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The Shape of Molecules

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The two most important molecular shape models are the Valence-Shell-Electron-Pair-Repulsion scheme and the Walsh-Mulliken Diagrams. These models, with illustrative examples, are described and a rigorous quantum mechanical definition of each is stated. A physical-mathematical proof ot their equivalence and of their origin is given along with an analysis of the failures to be expected. The theoretical prediction of bond angles is contrasted with the corresponding prediction of bond lengths, and the low information content inherent to the specification of bond angles shows their determination to be considerably easier than bond lengths.

Die beiden wichtigsten Modelle zur Molekülgeometrie sind das Modell der Valenzelektronen-Paar-Abstoßung und das Walsh-Mulliken-Diagramm. Beide Modelle werden anhand illustrativer Beispiele vorgestellt, eine quantenchemische Definition beider wird gegeben. Ihre physikalische Äquivalenz wird bewiesen; diese Analyse zeigt auch die Grenzen der Modelle. Die theoretische Voraussage von Winkeln wird der von Bindungslängen gegenübergestellt. Da der Informationsgehalt der Winkelspezifikation niedriger ist, ist diese Angabe wesentlich leichter als die der Bindungslängen.

Les deux modèles de forme moléculaire les plus importants sont le schéma de répulsion électronique des paires d'électrons des couches de valence et les diagrammes de Walsh-Mulliken. Ces modèles sont décrits, avec des examples illustratifs, et l'on donne une définition quantique rigoureuse de chacun d'entre eux. Une preuve physicomathématique de leur équivalence et de leur origine est fournie avec une analyse des échecs à attendre. La prédiction théorique des angles de valence est opposée aux prédictions théoriques des longueurs de liaison; le faible contenu informationnel inhérent à la spécification des angles de liaison montre que leur détermination est considérablement plus aisée que celle des longueurs de liaison.

Karl Heinz Hansen

Karl Hansen first attracted my attention in 1963 through his articles on group theory in the ligand field problem and on spin valence theory in the first volume of *Theoretica Chimica Acta*. Hansen's work on spin valence theory showed a fresh and creative approach to electronic structure theory. It marked him as the possessor of a superior intellect and demonstrated his mastery of mathematical technique. It was with keen interest that I followed the great variety and mathematical ingenuity displayed in his theoretical work during the succeeding half-dozen years. As a tribute to Karl, I have chosen to write on the geometry of molecules because our research came closest together on this subject.

I will always recall with pleasure his visit to Princeton in 1966 and the opportunity we had for scientific interchange. At this time I became acquainted with the man himself, and I was fascinated by his character and the nature of his ideas.

Much of his thought had clearly been influenced by the war. Although on opposing sides, the common experiences of low-ranking enlisted men quickly establish a cord of understanding, and I could well sense his terror and excitement in service with his antiaircraft battery. Very much on his mind during his Princeton visit was the planning, anxiety, and frustration attendant to finding a permanent academic position in the reemerging German university establishment. I also learned about the exhilaration Karl felt when driving a car at high speed and about the fatalism which pervaded his thoughts.

In 1967 my visit to Frankfurt was arranged in style by Karl. We had a number of meals together and again the chance to share a wide range of experiences and thoughts. Again I found him a stimulating colleague, and I retain many happy memories of this occasion.

More recently, I had been delighted to learn of Karl's appointment at Bonn. In this period he also undertook close collaboration with experimenters, and this was one promising new aspect in his career development. I was shocked indeed when I received notice of his untimely death. Karl Hansen made unique contributions to theoretical chemistry — he would have generated many more had time been allowed him.

Background

Two of the most successful models in all of chemistry are the valence-shell electron-pair repulsion model identified with Sidgwick and Powell [1] and Gillespie and Nyholm [2] and the orbital energy versus angle diagrams associated with Walsh [3] and Mulliken [4]. These two models have dominated the systematization and rationalization of non-transition metal inorganic chemistry and spectroscopy. Even though far more rigorous and accurate quantum mechanical solutions now have been obtained for many polyatomic molecules, these simple models continue to provide the conceptual framework for understanding molecular shape.

Although it has been known for some time that these two models generally provide similar predictions, they appear, at least superficially, to operate on entirely different principles: The valence-shell electron-pair repulsion (VSEPR) model utilizing classical electrostatics, the Walsh diagrams being a manifestation of atomic orbital hybridization with complete neglect of the nuclei and electron-electron interactions.

It is the purpose of this article to demonstrate the physical and mathematical equivalence of these two models and to derive their properties from Schrödinger's equation. Beyond the satisfaction of knowing that these two models are basically similar, the analysis brings out the conditions under which these models fail.

