Orbital Exchange Calculations: An Alternative View of the Chemical Bond

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Abstract

The purpose of this paper is to explore a model of the chemical bond which does not assume that the electrons of the chemical bonding electron pair can be unambiguously identified with either the left hand or right hand of the bonding atoms when their orbitals overlap to bond. In order to provide maximum flexibility in the selection of the electron's orbitals, the orbitals have been represented as spatial arrays and the calculations performed numerically. This model of the chemical bond assumes that the identifiability of the bonding electrons is a function of 1-(overlap/(1+overlap)) where the overlap of the two bonding electron's orbitals is calculated in the usual manner. The kinetic energy of the bonding electron pair and the energy required to meet the orthogonality requirements, mandated by the Pauli principle, are a function of overlap/(1+overlap). The model assumes that the bonding orbitals are straight-forward atomic orbitals or hybrids of these atomic orbitals. The results obtained by applying this simple approach to eleven di-atomics and seven common poly-atomics are quite good. The calculated bond lengths are generally within 0.005Å of the measured values and bond energies to within a few percent. Bond lengths for bonds to H are about 0.02 Å high. Except for H_2, bond lengths are determined, independent of bond energy, at that point where overlap/(1+overlap) equals 0.5.

I. INTRODUCTION

The purpose of the work described here is to test a model for the chemical bond that assumes that the two electrons of the bonding pair are not completely identifiable, with respect to their source atom, when their orbitals overlap. Were the bonding electrons not identifiable in the overlap region it would be impossible to unambiguously identify every element of the orbital's distribution with either the atom on the right hand or the atom on the left side of the bond. Since the identification is ambiguous, nature would allow one to make the most energy favorable identification, which is to picture the electrons spread out over the whole bond when calculating the kinetic energy.

Distributions are representations of order (as differentiated from disorder or randomness). Narrow distributions represent high order, broader distributions less order. When two distributions overlap the order associated with the system decreases with their overlap because, in the overlap region, one can no longer identify each distribution element with a particular distribution. Overlap introduces randomness. Electron kinetic energy relates to order and electron distributions to representations of order.

In his early work[1] applying LCAO-MO theory to H_2, Coulson assumed that the two electrons of the bonding pair were identifiable. In subsequent applications of LCAO-MO theory to this molecule and more complex molecules, the same assumption has been made[2]. This assumption apparently has its origin in the view that a single electron can be uniquely assigned to one of two non-orthogonal overlapping spatial orbitals of different spin.

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That the electrons of two overlapping *orthogonal* spatial orbitals *of the same spin* are not distinguishable is manifest in the so-called "exchange integral"[3]. The exchange integral evaluates the electron-electron repulsion in the overlap region. The total electron-electron repulsion is reduced by this quantity (Since an electron cannot repel itself.). Likewise, it is reasonable to hypothesize that the electrons of the bonding pair, which have *non-orthogonal* spatial orbitals *of different spin*, are also not distinguishable in the overlap region.

A. Numerical Methods

The calculations described herein are done numerically with the orbitals represented in huge identical spatial arrays of the form phi[i][j][k] where i is the index for the radius from the molecular axis, j represents the distance along the molecular axis and k is an array identifier. (Only two spatial coordinates are needed since the electron structure is axially symmetric or can be treated as such.) In a numerical calculation, integrals become summations. For example, the electron-electron repulsion becomes:

electron-electron repulsion = constant

$$\sum_{i=0}^{IMAX} \sum_{j=0}^{JMAX} \sum_{l=0}^{IMAX} \sum_{m=0}^{JMAX} \text{phi[i][j][left array] phi[l][m][right array] ovr[ndist][i][l]} ,$$

(1)

where

ovr[ndist][i][l] is the reciprocal of distance between phi[i][j][left array] and phi[l][m]{right array} and

ndist = absolute value(-j+m).

The value of the constant depends on the dimensions associated with the array elements.

As a practical matter, for the repulsion calculation, adjacent phi[i][j] and phi[l][m] are consolidated to reduce the number of array elements. The electron-electron repulsion calculation requires less resolution than the kinetic energy calculation described below.

Numerical methods are advantageous because they do not presume a particular functional form for the orbitals. These numerical methods are particularly advantageous in making bonding orbitals which are orthogonal to the opposite core 1s electrons. Numerical methods permit the use of iterative analytical methods to find the lowest energy orbitals which meet the orthogonalization requirements.

B. Kinetic Energy of Combined Orbital

Kinetic energy (KE) of an orbital is determined in the usual manner:

$$\text{KE} = \iint \phi \nabla^2 \phi \, 2\pi \, r \, dr \, dl,$$

(2)

where ϕ represents a generic orbital and ∇^2 is the Laplacian. The variable r represents the radial distance from the bond axis and l represents the distance along the bond axis. Using numerical methods this becomes:

KE =constant $\sum_{i=0}^{IMAX} \sum_{j=1}^{JMAX}$

$((\text{rrdn[i] (phi[i}-1][j] - \text{phi[i][j])} - \text{rrup[i](phi[i][j]} - \text{phi[i}+1][j]))) \text{phi[i][j]} +$

constant $\sum_{i=0}^{IMAX} \sum_{j=1}^{JMAX}$

$((\text{phi[i][j}+1] - \text{phi[i][j])} - (\text{phi[i][j]} - \text{phi[i][j}-1])) (\text{phi[i][j] rr[i]}) ,$

(3)

where

rr[i] is the axial radius at i

rrdn[i] is one-half unit down the axial radius from rr[i]

rrup[i] is one-half unit up the axial radius from rr[i].

(In the equation above i=0 leads to phi with a negative index (and therefore not determined). This is of no consequence because its factor, rrdn[i] = 0 when i=0.)

The value of the constant depends on the dimensions associated with the array elements.

As a practical matter, to increase accuracy while not sacrificing processing speed, finer arrays have been created for areas close to the nucleus (where phi changes faster) and coarser arrays at a distance from the nucleus.

