

On the Angular Independence of Sets of Atomic Orbitals*

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Abstract. The conditions under which a set of atomic orbitals becomes angularly independent are investigated for both atomic and molecular systems. How these results can be applied to various molecules is considered.

Keywords: angular independence, atomic orbitals, molecular orbitals, symmetry

INTRODUCTION

When presented in their real form, only the atomic orbitals having azimuthal quantum number $\ell = 0$ (the s orbitals) are spherical and have no angular dependence. The linear combination of spherical harmonics having the same azimuthal quantum number ℓ , with $\ell \geq 1$, yields atomic orbitals having angular dependence. For example, the p_x , p_y , and p_z orbitals (the real p orbitals) have dumbbell shapes that change sign as value of the angular variable goes from 0 to 180° , or π radians. Similarly, for $\ell = 2$, most of the real d orbitals have cloverleaf shapes that change sign every 90° , or $\pi/2$ radians. As ℓ increases in value, the shapes of the real orbitals become more complicated, e.g. the simplest drawing of an f orbital ($\ell = 3$) shows a 6-petalled flower that changes sign every 60° or $\pi/3$ radians. Parenthetically, it may be noted that the shapes of f orbitals are often not drawn correctly.

In 1927, Unsöld proved that if one sums the electron density of all three p orbitals, where each orbital is occupied by an electron pair, then all angular dependence disappears; that is, the resulting total density is as spherical as found from the use of s orbitals alone.¹⁻³ Similarly, if all five d orbitals are doubly occupied, or all seven f orbitals are doubly occupied, it was shown that the same spherical behavior results. Spherical density also occurs when each orbital is singly occupied, provided that all of the electron spins are parallel.

In other words, Unsöld's theorem states that the sum of the squares of all of the angular wave functions,

that is, the probability distribution, corresponding to a given value of ℓ , is a constant, independent of the orientation. While Unsöld's theorem has important implications for the structure of complicated atoms, most textbooks on quantum mechanics do not explicitly discuss it, notable exceptions being the classic textbooks by Linus Pauling and E. Bright Wilson, Jr.,² and by John C. Slater.³

In a previous publication by the present authors, the conditions required for the independence of sets of atomic orbitals were considered.⁴ In the present work, these conditions are investigated in more detail.

THE REQUIREMENTS FOR ANGULAR INDEPENDENCE

In 1995, Icke showed that angular dependence vanishes when an s orbital and some suitable real orbitals having $\ell \geq 1$ are added together.⁵ It is possible to understand this phenomenon by considering the combination of atomic orbitals as a sum of cosine functions:

$$s_n(\Theta) = N_0 + \sum_{j=1}^n \cos[(j-1) \cdot 2\pi\Theta] =$$

$$N_0 + 1 + \cos(2\pi\Theta) + \cos(2 \cdot 2\pi\Theta) + \dots + \cos[(n-1) \cdot 2\pi\Theta] \quad (1)$$

where Θ is an arbitrary angular coordinate that applies either to an atom or a molecular system with D_{nh} point-

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

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group symmetry. Here the leading terms $N_0 + 1$ reflect the different normalization of the s orbital from those other orbitals that have some angular dependence. Moreover, Eq. (1) may be rewritten as

$$s_n(\Theta) = N_0 + S_n(\Theta) \quad (2)$$

where

$$S_n(\Theta) = \sum_{j=1}^n \cos[(j-1) \cdot 2\pi\Theta] \quad (3)$$

One may now ask to what does this sum converge for the angle variables $0 \leq 2\pi\Theta \leq 2\pi$ (i.e., $0 \leq \Theta \leq 1$) as n goes to infinity. That is, what is the value of $s_n(\Theta)$ for arbitrary angles Θ and for limiting values of n ? Owing to the nature of the cosine function, the situation for $\Theta = 0$ and $\Theta = 1$ are identical. Thus, this is an example of periodic boundary conditions.