Valence-Shell Electron-Pair Repulsion Model

The original article by Sidgwick and Powell [1] related the angular arrangement of electrons around a central atom to the number of electrons in its outer shell plus the valence of the attached atoms. The resultant number of electron pairs (irrespective of whether lone pairs or bond pairs) was put in one-to-one correspondence with molecular shape: two pairs linear, three pairs a planar triangle, four pairs tetrahedral, five pairs a trigonal bipyramid, six pairs octahedral. These same results derive from the even simpler model of point charges on a spherical surface interacting through the force law $1/(r_{ij})^n$, irrespective of the value of n [5]. Seven particles is an exception [6]. However, both in the models and in nature itself, seven coordination is rare and special, and it is not appropriate for further discussion here because it obscures the central features of the model. The ultimate simplicity of the charges-on-a-sphere model as much as anything else has fixed in people's minds the idea of electrostatic repulsion as the basic origin of inorganic stereochemistry.

Gillespie and Nyholm [2] significantly enhanced the original Sidgwick and Powell model by recognizing a distinction between lone pairs and bond pairs. Lone pairs are closer to nuclear centers than bonds and occupy more space thereby leading them to the additional rule for interaction energies: lone pair − lone pair > lone pair − bond pair > bond pair − bond pair. This greatly increased the precision and scope of the model. By bringing together most all of the existing experimental data and by further refining the model, Gillespie [7] has been able to encompass and bring into systemization a larger body of structural knowledge than has been accomplished ever before. As examples we consider shape predictions for four simple cases. BH_2^+ has four valence electrons, two bond pairs, and therefore a linear configuration. BH_2^- has six valence electrons, two bond pairs plus a boron lone pair. Since lone pair − bond pair interaction energy > bond pair − bond pair interaction energy, the ion is strongly bent. XeF_2 obtains eight electrons from xenon, plus one from each fluorine, yielding three lone pairs and two bond pairs. The arrangement with the lowest electrostatic repulsion energy is the trigonal bipyramid with three lone pairs in a plane perpendicular to the linear F–Xe–F bond axis. The six electron pairs of XeF_4 divide into four bond pairs and two lone pairs. Electrostatic energy is minimized by keeping the lone pairs as far apart as possible, thereby producing a square planar arrangement of fluorines with lone pairs protruding above and below the plane.

A mathematically and physically rigorous definition of the VSEPR model exists, and in order to clearly state this definition, it is worthwhile recalling three of the well-established approximations of electronic structure theory. First is the non-relativistic assumption, second is the complete separation of electronic and vibrational motion (Born-Oppenheimer clamped nuclei). Third is the claim that a single determinant composed of one-electron spin orbitals is a satisfactory approximate solution to Schrödinger equation for predicting molecular geometry with an error of only a few percent. The validity of this assumption stands on consistent numerical results obtained from over a thousand polyatomic *ab initio* wavefunctions constructed during the last dozen years. The invariance of such single-determinant wavefunctions to an arbitrary unitary transformation has long been recognized, and over twenty years ago Lennard-Jones [8] proposed orbitals whose shapes would correspond to the elementary picture of a localized electron-pair bond. More recently Edmiston and Ruedenberg [9] have given a precise prescription for constructing these orbitals and worked out a number of examples [10]. Schematically the total molecular energy may be partitioned into the following components:

$$E_T = KE + V_{ne} + V_{nn} + V_{\text{Coulomb}} - V_{\text{exchange}} \,.$$

The energy localized orbitals of Edmiston and Ruedenberg are defined by minimizing the V_{exchange} *between different bond orbitals*. In physical terms this makes the quantum mechanical description behave as closely as possible to a classical electrostatic interaction between electron pairs. The numerical calculations they carried out for LiH, BH, NH, FH, Li_2, B_2, Be_2, N_2, F_2, CO, BF, LiF, H_2O, NH_3, C_2H_6, and CH_4 display just the sort of lone-pair and bond-pair charge lobes prescribed by the VSEPR model, and a rigorous, *ab initio* basis for this model is thereby established.

Walsh-Mulliken Diagrams

In his classic set of papers [3] Walsh deduced orbital energy versus bond angle diagrams for a series of generic species: AH_2, AH_3, AB_2, AB_3, HAB, A_3, HAAH, HAB_2 and H_2AB. A and B represent atoms such as C, N and O. His AH_2 diagram is illustrated by the dashed lines of Fig. 1. Only valence electrons are considered. To construct his diagrams, Walsh employed known results on molecular shape, observed molecular excitation energies and simple arguments concerning the mixing and relative weighting of atomic orbitals. These diagrams may be used to predict molecular shape by filling up the energy levels with pairs of valence electrons, summing the energies, and finding the bond angle that yields the smallest sum. For the four valence electrons of BH_2^+ only the lowest two states are occupied and a linear ion results. In BH_2^- the $3a_1$ is also occupied producing a sharply bent ion. An additional two valence electrons are present in H_2O, but they reside in the flat $1b_1$ level and again the molecule is strongly bent. Examples like these im-