Another important quantity is the overlap of the bonding orbitals which is calculated in the usual manner:

$$\text{overlap} = \int\int \phi_l \, \phi_r \, 2\pi \, r \; dr \, dl, \tag{4}$$

where ϕ_l represents the bonding atomic orbital on the left and ϕ_r the bonding atomic orbital on the right. The orbitals ϕ_l and ϕ_r are atomic orbitals which have been made orthogonal to the core electrons on the opposite atom. Overlap has a range from 0.0 to 1.0. The atomic orbitals which have been made orthogonal to the core electrons on the opposite atom have no net overlap with those core-electron orbitals:

$$\int\int \phi_l \, \phi_{1sr} \, 2\pi \, r \; dr \, dl = 0.0 \text{ and} \tag{5}$$

$$\int\int \phi_r \, \phi_{1sl} \, 2\pi \, r \; dr \, dl = 0.0. \tag{6}$$

To calculate the kinetic energy when the identification of components of the orbitals as right versus left is ambiguous, one creates a hypothetical orbital, referred to as the combined orbital, ϕ_{l+r} which distributes the electron equally on the atoms left and right of the bond while preserving the electron density map of the original left and right atomic orbitals combined and meeting the orthogonality requirements.

For each spatial array element one computes:

phi[i][j][combined] = square root
   (phi[i][j][right_ortho] phi[i][j][right_ortho]+phi[i][j][left_ortho] phi[i][j][left_ortho]) .

$$\tag{7}$$

When phi[i][j][left_ortho] and phi[i][j][right_ortho] are negative, a negative sign is given to the combined orbital. The array elements phi[i][j][left_ortho] and phi[i][j][right_ortho] are the array elements of atomic orbitals which have been altered to create orbitals which are orthogonal to the core electrons of the opposite atom (ϕ_l and ϕ_r). The analytic procedure used to convert the set of array elements, phi[i][j][left] and phi[i][j][right], the original atomic orbitals elements, designated as ϕ_l and ϕ_r, to the set phi[i][j][left_ortho] and phi[i][j][right_ortho] is described in Section IIIA below.

Note that the combined orbital is not the sum of the right and left orbitals as this would change the electron density map by adding electron density between the atoms. The author knows of no explicit functions which describe the set phi[i][j][left_ortho] and phi[i][j][right_ortho] or ϕ_{l+r}. These calculations can only be performed numerically.

The kinetic energy change associated with overlap of the atomic orbitals is designated KE_{bond}. KE_{bond} is calculated:

$$KE_{bond} = (\text{overlap}/(1+\text{overlap})) \, KE_{net} \tag{8}$$

$$\text{where} \quad KE_{net} = (KE_{\phi l+r} - KE_{\phi l} - KE_{\phi r}) \tag{9}$$

The total kinetic energy change for the bond is 2.0 times KE_{bond}. (KE_{bond} is for one electron.) This approach to the kinetic energy assumes that, to the extent of overlap/(1+overlap), the electrons are spread over the bonding orbitals of both of the bonding atoms. To the extent of 1-(overlap/(1+overlap)), the kinetic energy is that of the atomic orbitals which have been made orthogonal to the opposite core electrons (the set phi[i][j][left_ortho] and phi[i][j][right_ortho]).

C. H_2

Applying this approach to find the kinetic energy of the H_2 bonding electrons, I find a bond energy, D_e, of 4.06 eV at a bond length of 0.753Å using an orbital scale factor (orbital reduction factor) of 1.15. (See column B of Table I for the results of this calculation at 0.754 Å.) The actual values are D_e equal to 4.75 at a bond length of 0.741 Å. Some improvement can be made by polarizing the H 1s orbitals by adding a small amount of $2p_z$ (0.008) with a 2pz scale factor of 3.50 to the H 1s orbital while retaining an orbital scale factor of 1.15. This results in a bond energy, D_e, of 4.67 eV at a bond length of 0.754Å. (See column C of Table I for the results of this calculation at 0.754 Å.) These are remarkably good results for such a simple approach, but since the H_2 results could be fortuitous, the investigation needs to be extended to other molecules.

For purposes of comparison, Coulson's early MO calculations have been reproduced here. These results are shown in Table II. Coulson's MO approach gives poorer agreement with experiment, with D_e, of 3.49 eV.

Coulson gives a breakdown of similar calculations for H_2 at 1.41 Bohr (0.746Å) in his later book[4]. These are accurate to only about 0.1 eV. Coulson gives 17.8 eV, 19.3 eV, 27.2 eV and 16.2 eV for the electronic repulsion, nuclear repulsion, energy of two H atoms, and "energy of each separate molecular orbital", respectively. My similar calculations for the same quantities at 1.41 Bohr give 17.824 eV, 19.299 eV, 27.220 eV and 16.095 eV.

Table I. Components of H_2 calculations at 0.754 Å (Energy in electron volts)

A. Component	B. Unpolarized 1s Orbital orbital factor= 1.15	C. Polarized 1s Orbital $\phi = fs_b$ 1s+fp_b $2p_z$ fp_b fp_b=0.008 $2p_z$ orbital factor=3.50 1s orbital factor= 1.15
Kinetic energy gain associated with sigma orbital overlap (2 KE_{bond})	4.1416	4.1365
Nuclear-nuclear repulsion energy	-19.0957	-19.0957
Nuclear to opposite bonding orbital energy	34.3914	36.8282
Electron-electron repulsion energy	-14.7743	-16.0927
Energy for H atom compression/polarization	-0.6056	-1.1023

Total Energy	**4.06**	**4.67**

Table II. Reproduction of Coulson's MO H_2 calculation at 1.40 Bohr or 0.741 Å (Energy in electron volts)

Component	Contribution to total energy
Total kinetic energy of molecular orbitals	-30.8357
Nuclear-nuclear repulsion energy	-19.4367
Nuclear to molecular orbitals potential energy	98.8386
Electron-electron repulsion energy	-17.8501
Energy of two H atoms orbital factor=1.197	-27.2259
Total	**3.490**

Note: Actual energy minimum is at 0.731 Å

III. ATOMIC ORBITALS AND ORBITAL SCALE FACTORS

For the calculations described here, the atomic orbitals of Duncanson and Coulson[5] have been used. The quantities Duncanson and Coulson call μ and μc (These are equivalent to the effective nuclear charge [or orbital scale factor] for 2s and 2p electrons.), are increased by factors (called fact herein) ranging from 1.0 to 1.055. Contracting an atomic orbital raises an atom's energy but enables a stronger bond. Table III gives the approximate energy impact of these small changes in the atomic parameters. The energy impact of these changes is usually less than 0.4 eV and is spread among several bonds in a polyatomic molecule. The factors are usually not difficult to establish since the energy increases exponentially as the factor is increased. (The orbital scale factor for C+ is taken as 1.10 and that for O- as 0.93.)