Since i is defined as $\sqrt{-1}$ and the real part of any complex number may be written as

$$\Re(a + bi) = a \quad (4)$$

the following identity holds for all (angles) α

$$\cos(\alpha) = \Re[\exp(i\alpha)] \quad (5)$$

Then the series in Eq. (3) can thus be rewritten as

$$S_n(\Theta) = 1 + \Re[\exp(i(2\pi\Theta))] + \Re[\exp(i(2 \cdot 2\pi\Theta))] + \dots + \Re[\exp[i(n-1) \cdot 2\pi\Theta]] \quad (6)$$

Moreover, for any two arbitrary complex numbers u and v ,

$$\Re(u + v) = \Re(u) + \Re(v) \quad (7)$$

accordingly,

$$S_n(\Theta) = \Re \left\{ \begin{array}{l} 1 + \exp[i(2\pi\Theta)] + \\ \exp[i(2 \cdot 2\pi\Theta)] + \\ \dots + \exp[i(n-1) \cdot 2\pi\Theta] \end{array} \right\} \quad (8)$$

Now define

$$x \equiv \exp[i(2\pi\Theta)] \quad (9)$$

so that Eq. (8) may be rewritten as

$$S_n(x) = \Re[1 + x + x^2 + \dots + x^{n-1}] \quad (10)$$

Therefore, for all finite n and $x \neq 1$,

$$S_n(x) = \Re[(1 - x^n)/(1 - x)] \quad (11)$$

It is now possible to investigate under which conditions the sums $S_n(\Theta)$ and $S_n(x)$ have values equal to zero. This situation occurs if two conditions are met:

$$x^n = 1 \quad (12)$$

and

$$x \neq 1 \quad (13)$$

Thus,

$$x^n = \exp[i(2\pi n\Theta)] = 1, x \neq 1 \quad (14)$$

At this stage, one must consider whether Θ is a rational or irrational number. If Θ is rational, then must equal m/n , where m and n are integers, and Θ is real. By periodicity or modulus n , only those cases where m does not exceed n need be considered. Since it is also required that x does not equal 1, one may exclude the cases where Θ equals either 0 or 1. Does this mean that all (or more precisely, almost all) rational numbers between 0 and 1 result in a sum of 0? In other words, does this mean that exclusive of the end points result in a sum of 0?

For the values of real x chosen, it was required that $S_n(\Theta)$ and $S_n(x)$ equal 0. The defining equation for $S_n(x)$ is an n^{th} order equation in x . There are but n roots, which have already been found. For integer m and $n \rightarrow \infty$, the set of numbers m/n includes all rational numbers between 0 and 1. If n is set equal to $p!$, then the set of numbers m/n for all m not equal to n includes all quotients m'/n' not equal to 0 and 1 for all $n' \leq p$. As $p \rightarrow \infty$, and setting $p! = n$ which in turn goes to ∞ , all rational numbers between 0 and 1 are included. Thus, it would seem as if an infinite number of angles sum to zero.

Next, one must consider the infinite set of numbers between 0 and 1 not yet discussed, namely, the irrational values of x . The size of the set of such numbers is recognized to equal \aleph_1 , and is larger than the number of rational numbers, recognized to equal \aleph_0 - indeed, \aleph_1 is infinitely larger than \aleph_0 . What is their sum corresponding to $S_n(\Theta)$ and $S_n(x)$? Since each irrational number is arbitrarily close to a rational number and

since the sum for all rational numbers is 0, then one might surmise that the sum for irrational numbers also has the value 0 if the sum does not diverge. More precisely, can the sum diverge? If the sum $S_n(x)$ were to equal 0 at all points - at least for "large enough" n , and not just the rational values of x , then its derivative $S'_n(x)$ would equal 0 as well. This may be determined by recognizing that $S_n(x)$ is of the form $N(x)/D(x)$. From simple calculus,

$$S'_n(x) = \frac{[D(n)N'(x) - D'(x)N(x)]}{D^2(x)} \quad (15)$$

By construction, $D(x)$ never equals 0 while $N(x)$ always does. Recall $x^n = 1; x \neq 1$.