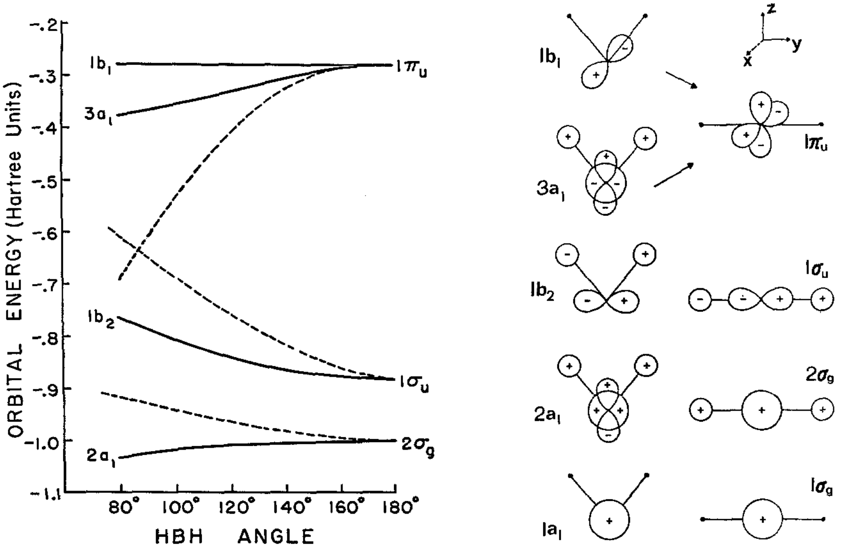


Fig. 1. Walsh-Mulliken Diagram for AH_2 molecules (dashed lines). *Ab initio* one-electron molecular orbital energies for BH_2^+ (solid lines). Right side: atomic orbital mixing for bent and linear AH_2

mediately demonstrate that molecular shape – a bent or linear AH_2 species in our example – is determined solely by the *number* of valence electrons.

In a manner parallel to that described for the VSEPR model, Walsh-Mulliken diagrams can be generated directly from *ab initio*, single-determinant wavefunctions. The one-electron molecular spin orbitals which make up the determinant are expressed as a linear combination of the atomic-like functions mounted on the various nuclear centers:

$$\varphi_i^{\text{Mol.}}(1) = \sum_j C_{ij}\eta_j^{\text{Atom}}(1)\,.$$

The linear coefficients, C_{ij}, are varied to minimize the energy with the molecular orbitals and corresponding orbital energies (ε_i) expressed in canonical (diagonal) eigenvalue form:

$$\mathscr{H}\,\varphi_i^{\text{Mol.}}(1) = \varepsilon_i\varphi_i^{\text{Mol.}}(1)\,.$$

The solid lines of Fig. 1 result from an *ab initio* calculation of BH_2^+ [11], and *ab initio* Walsh-Mulliken diagrams now exist for over fifty polyatomic molecules [12]. In each case they closely resemble Walsh's original constructs, and they preserve their generic form for sequences of A and B atoms. The atomic orbital mixing combinations allowed by symmetry, along with their irreducible representation labels, are displayed schematically in both linear and bent configurations on the right-hand side of Fig. 1. From the schematics it is obvious that there is an intimate mixture of $2s$ and $2p$ orbitals in $2a_1$ and $3a_1$. Actual calculations reveal that around 90° $2s$ dominates $2a_1$, and correspondingly $2p$ dominates $3a_1$ in this angular range. As noted by Mulliken long ago [13], Walsh neglected a $2s$ contribution from $3a_1$ in the 90° region leading to incorrect slopes for these two molecular orbitals, but fortunately, Walsh's error was not so severe as to vitiate his qualitative conclusions.

There is another way of obtaining bond angles from the molecular orbitals generated by the diagonal eigenvalue equation stated above. This is *via* the second-order ("pseudo") Jahn-Teller perturbation theory [14] and, although entirely equivalent to the Walsh diagram approach, it sometimes provides a useful viewpoint. Bartell has applied it to shape prediction [15], and I note it here for completeness. The scheme starts with a high-symmetry reference configuration-linear for AH_2 systems. Standard perturbation theory arguments then show that the sign of the coefficient of the square of the appropriate normal mode vibration coordinate, S_i, determines whether or not the high-symmetry reference configuration will deform:

$$\left\langle \psi_0 \left| \frac{\partial^2 H}{\partial S_i^2} \right| \psi_0 \right\rangle - 2\sum_n \frac{\left| \left\langle \psi_n \left| \frac{\partial H}{\partial S_i} \right| \psi_0 \right\rangle \right|^2}{E_n - E_0}\,.$$

The possibility of energy lowering under deformation is controlled by the summation because this term comes in with a negative sign. Thus a bent molecule results when the first excited states are sufficiently low and their symmetry such as to produce non-vanishing matrix elements of the force operator.