Table II. Estimated Energy (eV) Associated with Orbital Scale Factor

	Factors					
Atom	1.01	1.02	1.03	1.04	1.05	1.055
B	—	0.01	0.05	0.09	0.15	
C	0.01	0.04	0.11	0.20	0.33	0.44
N	0.03	0.11	0.22	0.41		
O	0	0.10	0.27	0.54		
F	0.04	0.20	0.50			

III. ORTHOGONALITY

For calculations involving multi-electron atoms, orthogonality requirements must be considered. Consistent with the Pauli principle, the orbitals of electrons of the same spin must be orthogonal. When an atom presents a bonding orbital to the opposite atom two types of changes must be made to meet the orthogonality requirements: the bonding orbital must be made orthogonal to the "core" electrons on the opposite atom and the not-bonding electron orbitals must be changed/reconfigured to be orthogonal to the bonding orbital from the opposite atom.

A. Core Orthogonality

Herein, a bonding atomic orbital is made orthogonal to the opposite core by placing a node(s) in the orbital at the position of the nodes in the opposite bonding orbital. Since these calculations are performed analytically, using arrays to represent the orbitals, the orthogonalization is relatively easy. The goal is to find an orthogonal orbital with the same charge distribution (and potential energy) as the original atomic orbital. An orthogonal orbital with exactly the same charge density as the original atomic orbital is impossible because this would require a discontinuity in the function at the node. However, an iterative analytical procedure produces a satisfactory approximation of an orthogonal orbital, with approximately the same charge density as the original atomic orbital, but without a discontinuity.

An approximate, and normalized orbital is constructed from the atomic orbital which has a relatively gentle transition at the node. The approximation procedure does not permit a displacement of charge density from one side of the nucleus to another or cause a net displacement of charge toward, or away from, the nucleus. The bond energy is calculated for successively sharper node transitions. [Alternatively, just the difference $KE_{bond} - (KE_\phi - KE_\phi)$ could be calculated]. Usually, as the transition becomes sharper, the bond energy will improve slowly, and the overlap change little. At some point the bond energy will decrease. The orbital that has the best energy is utilized. Sometimes, usually when one or both of the bonding atoms are "soft" (H, light elements), the bond energy does not improve as the node transition becomes sharper. In these cases the bond energy decreases slowly as the node transition sharpens. At some point the bond energy will begin to deteriorate more quickly for a given change in the node transition. The function just prior to the inflection point is chosen. Although the selection of the orthogonal bonding orbital is sometimes not precise, the process does not appear to introduce an error of more than a few percent even in the worst cases.

There is a reason that the bond energy is relatively stable with changes in the bonding orbital. As the node transition sharpens, KE_ϕ increases. The increase in KE_ϕ is accompanied by a corresponding increase in $KE_{\phi l+r}$. The difference between these two quantities remains relatively constant.

Making the bonding atomic orbital orthogonal to the opposite core has the salubrious effect of making the two overlapping bonding orbitals positive where the other is positive, and negative where the other is negative. The combined orbital, ϕ_{l+r} has no discontinuities.

B. Valence Orthogonality

When an atom presents a bonding orbital to the opposite atom, the opposite atom must change/reconfigure so that its orbitals, with the exception of its bonding orbital, are orthogonal to the bonding orbital. This is referred to here as valence electron orthogonalization. Consider atoms in di-atomic molecules. The atoms in di-atomic molecules typically have an s^2p^n configuration. To orthogonalize, the atoms reconfigure to $sp_z p_\perp^{n-1} sp_o$ where sp_o is an opposing hybrid orbital (taking z as the bond axis). The 2s and $2p_z$ orbitals of the atom hybridize to form an opposing orbital of the form $fs_o\,2s - fp_o\,2p_z$, (fs_o stands for fraction s opposing) and a bonding orbital of the form $fs_b\,2s + fp_b\,2p_z$ (fs_b stands for fraction s bonding),where $fs_o fs_o + fp_o fp_o = 1$. The coefficients fs_o and fp_o are chosen to make the opposing orbital orthogonal to the opposite bonding orbital. The opposing orbitals determine the bonding orbitals ($fs_b = fp_o$ and $fp_b = fs_o$). In the case of a di-atomic, fs_{or} (the subscripts $_r$ and $_l$ indicate right and left) and fp_{or} and fs_{ol} and fp_{ol} are chosen to satisfy the simultaneous equations:

$$fs_{bl}\,fs_{or}\,\text{overlap}_{s\_s\_n} - fp_{bl}\,fp_{or}\,\text{overlap}_{pz\_pz\_n} +$$
$$fs_{or}\,fp_{bl}\,\text{overlap}_{pz\_s\_n} - fp_{or}\,fs_{bl}\,\text{overlap}_{s\_pz\_n} = 0.0 \ \text{and} \tag{10a}$$

$$fs_{br}\,fs_{ol}\,\text{overlap}_{s\_s\_n} - fp_{br}\,fp_{ol}\,\text{overlap}_{pz\_pz\_n} +$$
$$fs_{al}\,fp_{br}\,\text{overlap}_{pz\_s\_n} - fp_{al}\,fs_{br}\,\text{overlap}_{s\_pz\_n} = 0.0\ . \tag{10b}$$

The overlap $_{s\_s\_n}$ is the overlap of the 2s atomic orbitals (not core orthogonalized) and etc.