Therefore,

$$S'_n(x) = N'(x)/D(x) = -nx^{n-1}/(1-x) \quad (16)$$

and so $N'(x)$ must equal 0. This means that

$$nx^{n-1} = 0 \quad (17)$$

Since $x^n = 1$, one obtains

$$n/x = 0 \quad (18)$$

Remembering that n becomes arbitrarily large while x is never larger than 1 means that Eq. (18) is never realized. $S'_n(x)$ never equals 0, and so $S_n(x)$ does not equal 0 at all points. Indeed, since \aleph_0 is infinitely smaller than \aleph_1 , $S_n(x)$ almost never equals 0. Thus, the initial conclusion is, in fact, false.

Lest the reader be unsold by the preceding discussion, there is an alternative way to investigate the sum given in Eq. (6) and rewritten as Eq. (7). Indeed, one may recast the sum $[1 + x + x^2 + \dots + x^{n-1}]$ as

$$T_n(x) = T_{n,0}(x) + T_{n,1}(x) + T_{n,2}(x) + \dots + T_{n,n-1}(x) \quad (19)$$

For all x chosen such that $\Theta = m/n$, where m and n are integers,

$$xT_n(x) = T_n(x) \quad (20)$$

Then, either $x = 0$, in which case $n = 1$, or $T_n(x) = 0$. Therefore, $S_n(x) = 0$ for all $n \neq 1$.

Similarly, for all x chosen such that $\Theta = m/n$, where m and n are integers,

$$[T_n(x)]^2 = nT_n(x) \quad (21)$$

For this situation, $n = 1$ is an allowed solution. Other solutions are $[T_n(x)] = n$ and $[T_n(x)] = 0$. Consider the individual terms, e.g., $T_{n,k}(x)$. Then it might appear that

$$\Re[T_n(x)] = n \quad (22)$$

However, $\Re[T_{n,k}(x)] < 1$ for all $k \neq 0$. Therefore, the sum of the terms $\Re[T_{n,k}(x)] \leq n$, where equality is found only for $n = 1$. This implies that the only general solution for arbitrary integer n is $T_n(x) = 0$.

CHEMICAL SIGNIFICANCE

The foregoing investigation of the angular independence of certain sets of atomic orbitals has implications for chemistry. First, consider homoleptic ions and molecules such as BBr_3 , $[\text{ICl}_4]^-$, and $[\text{XeF}_5]^-$, with 3-, 4-, and 5-fold symmetry and bond angles of $2\pi/3$, $\pi/2$, and $2\pi/5$, respectively. These species can be compared to NF_3 , $[\text{IF}_4]^+$, and IF_5 , which lack the symmetries of the first set of species. Second, there are also regular polygonal rings such as $[\text{C}_5\text{H}_5]^-$, C_6H_6 , $[\text{C}_7\text{H}_7]^+$, and $[\text{C}_8\text{H}_8]^{2-}$, with 5-, 6-, 7-, and 8-fold symmetry and bond angles (formed by two adjacent carbons and the n -fold symmetry axes) such as $\pi/5$, $\pi/3$, $2\pi/7$, and $\pi/4$. These species contrast with $[\text{C}_5\text{H}_5]^-$, $[\text{C}_6\text{H}_6]^+$, $[\text{C}_7\text{H}_7]^-$, and C_8H_8 . In other words, the geometry is not merely due to the fact that these species are of the type AB_3 , AB_4 , and AB_5 for the first set and C_nH_n , ($n = 5, 6, 7, 8$) for the second. A close examination of the coefficients of the real molecular orbitals, as opposed to the complex formulation, indicates unequal electron densities for all atoms in systems having D_{nh} point-group symmetry.