In discussing the VSEPR scheme, we noted that the extreme simplicity of the charges-on-a-sphere model appeared to reveal the underlying operating principle through which molecular shape was determined. Several simple semi-empirical and parametric electronic structure schemes have been shown capable of generating Walsh-Mulliken diagrams, and they similarly claim to shed light on the origin of these diagrams. Thus Schmidtke and Preuss [16] were able to reproduce AH_2 and AH_3 diagrams using a Hamiltonian that only contained the one-electron terms: kinetic energy and electron-nuclear attraction. Bingle [17] produced correct AH_2 and AH_3 diagrams from a united atom perturbation theory approach that omits most of the influence of the nuclear framework potential. Reasonable AH_2 and AH_3 diagrams were obtained by Leclerc and Lorquet [18] with extended Hückel theory which employs an attractive bond-forming interaction, but omits explicit expressions for kinetic energy, nuclear framework potential, and electron-electron interactions. A paper by Allen and Russell [19] showed the remarkable degree of parallelism between diagrams generated by extended Hückel and *ab initio* methods, and a series of articles by Gimarc [20] has verified the qualitative capability of extended Hückel theory to produce all nine types of Walsh-Mulliken diagrams.

Equivalence of VSEPR and Walsh-Mulliken Diagrams

In all three sections above we have pointed out the similar shape predictions generally given by VSEPR and Walsh-Mulliken, and this provides circumstantial evidence for the equivalence of these two models. But we seem to be faced with a severe dichotomy when the two models are examined in detail. The electron repulsions which appear to dominate VSEPR can be omitted entirely from theories which satisfactorily construct Walsh-Mulliken diagrams while the details of atomic orbital hybridization that are central to the Walsh-Mulliken diagrams are nowhere put into VSEPR. In spite of these contradictions the two models *are* equivalent and the physical-mathematical proof is given below.

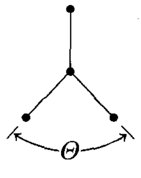
Pauli Principle. In Gillespie's later writings he has stated his belief that it is primarily the workings of the Pauli principle rather than electrostatic repulsion which provides the driving force for VSEPR. This is certainly correct. Two electrons of opposite spin in the same orbital act toward a nearby similar pair as two helium atoms. Their effective repulsion can be represented by an inverse power of r. Opposite spin pairs (in the same orbital) moving on the surface of a sphere will obviously produce the same geometries as the charges-on-a-sphere model. The difference between lone-pairs and bond-pairs is mainly manifest through size and shape rather than charge density, thus the rule:

$$\text{lone pair} - \text{lone pair} > \text{lone pair} - \text{bond pair} > \text{bond pair} - \text{bond pair}$$

is a size-Pauli exclusion principle result. This reasoning in no way denies the existence of electrostatic repulsion between bond pairs and lone pairs, but rather shows that shape does not follow directly from simple electrostatics.

Trace Invariance. Unitary transformations of a single determinant wavefunction preserve the trace of the canonical Hamiltonian matrix. That is, the sum of ε_i's over occupied orbitals in the molecular orbital determining eigenvalue equation given in the previous section is unchanged when a transformation to Edmiston-Ruedenberg localized orbitals is made. It is $\sum_i^{\text{val.}} \varepsilon_i$ which is the shape criteria of the Walsh-Mulliken diagrams, and we have already noted that a single determinant *ab initio* wavefunction is adequate to yield both these diagrams and the VSEPR-like localized lone pairs and bond pairs. In fact the localized orbital pictures computed by Edmiston and Ruedenberg [10] were obtained by transforming solutions of the canonical eigenvalue equation, and solutions to this equation have been shown by direct construction capable of generating Walsh-Mulliken diagrams.