C. Orthogonality Energy

The orthogonalizations described above in Section IIIA need only be taken to the extent that the bonding atomic orbitals are identifiable (when the orbitals are identifiable the bond is said to be "not bonding"). The measure of identifiability (bond is "bonding") is termed fraction_bonding and is calculated:

$$\text{fraction\_bonding} = \text{overlap}/(1.0 + \text{overlap}). \tag{11}$$

The energy required to core orthogonalize a bonding orbital, KE_{core_ortho}, is:

$$KE_{core\_ortho} = (1.0 - \text{fraction\_bonding})\,(KE_\phi - KE_\phi) \tag{12}$$

where KE_ϕ is the kinetic energy of the core orthogonalized atomic orbital and KE_ϕ is the kinetic energy of the original atomic orbital.

For two hybrid sigma bonding orbitals (comprised of the 2s and $2p_z$ atomic orbitals) of the form $\phi_r = fs_{br}\,2s + fp_{br}\,2p_z$ and $\phi_l = fs_{bl}\,2s + fp_{bl}\,2p_z$, the energy to core orthogonalize the hybrid orbitals, KE_{core_ortho}, is:

$$KE_{core\_ortho} = (1 - \text{fraction\_bonding})$$
$$((\ fs_{bl}\,fs_{br}\,fs_{bl}\,fs_{br}\,(KE_{s\_sal} - KE_{sl}) + fs_{bl}\,fs_{br}\,fs_{bl}\,fs_{br}\,(KE_{s\_sar} - KE_{sr}) +$$
$$fs_{bl}\,fp_{br}\,fs_{bl}\,fp_{br}\,(KE_{s\_pzal} - KE_{sl}) + fs_{bl}\,fp_{br}\,fs_{bl}\,fp_{br}\,(KE_{pz\_sar} - KE_{pzr}) +$$
$$fp_{bl}\,fs_{br}\,fp_{bl}\,fs_{br}\,(KE_{pz\_sal} - KE_{pzl}) + fp_{bl}\,fs_{br}\,fp_{bl}\,fs_{br}\,(KE_{s\_pzar} - KE_{sr}) +$$

$$fp_{bl}\ fp_{br}\ fp_{bl}\ fp_{br}\ (KE_{pz\_pzal} - KE_{pzl}) + fp_{bl}\ fp_{br}\ fp_{bl}\ fp_{br}\ (KE_{pz\_pzar} - KE_{pzr}))$$

$$(13)$$

where KE_{sl} and KE_{pzl} are the kinetic energies of the left 2s and $2p_z$ initial atomic orbitals and, KE_{sr} and KE_{pzr} are those on the right. KE_{s_sal} is the kinetic energy of the s orbital on the left which has been orthogonalized with the right hand s (the subscript "a" indicates the orthogonalized orbital). KE_{s_pzal} is the kinetic energy of the s orbital on the left which has been orthogonalized with the right hand $2p_z$. KE_{pz_sal} is kinetic energy of the $2p_z$ orbital on the left which has been orthogonalized with the right hand s. KE_{pz_pzal} is kinetic energy of the $2p_z$ orbital on the left which has been orthogonalized with the right hand p_z. The suffix $_r$ indicates the corresponding orbitals on the right.

In the potential energy calculations, the reconfiguration required to meet the valence orthogonalization requirement need only to be taken to the extent of (1.0-fraction_bonding). If a 2s orbital is reconfigured to a fs_o 2s-fp_o $2p_z$ hybrid to become orthogonal, then, in the potential energy calculations, the electron is considered to be in an 2s orbital for fraction_bonding and in a fs_o 2s-fp_o $2p_z$ hybrid orbital for (1.0-fraction_bonding). In this latter case, the bond energy is also adjusted for the energy required to promote the s to p. If the energy to promote an s to p is given by stop, then the bond energy is decreased by stop fp_o fp_o (1.0-fraction_bonding).

A table of the energies required for the 2s to 2p promotion for the first row atoms has been developed for this work. The stop values are in the order B≤C<N≤O≤F, positive atom≤neutral atom≤negative atom, high symmetry≤low symmetry and unpaired≤paired. The stop values used in this work are presented in Table IV. While stop values could be calculated for each bond, a table-driven approach has been utilized because it results in shorter computation times and does not appear to degrade accuracy. The stop values have been applied consistently (For example, the C sp_o (paired) value is used in three calculations and the N sp_o (paired) value in four.). Since fraction_bonding is typically 0.5 and fp_o fp_o~0.5, the energy charged to a bond for 2s to 2p promotion is typically less than or equal to half the stop value.

Table IV. Estimated Energy to Promote 2s to 2p (stop) Values

Species	2p Orbital Type	stop Energy/eV
B	sp_o (unpaired)	4.35
B	sp_o (paired)	6.55
C+	sp_o (unpaired)	4.35
C+	p_π	5.05
C	T_d	6.55
C	sp_o (unpaired)	6.55
C	$p_\perp$ (unbonded)	6.95
C	p_π	7.50
C	sp_o (paired,bonding)	7.90
N	sp_o (paired)	12.40
O	sp_o (paired)	16.60
O-	sp_o (paired)	16.60

D. Core Orthogonality of a Second Sigma Pair

Most atoms in di-atomic molecules and some atoms in other molecules have more than one bond pair of electrons with sigma symmetry. For example consider N_2. N has the configuration $1s^2 2s^2 2p^3$ or $1s^2 2s^2 2p_{\perp}^2 2p_z$. There are two possibilities for sigma bonds: an sp hybrid to sp hybrid bond and an s to s bond. To the extent that one pair (or both pairs) of the bonding electrons are not identifiable, (fraction_bonding), the second 2s electron remains in place. To the extent that this s to s bond pair is not bonding (1-fraction_bonding$_{second\_set}$), the second 2s must also be made orthogonal to the opposite core electrons. The energy to core orthogonalize a second sigma orbital $KE_{core\_ortho\_x}$, is, in general, for the left:

$$KE_{core\_ortho\_xl} = fraction\_bonding \ (1.0\text{-}fraction\_bonding_{second\_set})$$
$$(fs_{bl} \ fs_{br} \ fs_{bl} \ fs_{br} \ (KE_{s\_sal} - KE_{sl}) +$$
$$fs_{bl} \ fp_{br} \ fs_{bl} \ fp_{br} \ (KE_{s\_pzal} - KE_{sl}) +$$
$$fp_{bl} \ fs_{br} \ fp_{bl} \ fs_{br} \ (KE_{pz\_sal} - KE_{pzl}) +$$
$$fp_{bl} \ fp_{br} \ fp_{bl} \ fp_{br} \ (KE_{pz\_pzal} - KE_{pzl})). \tag{14}$$

The calculations for the right side are analogous to those on the left.

