle values were found to be $r_{C=C}$ = 1.349 (6) Å, r_{C-C} = 1.483 (18) Å, r_{C-Cl} = 1.715 (2) Å, ∠C=C—C = 123.4 (6)°, ∠C=C—Cl(terminal) = 122.5 (2)°, ∠C=C—Cl(central) = 122.0 (7)°, and θ (the CCCC dihedral angle relative to 0° for the anti form) = 101.9 (11)°; parenthesized values are 2σ and refer to the last digit given.

Based on interpretation of the Raman spectrum of hexachlorobutadiene, C_4Cl_6, Kohlrausch and Wittek[1] concluded that the molecule was noncoplanar, a result supported by their energy calculations which predicted a value of 98° for the angle of torsion about the central single bond (0° corresponds to the coplanar anti form). The noncoplanar structure of C_4Cl_6 was confirmed in 1953 by an ir study by Szasz and Sheppard.[2] Their low-temperature results also eliminated the possibility that the substance is a mixture of noncoplanar rotational isomers, and they judged the steric effects to be so great that one single minimum in the potential energy curve located in the near 90° position should be possible. Results from a new Raman investigation[3] and two uv studies[4,5] have been taken as further evidence against a coplanar anti conformation.

Butadiene[6,7] as well as many of the substituted butadienes[8] have been found to exist predominantly in the coplanar anti form at normal temperatures. The coexistence of a second conformer syn or gauche has been widely discussed but not conclusively verified.[9] Although high-temperature studies of butadiene[10] seem to indicate that a gauche conformer may be present, no second conformer has yet been observed for substituted butadienes for which the coplanar anti conformation has been established.[11-14] Sub-