Another way to check the equivalence of VSEPR and Walsh-Mulliken is by investigating the symmetry properties of the transformation that takes orbitals from one model to the other. A simple and effective way of doing this for seven of Walsh's generic types has been carried out by Thompson [21]. Assuming a particular point group, he constructs a mechanical ball-and-stick model representing localized bond pairs and lone pairs. Following Gillespie, a lone pair is assumed to preempt more solid angle around a nucleus than a bond pair, and, where ambiguity exists, lone pairs are oriented to match the molecular framework symmetry. Linear combinations of bond pairs and of lone pairs that transform as irreducible representations can generally be made up by inspection or formally by employing character projection operators. Thompson then finds a one-to-one correspondence between the number and symmetry type of molecular symmetry orbitals constructed in this manner and the corresponding number and type found in Walsh's original diagrams. For AH_3 and AB_3 types Thompson also works out molecular symmetry orbitals for the now well-established T-shaped molecules, such as ClF_3 and BrF_3. Walsh did not include this possibility, and Thompson suggests that these species may be outside the Walsh systemization scheme. This problem can be stated and resolved as follows: Walsh AH_3 and AB_3 systems transform from C_{3v} to D_{3h} by change of a single angle, but there is no single angle that transforms the T point group, C_{2v}, to C_{3v} or D_{3h}. Therefore there are basically two classes of AH_3 and AB_3 molecules, and the one that is realized can only be determined by computing which structure has the lowest total energy [22]. The appropriate Walsh-Mulliken abscissa for T-shaped molecules is the in-plane angle Θ which converts a Y-shaped molecule into T shape for $\Theta = 180°$. For $\Theta = 120°$ the symmetry is D_{3h} and therefore a common point between the two classes of AH_3 and AB_3 molecules. The series of extended Hückel generated Walsh-Mulliken diagrams computrd by Gimarc [20] contains a $Y - T$ diagram for AH_3 and results for LiH_3^+ (Y-shaped). Qualitative slopes and energy ordering for the first few levels of the $Y - T$ diagram from 120° to 180° can be directly inferred from the AH_2 diagram because both reflection planes of C_{2v} pass through the added bond in a $Y - T$ molecule. Thus the first four valence molecular orbitals will be $2a_1$, $1b_2$, $3a_1$, and $1b_1$ – just as in AH_2. Thompson's analysis and Gimarc's diagrams are both compatible with this simple reasoning. It is also worth noting that in this case as well as others, d-orbitals are not required as they are in the valence bond hybridization scheme of Kimball [23].



There is still another line of argument which brings out the equivalence of the two models, and this concerns cases where both models fail. It has frequently been pointed out that VSEPR fails for bonds which are highly ionic [7, 15]. The same is true for Walsh's rules. Li_2O is the simplest example. According to VSEPR there are two bond pairs and two lone pairs leading to a bent molecule. Assigning eight electrons to the AH_2 Walsh-Mulliken diagram also leads to a bent molecule – just like H_2O. Actually, of course, Li_2O is almost $Li^+O^=Li^+$ and definitely linear. Both models fail for lack of a Madelung potential term. When the Edmiston-Ruedenberg transformation is applied to a high-accuracy *ab initio* calculation of Li_2O, the charge lobes arrange themselves in an approximately tetrahedral fashion around oxygen – none of them pointing toward the lithium nuclei [24]. This result is indicative of the faithful representation of VSEPR provided by the Edmiston-Ruedenberg localized orbital definition.

An important observation arising from the large amount of research done on molecular shape is that almost any model or computational scheme yields reasonable bond angle predictions, and this suggests a low information content inherent to the specification of molecular shape. The most dramatic and elegant manifestation of this observation is Karl Hansen's development of spin valence theory and the results he obtained from it [25, 26, 27]. Using only the *ab initio* determinantal formalism for constructing wavefunctions, group theory, and the assumption of maximum multiplicity on the central atom, Hansen was able to determine the electronic ground state configuration and shape (point group) for AH_2 and AH_3 species without numerical computations. He made 24 predictions – all in complete accord with Walsh-Mulliken diagram results.

The Origin of Walsh's Rules

Having demonstrated the equivalence of VSEPR and Walsh-Mulliken, it remains to elucidate their basic origin. Because of their quantitative association with molecular orbital theory, Walsh-Mulliken diagrams are much easier to treat theoretically. Although schemes for computing these diagrams have been available for many years now, the progress toward understanding the physical-mathematical principles behind them has been slower to evolve. In particular there was a long period of uncertainty over the precise definition of Walsh's "orbital energies". An important paper by Coulson and Neilson [28] concluded that these were the "partitioned energies", $e_i = \frac{1}{2}[\varepsilon_i + (i\,|\,\text{one-electron terms in the Hamiltonian}\,|\,i)]$, whose sum equals the total energy. Bingel used the one-electron eigenvalue of his total energy united atom Hamiltonian, and this quantity is different from either ε_i or e_i, but, in practice, it behaves much like e_i. Schmidtke and Preuss employed the eigenvalues of a secular equation over a one-electron Hamiltonian composed of kinetic and electron-nuclear potential terms with an effective nuclear charge for the central atom. Their energies also have an angular dependence very similar to e_i. Coulson and Neilson's H_2O, Bingel's AH_2 and AH_3, and Schmidtke and Preuss's AH_2 and AH_3 all yielded diagrams in qualitative agreement with Walsh. On the other hand Bingel's A_3 and AB_3 and Schmidtke's AB_2 yield curves that all fall off very strongly at small angles and are essentially identical to the e_i curves for F_2O [29]. None of these resemble the corresponding Walsh diagrams.