As (12) indicates the $KE_{core\_ortho\_x}$ penalty is taken only to the extent of overall fraction_bonding. If there are second sigma bonding orbitals on both sides of the bond and these bond, then the $KE_{core\_ortho\_x}$ penalty is further reduced to the extent that the second set of sigma orbitals themselves bond, fraction_bonding$_{second\_set}$.

IV. SIGMA HYBRID ORBITAL OVERLAP AND KINETIC ENERGY

For a single set of hybrid sigma bonding orbitals of the form $\phi_r = fs_{br} \, 2s + fp_{br} \, 2p_z$ and $\phi_l = fs_{brl} \, 2s + fp_{bl} \, 2p_z$, the quantities overlap and KE_{bond} are:

$$overlap = fs_{bl} \ fs_{br} \ overlap_{s\text{-}s} + fp_{bl} \ fp_{br} \ overlap_{pz\text{-}pz} +$$
$$fp_{bl} \ fs_{br} \ overlap_{pz\text{-}s} + fs_{bl} \ fp_{br} \ overlap_{s\text{-}pz} \ and \tag{15}$$

$$KE_{bond} = (1.0/(1.0 + overlap)) \ (fs_{bl} \ fs_{br} \ overlap_{s\text{-}s} \ KE_{net\ s\text{-}s} +$$
$$fp_{bl} \ fp_{br} \ overlap_{pz\text{-}pz} \ KE_{net\ pz\text{-}pz} + fp_{bl} \ fs_{br} \ overlap_{pz\text{-}s} \ KE_{net\ pz\text{-}s} +$$
$$fs_{bl} \ fp_{br} \ overlap_{s\text{-}pz} \ KE_{net\ s\text{-}pz}). \tag{16}$$

Obviously, overlap cannot exceed 1.0, nor can fraction_bonding exceed 0.5. Except for the bonds of some "soft" atoms (H typically) fraction_bonding generally reaches the limit of 0.5. The limitation on overlap makes it possible, in most cases, to determine bond lengths without a complete treatment of bond energy. With a few exceptions, bond energy increases as the bond length decreases until fraction_bonding = 0.5 is reached.

V. DUAL AND PARALLEL BONDS

As mentioned above, most atoms in di-atomic molecules and some atoms in other molecules have more than single pair of electrons that have the appropriate symmetry for sigma

bonding. Both of these pairs bond. This results in what is described herein as dual bonding or parallel bonding. Dual/parallel bonds are not double bonds in the traditional sense, *i.e* a sigma bond and a pi bond. Dual/parallel bonds entail two sigma bonds. Parallel bonding differs from dual bonding in that the second set of bonding orbitals does not reconfigure when the bond is not bonding. Dual bonding is far more common than parallel bonding. Parallel bonding is exhibited in F_2, He_2^+ and partially in other compounds.

A. Dual Bonding

The calculation of dual overlap, fraction_bonding and KE_{bond} differs somewhat from that of the single sigma bond because simultaneous overlaps must be taken in account.

Consider two atoms each with a sigma bonding configuration of $2s^2 2p_z$ (e.g. N_2). The dual bond between these atoms could be considered as an sp-sp hybrid bond and an s-s bond with each weighted by 0.5. Alternatively, the dual bond between these atoms could be considered as an sp-sp hybrid bond, an s-s bond, an sp-s bond and an s-sp bond with each weighted by 0.25. In the latter case ($s^2 p_z$ on both sides), the relevant quantities are:

$$\text{fraction\_bonding }_{s\text{-}s} = \text{overlap }_{s\_s}/(1.0 + \text{overlap }_{s\_s}) \tag{17a}$$

$$\text{fraction\_bonding }_{s\text{-}sp} = \text{overlap }_{s\_sp}/(1.0 + \text{overlap }_{s\_sp}) \tag{17b}$$

$$\text{fraction\_bonding }_{sp\text{-}s} = \text{overlap }_{sp\_s}/(1.0 + \text{overlap }_{sp\_s}) \tag{17c}$$

$$\text{fraction\_bonding }_{sp\text{-}sp} = \text{overlap }_{sp\_sp}/(1.0 + \text{overlap }_{sp\_sp}) \tag{17d}$$

$$\text{fraction\_bonding }_{ave} = 0.25 \,(\text{fraction\_bonding }_{s\text{-}s} + \text{fraction\_bonding }_{s\text{-}sp} +$$
$$\text{fraction\_bonding }_{sp\text{-}s} + \text{fraction\_bonding }_{sp\text{-}sp}) \tag{18}$$

$$\text{overlap }_{ave} = \text{fraction\_bonding }_{ave}/(1.0 - \text{fraction\_bonding }_{ave}) \tag{19}$$

$$\text{simultaneous\_bond }_{s\text{-}s/sp\text{-}sp} = \text{fraction\_bonding }_{s\text{-}s} \,\text{fraction\_bonding }_{sp\text{-}sp} \tag{20a}$$

$$\text{simultaneous\_bond }_{s\text{-}sp/sp\text{-}s} = \text{fraction\_bonding }_{s\text{-}sp} \,\text{fraction\_bonding }_{sp\text{-}s} \tag{20b}$$

$$\text{overlap }_{s\text{-}s/sp\text{-}sp} = \text{simultaneous\_bond }_{s\text{-}s/sp\text{-}sp} /(1.0 - \text{simultaneous\_bond }_{s\text{-}s/sp\text{-}sp}) \tag{20a}$$

$$\text{overlap }_{s\text{-}sp/sp\text{-}s} = \text{simultaneous\_bond }_{s\text{-}sp/sp\text{-}s}/(1.0 - \text{simultaneous\_bond }_{s\text{-}sp/sp\text{-}s}) \tag{20b}$$

$$\text{overlap} = 2 \,\text{overlap }_{ave} - \text{overlap }_{sp\text{-}s/s\text{-}sp} - \text{overlap }_{s\text{-}sp/sp\text{-}s} \tag{21}$$

$$\text{fraction\_bonding} = \text{overlap}/(1.0 + \text{overlap})$$

$$\text{factor} = \text{fraction\_bonding}/\text{fraction\_bonding }_{ave} \tag{22}$$

$$KE_{bond} =$$
$$\text{factor } 0.25 \,(KE_{bond\ s\text{-}s} + KE_{bond\ s\text{-}sp} + KE_{bond\ sp\text{-}s} + KE_{bond\ sp\text{-}sp}) \tag{23}$$