Interestingly, the first set of carbon-containing rings gives us an even simpler proof of our angular independence result. According to the textbook literature,⁶ within the Hückel molecular orbital approximation for an N -carbon ring, a simple expression for the coefficient $b_m^{(k)}$ on of the m^{th} orbital, ψ_m on carbon atom k is given by

$$b_m^{(k)} = C_k \cos(2\pi mk / N) \quad (23)$$

C_k is the normalization factor and is the same for all $k \neq N$. It is seen that $k = N$ is a constant function because $\cos(0)$ equals 1 and so has a different normalization factor from the other solutions.

However, the N -dimensional vector that corresponds to the m^{th} molecular orbital, ψ_m , is orthogonal to

other all eigenfunction solutions including ψ_N . Since the coefficient at all atoms in the lowest energy solution for the n -atom ring equals the constant $(1/\sqrt{N})$, this means that the sum over all k (including N) vanishes:

$$\sum_{k=1}^N (1/\sqrt{N}) C_k [\cos(2\pi mk/N)] = 0 \quad (24)$$

However, the common factors $(1/\sqrt{N})$ and C_k cannot equal zero. Therefore, one concludes that

$$\sum_{k=1}^N \cos(2\pi mk/N) = 0 \quad (25)$$

Thus, for specified angles, one apiece for each size of the carbon ring, and within a multiplicative factor, angular independence has been demonstrated, at least for the class of ions and molecules considered.

Therefore, rational numbers appear to be adequate for the understanding and, at least heuristic, validity of the conditions required for angular independence. Indeed, for a planar homocyclic system, most often carbocyclic C_nH_n with some charge or another, consider the molecular orbitals. If each member of a degenerate set of molecular orbitals is equally occupied (either both singly or both doubly occupied), then equal electron density occurs at each atom. Accordingly, C_6H_6 , with point-group symmetry D_{6h} , has uniform electron density at each atom. So does $[C_5H_5]^-$, with point-group symmetry D_{5h} , but neutral C_5H_5 does not, even with with point-group symmetry D_{5h} . That the last system also will undergo Jahn-Teller distortion only exacerbates or exaggerates the nonuniformity of charges on carbon.

There are some other species that are worthy of mention at this point. For example, consider the cyclononatetraenide ion, $[C_9H_9]^-$, which has D_{9h} point-group symmetry in both solution, and in numerous diverse salts and complexes.⁷ However, the nonacyano derivative, $[C_9(CN)_9]^-$, is expected to have only 2-fold symmetry because of repulsion between the substituents according to calculational theory.⁸ Nonetheless, this anion is still expected to remain the conjugate base of an exceptionally strong acid as well as a desirable synthetic goal for the organic chemist.

Furthermore, higher species with the formula C_nH_n (neutral and charged, $n > 9$) lack D_{nh} symmetry. For example, calculational theory shows the still-unknown

$[C_{11}H_{11}]^+$ to have 6 minima, none of which have D_{11h} symmetry.⁹ Indeed, the well-known and highly stable [18]-annulene $C_{18}H_{18}$, not only lacks D_{18h} symmetry, but seemingly lacks even the customarily believed D_{6h} point-group symmetry.¹⁰ Even for these species with $n \leq 9$, when unequal occupancy of degenerate molecular orbitals occurs, there exists the possibility of blocking D_{nh} point-group symmetry. After all, as drawn, some of the degenerate molecular orbitals have nodes at some of the atoms and, therefore, zero electron density at those atoms. Since the other atoms have nonzero coefficients, the electron density is positive, and the orbital electron density lacks D_{nh} point-group symmetry.

CONCLUSION

Within the spirit of Unsöld's theorem, certain conditions have been found under which a collection of atomic orbitals or molecular orbitals are angularly independent.

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SAŽETAK

O kutnoj neovisnosti setova atomskih orbitala

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Istraživani su uvjeti pod kojima set atomskih orbitala postaje kutno neovisan, za atomske i molekulske sisteme. Razmatrano je kako se ovi rezultati mogu primjeniti na različite molekule.