As displayed above, e_i differs from ε_i by the addition of the one-electron terms in the Hamiltonian, and at small angles electrons of one ligand atom are attracted to the nucleus of a nearby "non-bonded" ligand atom, and this pulls down the e_i curves. For a light ligand atom like hydrogen, this effect is relatively small, and therefore qualitatively acceptable results were obtained for the hydrides. Another approach to the origin of Walsh's rules was proposed by Peters [30]. He equated the orbital energies with the *change* in ionization potential of the molecular orbital upon molecule formation. All of these previous hypotheses are incorrect, and they reflect the fact that an adequate supply of accurate *ab initio* computational results was unavailable to these authors. It has been numerical reproduction of Walsh-Mulliken diagrams for many individual cases that has clearly focused on ε_i, the eigenvalue in the canonical molecular orbital determining equation, as the correct definition of "orbital energy". As everyone knows, ε_i enjoys the great advantage of being identified with experimentally determined ionization potentials via Koopmans' theorem. When the Edmiston-Ruedenberg transformation is applied to canonical molecular orbitals, off-diagonal ε_{ij}'s are introduced, and the problem of physically interpreting or experimentally determining these quantities is the principal reason why it is difficult to carry out a detailed and complete analysis of VSEPR.

Central to the origin of Walsh's rules is a mathematical and computational justification of how a minimum in $\sum_i^{\text{val.}} \varepsilon_i$ can determine bond angles when it is well known that this sum has a grossly different value from the total energy, E_T:

$$E_T = \sum_i^{\text{val.}} \varepsilon_i + \left[\sum_i^{\text{core}} \varepsilon_i - V_{ee} + V_{nn} \right].$$

The key is to consider the derivative of E_T with respect to Θ rather than E_T itself, because it is an extremum in the derivative which governs the angle. Thus if

$$\frac{\dfrac{\partial}{\partial\Theta}\left[\sum_i^{\text{val.}} \varepsilon_i\right]}{\dfrac{\partial}{\partial\Theta}\left[\sum_i^{\text{core}} \varepsilon_i - V_{ee} + V_{nn}\right]} > 0$$

or if

$$\left|\frac{\partial}{\partial\Theta}\left[\sum_i^{\text{val.}} \varepsilon_i\right]\right| > \left|\frac{\partial}{\partial\Theta}\left[\sum_i^{\text{core}} \varepsilon_i - V_{ee} + V_{nn}\right]\right|.$$

$\dfrac{\partial}{\partial\Theta}\left[\sum_i^{\text{val.}} \varepsilon_i\right]$ will have the same sign as $\dfrac{\partial}{\partial\Theta}[E_T]$ and the minimum in $\sum_i^{\text{val.}} \varepsilon_i$ will occur at the same angle as the E_T minimum [31]. Physically, the inequalities will be satisfied if there is little charge transfer from one atom to another because then the effective screening potential, V_{ee}, will shield V_{nn} and changing bond angle will be like moving neutral bonds. Numerical proof of the inequalities has been obtained for a number of cases, two of which (BH_2^- and F_2O) are shown in Fig. 2 $\left(E_T\text{, solid lines, compared to } \sum_i^{\text{val.}} \varepsilon_i\text{, dashed lines, from the same } ab\ initio \text{ calculation}\right)$.

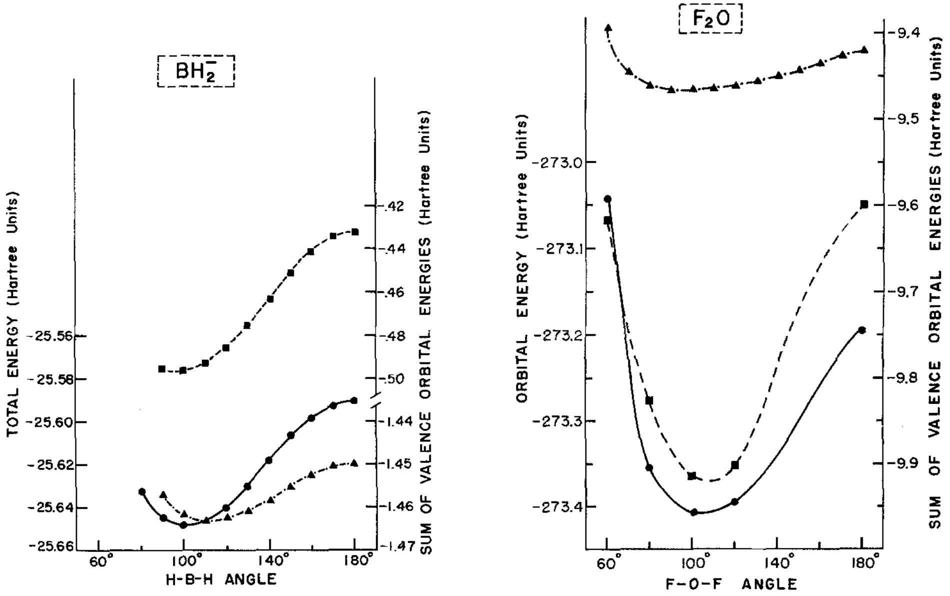


Fig. 2. Numerical proof of inequalities for covalent molecules. *Ab initio* E_T (solid lines), *ab initio* $\sum^{\text{val.}} \varepsilon$ (dashed lines), extended Hückel $\sum^{\text{val.}} \varepsilon$ (staggered lines)