With the N_2 bonding configurations, both sides $2s^2 2p_z$, the dual bond overlap is actually somewhat less than the overlap of the sp-sp overlap alone. This is because the s-s overlap is much less than the sp-sp overlap.

Consider two atoms each with a sigma bonding configuration of $2s^2 2p_z^2$ (e.g. O_2). In this case the relevant quantities are:

$$\text{fraction\_bonding}_{\text{sp-sp}} = \text{overlap}_{\text{sp\_sp}}/(1.0+\text{overlap}_{\text{sp\_sp}}) \tag{24}$$

$$\text{fraction\_bonding}_{\text{ave}} = \text{fraction\_bonding}_{\text{sp-sp}} \tag{25}$$

$$\text{overlap}_{\text{ave}} = \text{fraction\_bonding}_{\text{ave}}/(1.0-\text{fraction\_bonding}_{\text{ave}}) \tag{26}$$

$$\text{simultaneous\_bond}_{\text{sp-sp/sp-sp}} = \text{fraction\_bonding}_{\text{sp-sp}}\,\text{fraction\_bonding}_{\text{sp-sp}} \tag{27}$$

$$\text{overlap}_{\text{sp-sp/sp-sp}} = \text{simultaneous\_bond}_{\text{sp-sp/sp-sp}}/(1.0-\text{simultaneous\_bond}_{\text{sp-sp/sp-sp}}) \tag{28}$$

$$\text{overlap} = 2\,\text{overlap}_{\text{ave}} - 2\,\text{overlap}_{\text{sp-sp/sp-sp}} \tag{29}$$

$$\text{fraction\_bonding} = \text{overlap}/(1.0+\text{overlap})$$

$$\text{factor} = \text{fraction\_bonding}/\text{fraction\_bonding}_{\text{ave}} \tag{30}$$

$$KE_{\text{bond}} = \text{factor}\; KE_{\text{bond sp-sp}} \tag{31}$$

With these bonding configurations, both atoms $2s^2 2p_z^2$, the dual bond overlap is somewhat more than the overlap of the sp-sp overlap alone.

Consider two atoms, one with a sigma bonding configuration of $2s^2 2p_z$ and one with a sigma bonding configuration of $2s^2 2p_z^2$ (e.g. NO). In this case the relevant quantities are:

$$\text{fraction\_bonding}_{\text{s-sp}} = \text{overlap}_{\text{s\_sp}}/(1.0+\text{overlap}_{\text{s\_sp}}) \tag{32}$$

$$\text{fraction\_bonding}_{\text{sp-sp}} = \text{overlap}_{\text{sp\_sp}}/(1.0+\text{overlap}_{\text{sp\_sp}}) \tag{33}$$

$$\text{fraction\_bonding}_{\text{ave}} = 0.5\,(\text{fraction\_bonding}_{\text{s-sp}} + \text{fraction\_bonding}_{\text{sp-sp}}) \tag{34}$$

$$\text{overlap}_{\text{ave}} = \text{fraction\_bonding}_{\text{ave}}/(1.0-\text{fraction\_bonding}_{\text{ave}}) \tag{35}$$

$$\text{simultaneous\_bond}_{\text{s-sp/sp-sp}} = \text{fraction\_bonding}_{\text{s-sp}}\,\text{fraction\_bonding}_{\text{sp-sp}} \tag{36}$$

$$\text{overlap}_{\text{s-sp/sp-sp}} = \text{simultaneous\_bond}_{\text{s-sp/sp-sp}}/(1.0-\text{simultaneous\_bond}_{\text{s-sp/sp-sp}}) \tag{37}$$

$$\text{overlap} = 2\,\text{overlap}_{\text{ave}} - 2\,\text{overlap}_{\text{s-sp/sp-sp}} \tag{38}$$

$$\text{fraction\_bonding} = \text{overlap}/(1.0+\text{overlap})$$

$$\text{factor} = \text{fraction\_bonding}/\text{fraction\_bonding}_{\text{ave}} \tag{39}$$

$$KE_{\text{bond}} = \text{factor}\; 0.5\,(KE_{\text{bond s-sp}} + KE_{\text{bond sp-sp}}) \tag{40}$$

B. Parallel Bonding

Parallel bonding is a type of dual bonding that occurs when, instead of reconfiguring to orthogonalize, a second sigma orbital remains in place and forms a node to make it orthogonal to the opposite side bonding orbital. The best example of parallel bonding is F_2. F has a bonding configuration of $1s^2 2s^2 2p_z^2 2p_{xy}^3$. For parallel bonding, fraction_bonding is simply the sum of fraction_bonding for each of the two sigma bonds. So for the F_2 parallel bond:

$$\text{fraction\_bonding} = \text{fraction\_bonding}_{sp\text{-}sp} + \text{fraction\_bonding}_{sp\text{-}sp} \quad \text{and} \tag{41}$$

$$KE_{bond} = KE_{bond\ sp\text{-}sp} + KE_{bond\ sp\text{-}sp}. \tag{42}$$

Since fraction_bonding calculated in this manner is subject to the usual constraint (fraction_bonding ≤ 0.5) parallel bonding results in relatively long bond lengths and is usually associated with molecules which require p_π orthogonalization (e.g. F_2)(See Section VI.C below).