It is a remarkable fact (already noted in a section above) that the simplest of all electronic structure models, extended Hückel theory, is able to generate reasonable Walsh-Mulliken diagrams. I have discussed the origin of this model at length elsewhere [32], here the most important point is demonstration that $\sum_i^{\text{val.}} \varepsilon_i$ from extended Hückel theory maintains the same sign of derivative versus angle as *ab initio* E_T and *ab initio* $\sum_i^{\text{val.}} \varepsilon_i$. Fig. 2 (staggered lines) shows that it does. The rather large differences in detail between extended Hückel $\sum_i^{\text{val.}} \varepsilon_i$ and *ab initio* $\sum_i^{\text{val.}} \varepsilon_i$ is one measure of the crudity of extended Hückel theory, but because of the low information content inherent to angle specification, extended Hückel angle predictions can be quantitatively useful.

The origin of the Walsh rule breakdown for highly ionic bonds is nicely brought out in the inequalities. Changes with angle of $\sum_i^{\text{core}} \varepsilon_i - V_{ee}$ no longer cancel changes with angle of V_{nn}, and the resultant Coulomb term destroys the inequality. This is illustrated in Fig. 3 by *ab initio* calculations on Li_2O $\left(E_T \text{ solid line, } \sum_i^{\text{val.}} \varepsilon_i \text{ dashed lines}\right)$. The sign of $\partial/\partial\Theta\left[\sum_i^{\text{val.}} \varepsilon_i\right]$ for extended Hückel theory is also opposite to that of $\partial/\partial\Theta(E_T)$. For extended Hückel theory the failure in $\sum_i^{\text{val.}} \varepsilon_i$ is paralleled by large

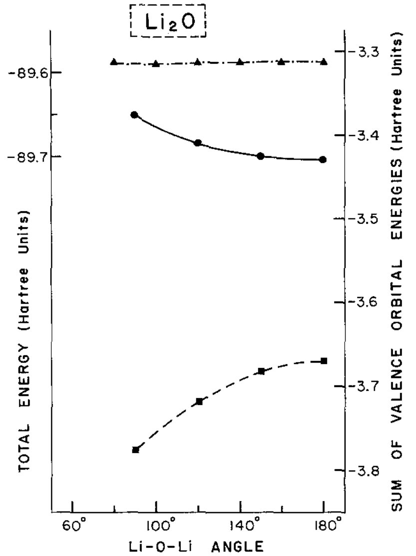


Fig. 3. Break of Walsh's rules for ionic molecules. *Ab initio* E_T (solid line), *ab initio* $\sum^{\text{val.}} \varepsilon$ (dashed line), extended Hückel $\sum^{\text{val.}} \varepsilon$ (staggered line)

inaccuracies in ε_i and in the molecular orbital coefficients. Since these quantities are the sole output of extended Hückel theory, it is clear that this model is only valid when Walsh's rules hold, and from a chemical viewpoint this implies small bond dipoles and a relatively smooth charge distribution.

Bond Lengths

In its simplest form, VSEPR does not address itself to bond length predictions, but some elaborations by Gillespie [7] have enabled him to account for trends in sequences of compounds. These additional postulates are: (a) Successive addition of electronegative ligands increases the effective electronegativity of the central atom and decreases bond lengths. (b) Different ligands have different environments, therefore different bond lengths. For example, five electron pairs lead to a trigonal-bipyramid with two axial positions and three equatorial ones. Results from the charges-on-a-sphere model (for $n \geqq 4$ in $1/r_{ij}^n$) show a greater force at the axial position than equatorial, and this gives qualitative rationalization to the 10–20% longer axial bond observed for AX_5, AX_4E, and AX_3E_2 species. Application of both these additional rules to noble gas compounds has led to a useful systematization of bond length trends in these molecules [33].

Walsh-Mulliken diagrams likewise do not address themselves to bond lengths, but it is informative to apply the same analytical techniques to bond lengths as proved successful for bond angles. We carried this out in my laboratory [34] and found that $\sum_i^{\text{val.}} \varepsilon_i$ provides no guide at all to bond length, and the corresponding inequalities do not hold.