VI. PI BONDING, PI RESONANCE AND PI ORTHOGONALIZATION

A. Pi Bonding

The kinetic energy reduction associated with pi bonding, analogous to that of sigma bonding, is:

$$KE_{bond\_\pi} = \text{fraction\_bonding}_\pi \ (KE_{combined\_\pi} - KE_{\pi\_l} - KE_{\pi\_r}) \tag{43}$$
where
$$\text{fraction\_bonding}_\pi = \text{overlap}_\pi/(1.0 + \text{overlap}_\pi). \tag{44}$$

Pi overlaps are much smaller than sigma overlaps, usually in the range of 0.1 to 0.3. Pi bonding only occurs to the extent that both pi bonding orbitals have the appropriate symmetry.

B. Pi Resonance

When the bonding electron is free to move from the right bonding orbital to the left, or from the left to the right, fraction_bonding in (39) above is 0.5. The kinetic energy reduction associated with full pi resonance, $KE_{bond\_\pi\_res}$, is:

$$KE_{bond\_\pi\_res} = 0.5 \ (KE_{combined\_\pi} - KE_{\pi\_l} - KE_{\pi\_r}) \tag{45}$$

For these calculations, the energy associated with the formation of a positively charge species in a resonance is obtained from tables of ionization potentials[6]. The energy associated with the formation of negatively charged species is obtained from tables of electron affinities[7].

C. Pi Orthogonalization

When the p_π orbitals on the atom on one side of the bond are more than half full (three or four electrons) and the p_π orbitals on the other side are at least half full, then, one of each of the spin paired pi orbitals must be made orthogonal to the pi bonding orbitals from the opposite side. This orthogonalization is analogous to that described in Section IIIA above with respect to sigma bonding, with a node placed in the p_π orbital to make it orthogonal to the opposite pi bonding orbital. An analytical procedure, similar to the one used for core orthogonalization described

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above, is used to find the optimal node position and node transition. As in core orthogonalization, this procedure attempts to maintain the atomic orbital density distribution as closely as possible. Analogous to sigma bonding, the pi orthogonalization penalty is taken only to the extent of $(1.0 - \text{fraction\_bonding}_\pi)$.

VII. SECONDARY BONDING

In poly-atomic molecules, bonding occurs not only to the closest atom, but also to all atoms in the molecule with which it significantly overlaps. Secondary/tertiary bonding differs from primary bonding in three ways. First, the bond axis of the primary is retained in the secondary, tertiary, etc.. Secondly, secondary bonding is reduced by the extent of primary bonding (and the tertiary by the extent of primary and secondary and etc.). The reduction in secondary bonding, by primary bonding, is determined by the least primary bonding of the two secondary bonding orbitals. Thirdly, total overlap, including contributions from secondary and subsequent bonds, is calculated along the principle axis which is usually the primary bond axis.

The secondary (tertiary, etc.) overlap between the primary bonding orbital on the left and the secondary bonding orbital on the right is as follows:

$$\text{overlap}_{sec\_1} = fs_{bl}\, fs_{br}\, \text{overlap}_{s\text{-}s} + \cos\theta_l \cos\theta_r\, fp_{bl}\, fp_{br}\, \text{overlap}_{pz\text{-}pz} +$$
$$\cos\theta_l\, fp_{bl}\, fs_{br}\, \text{overlap}_{pz\text{-}s} + \cos\theta_r\, fs_{bl}\, fp_{br}\, \text{overlap}_{s\text{-}pz}\,, \qquad (46)$$

where θ_l is the angle between the primary axis of the left atom and the secondary (tertiary, etc.) bond axis and where θ_r is the angle between the primary axis of the right atom and the secondary (tertiary, etc.) bond axis. Notice that fs_{bl} and fp_{bl} refer to the hybridization of the primary orbital on the left and fs_{br} and fp_{br} refer to the hybridization of the secondary orbital on the right. Note also that, in general, the secondary for the left is different from the secondary on the right. The calculation of overlap_{sec_r} is analogous to that on the left. Sometimes there is a secondary on one side but none on the other (e.g. CH_4).

The overlap component along the primary bond axis, $\text{overlap}_{sec\_1\_z}$, is:

$$\text{overlap}_{sec\_1\_z} = \cos^2\theta\ \text{overlap}_{sec\_1}\,, \qquad (47)$$

where θ is the angle between the primary bond axis and the secondary (tertiary, etc.) bond axis. The secondary fraction_bonding increment, $\text{fraction\_bonding}_{sec\_1\_inc}$, is:

$$\text{fraction\_bonding}_{sec\_1\_inc} = 0.5\ (1 - \text{fraction\_bonding}_{lessor\_primary\_1})$$
$$(\text{overlap}_{sec\_1\_z} / (1 + \text{overlap}_{sec\_1\_z}) \qquad (48)$$

where $\text{fraction\_bonding}_{lessor\_primary\_1}$ is the lessor of the two $\text{fraction\_bonding}_{primary}$ associated with the secondary. The factor of 0.5 arises because the secondary bond spans two primary bonds. The contribution of the secondary overlap to the total overlap, the secondary overlap increment, $\text{overlap}_{sec\_1\_inc}$, is:

$$\text{overlap}_{sec\_1\_inc} = \text{fraction\_bonding}_{sec\_1\_inc} / (1 - \text{fraction\_bonding}_{sec\_1\_inc})\,. \qquad (49)$$

The calculations for the right side are analogous to those on the left. The overlap subtotal, overlap$_{subtotal}$, is:

$$\text{overlap}_{subtotal} = \text{overlap}_{primary} + \text{overlap}_{sec\_l\_inc} + \text{overlap}_{sec\_r\_inc}, \text{ and} \qquad (50)$$

$$\text{fraction\_bonding}_{subtotal} = \text{overlap}_{subtotal} / (1 + \text{overlap}_{subtotal}). \qquad (51)$$

Subsequent, secondary (or tertiary and etc.) are treated similarly.