There are four other model schemes that are used for estimating and rationalizing bond lengths, and a review of them sheds light on the further analysis to be given below. The oldest, simplest and most used is tabulation of atomic and ionic radii. Pauling [35] has been principally responsible for developing this scheme. Mulliken [36] proposed that bond length trends be related to change in the occupancy of bonding and antibonding orbitals along a sequence of neutral or ionic species. The correctness of this hypothesis has been proved many times, but no general quantification of this model has yet arisen. Pauling's and Mulliken's models apply to any molecule but lack precision. If attention is restricted to hydrocarbons, much higher accuracy can be obtained, and two model theories have been widely employed: "molecular mechanics" [37] and the bond-order versus bond-length diagrams originated by Coulson [38]. The latter have been mostly applied to bond-length changes arising from changes in the number of π-electrons, and π-orbital Hückel theory has proved adequate for generating bond orders. Coulson's model may be thought of as a special case of Mulliken's general orbital occupancy concept. A review of molecular mechanics is beyond the scope of this article, but Bartell [15] has given examples and pointed out inherent difficulties in the method that are relevant to our discussion here. Overall, one can say that the precision achieved for hydrocarbon bond-length trends by molecular mechanics and bond-orders is to be viewed as the result of a sophisticated interpolation scheme rather than due to an intrinsically accurate description of the basic force laws involved.

Beyond the six models discussed so far in this section, there are the quantum mechanical calculational methods. The method with the highest level of reliability which is still able to handle large enough systems to be of practical interest to many inorganic and organic chemists is the single determinant, self-consistent field molecular orbital method. We have displayed the canonical orbital determining equation for this method, and even when a relatively crude basis set is used to expand the molecular orbitals, generally correct trends are found and absolute errors are 1–10%. Fortunately, the efficiency of this *ab initio* method is rapidly improving, and molecules composed of twenty atoms and sixty electrons are practical at this time. Extended Hückel theory with its high computation speed and low *a priori* reliability for predicting bond lengths is at the opposite end of the scale. Detailed examination shows [32] that extended Hückel theory generates its bond lengths by a physically incorrect process and this scheme is essentially useless for their prediction. There exist a number of methods that are intermediate in all respects to these extremes. A great deal of everyday chemical utility has been achieved through their use and the absolute error in bond lengths does not generally exceed 12%. However, the trends through a chemical sequence are often incorrectly ordered.

Two quite general results from theoretical chemistry suggest why the precise determination of bond lengths is so difficult. First is the well-known united atom – separated atom energy level correlation diagram [39]. Examination of the numerous cases given by Herzberg shows that the pattern of level spacings is vastly different between the two sides of these diagrams. The actual levels manifest by the molecule may be close to one side or to the other or somewhere near the middle. Second is the plot of average kinetic energy and average potential energy versus internuclear separation found in several textbooks [40]. These show that around the equilibrium separation both average kinetic and average potential energies are changing very rapidly in opposite directions while the total energy has a very much slower change. These rapid opposing changes cannot cancel because, of course, their sum is the total energy curve. Bond lengths are clearly a delicate balance between electron-nuclear attraction, screening, and nuclear repulsions as well as between the total potential and kinetic energies, and a considerable amount of detailed information is required about these terms to specify bond lengths.

Summary and Conclusions

Because of its name, the fact that repelling charges on a sphere can produce its results, and because the relative repulsion of bond pairs and lone pairs successfully rationalizes their observed positions, the origin of the VSEPR model has been popularly associated with electron-electron repulsion. Walsh-Mulliken diagrams, on the other hand, are associated with molecular ionization potentials and omit electron-electron and nuclear-nuclear repulsions. That these two models are, in fact, equivalent follows from four considerations: (a) The same single determinant *ab initio* wavefunction can produce all of the directly identifiable features of both models. (b) The trace of the Hamiltonian matrix for this wavefunction is invariant under transformation from a localized (VSEPR) representation to a delocalized (Walsh-Mulliken) representation. (c) Size and Pauli exclusion principle repulsion of closed shells replaces electron-electron repulsion as the true driving force in VSEPR. (d) Both models fail simultaneously when bonds become sufficiently ionic that a significant Madelung term is introduced.

Many early papers misinterpreted the dependent variable in Walsh-Mulliken diagrams, and it has only been relatively recently that "orbital energy" has been unequivocally established as the Koopman-theorem related ε. The basic mathematical-physical origin of Walsh's rules resides in the dominance of $\partial/\partial\Theta\left[\sum_i^{\text{val.}}\varepsilon_i\right]$ over other terms in the total energy expression, and this holds only when the molecular charge distribution is rather smooth and no significant between-atom charge transfer occurs. Because only sign information concerning $\partial/\partial\Theta\left[\sum_i^{\text{val.}}\varepsilon_i\right]$ is required, many highly approximate quantum mechanical schemes, such as extended Hückel theory, are able to yield useful predictions.

In sharp contrast to angles, bond lengths are difficult to predict with precision. This is due to the delicate balance of energy components that occurs around equilibrium bond separations. Model schemes, such as sum of radii or number of occupied bonding and anti-bonding orbitals, are not adequately quantitative, while some schemes only apply to special classes of hydrocarbons. At present, *ab initio* calculation is the only method that yields reliable *a priori* bond length predictions.

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