Summing overlap contributions in this manner is very important because they make up a very significant portion of the total overlap (typically around 10-25%) and therefore have a very large impact on the bond length and, indirectly, via the overlap$_{total}$=1.0 constraint, on the bond energy. The direct secondary contributions to the bond energy (described below) can sometimes be ignored for an approximate result but the secondary contributions to overlap cannot be ignored.

The core orthogonalization penalty associated with the overlap of the primary bonding orbital on the left and the core electrons of the secondary atom on the right is as follows:

$$\begin{aligned}
KE_{core\_ortho\_sec\_l} = &(fs_{bl}\, fs_{br}\, fs_{bl}\, fs_{br}\, (KE_{s\_sal} - KE_{sl}) + \\
&fs_{bl}\, fp_{br}\, fs_{bl}\, fp_{br}\, (KE_{s\_pzal} - KE_{sl}) + \\
&\cos(\theta)\, fp_{bl}\, fs_{br}\, fp_{bl}\, fs_{br}\, (KE_{pz\_sal} - KE_{pzl}) + \\
&\cos(\theta)\, fp_{bl}\, fp_{br}\, fp_{bl}\, fp_{br}\, (KE_{pz\_pzal} - KE_{pzl})). \qquad (52)
\end{aligned}$$

The calculations for the right side are analogous to those on the left. The $_{core\_orth}$ contributions are taken only to the extent of (1-fraction_bonding$_{total}$). Fraction_bonding$_{total}$ generally reaches 0.5. The $KE_{core\_orth\_sec}$ contributions to the bond energy are generally quite small.

Secondary potential energy terms are calculated in the same manner as those of the primary terms. The secondary and subsequent contributions are much smaller than the primary due to the longer atomic distances, but they are nonetheless usually significant.

Table V provides a complete breakdown of the many components that contribute to the total overlap in diamond.

Table V. Components of the Calculation of Overlap in Diamond at 1.541 Å

The configuration of C in diamond is $1s^2 2s 2p_z 2p_{xy}^2$.

Component	Value	Overlap Increment

Sigma overlap of primary orbitals (overlap $_{1st}$)
   overlap $_{1st}$ = 0.25 overlap $_{s-s}$ + 0.25 overlap $_{s-p}$+0.25 overlap $_{p-s}$+ 0.25 overlap $_{p-p}$
   $fs_{br} = fs_{bl} = fp_{br} = fp_{bl} = 0.5$
	0.7960	0.7960

Fraction_bonding of primary (fraction_bonding $_{1st}$) fraction_bonding $_{1st}$ = overlap $_{1st}$ /(1+ overlap $_{1st}$)	0.4432	

Component	Value	Overlap Increment

Sigma overlap to secondary along primary axis (overlap 2_{nd})
    3 secondary atoms are at (0,1/2,1/2) at 2.517 Å
    The angle from bond axis is 35.265 degrees.   cos(35.265)=0.8165
    overlap 2_{nd} = 0.8165 0.8165 (0.25 overlap $_{s\text{-}s}$+0.8165 0.25 overlap $_{s\text{-}p}$+
      0.8165 0.25 overlap $_{p\text{-}s}$+0.8165 0.8165·0.25 overlap $_{p\text{-}p}$)
	0.0949	

Secondary fraction_bonding (fraction_bonding$_{2nd}$) fraction_bonding$_{2nd}$ = overlap $_{2nd}$ /(1+overlap $_{2nd}$)	0.0867	

First secondary fraction_bonding increment (fraction_bonding$_{2nd\_inc}$)
    fraction_bonding$_{2nd\_inc}$ = 2 0.5 (1- fraction_bonding $_{1st}$) fraction_bonding$_{2nd}$
    Secondary fraction_bonding is reduced by previous, coincident, 1st order bonding.
      0.5 because secondary spans 2 primary
      2 because primary C is also a secondary
	0.0483	

First secondary overlap first secondary overlap = fraction_bonding$_{2nd\_inc}$/(1- fraction_bonding $_{2nd\_inc}$)	0.0507	

Total secondary overlap for 3 atoms
    Note that coincident bonding increases as previous fraction_bonding
    increases with successive bonds.   0.1479<3 0.0507
	0.1479	0.1479

Sigma overlap to tertiary #1 (overlap 3_{rd} #1)
    6 tertiary atoms are at (1/4,3/4,-1/4) and (3/4,1/4,-1/4) at 2.9512 Å
     cos(angle)=0.5222
    overlap 3_{rd} #1 = 0.5222 0.5222 (0.25 overlap $_{s\text{-}s}$+0.5222 0.25 overlap $_{s\text{-}p}$+
      0.5222 0.25 overlap $_{p\text{-}s}$+0.5222 0.5222 0.25 overlap $_{p\text{-}p}$)
	0.0108	

Total tertiary overlap #1 for 6 atoms	0.0329	0.0329

Sigma overlap to tertiary #2 (overlap 3_{rd} #2)
    3 tertiary atoms are at (1/4,3/4,3/4) at 3.8781 Å
    cos(angle)=0.9270
	0.0089	

Total tertiary overlap #2 for 3 atoms	0.0134	0.0134

Sigma overlap to tertiary #3 (overlap 3_{rd} #3)
    7 tertiary atoms are at opposite faces at 4.3592 Å (4 above unit cell)
    cos(angle)=0.4717
	0.0004	

Total tertiary overlap #3 for 7 atoms	0.0013	0.0013

Sigma overlap to tertiary #4 (overlap 3_{rd} #4)
    3 tertiary atoms are at adjacent corner at 3.5593 Å
    cos(angle)=0.5774
	0.0041	

Total tertiary overlap #4 for 3 atoms	0.0061	0.0061

Sigma overlap to tertiary #5 (overlap 3_{rd} #5)
    3 tertiary atoms are at one off from adjacent corner at 5.5372 Å
    cos(angle)=0.7360
	0.0009	

Total tertiary overlap #5 for 3 atoms	0.0014	0.0014

Component	Value	Overlap Increment

Sigma overlap to tertiary #6 (overlap 3_{rd} #6)
    3 tertiary atoms are at corners at (1,1,0),(1,0,1)and (0,1,1) at 5.0336 Å
    cos(angle)=0.8167
	0.0004	

Total tertiary overlap #6 for 3 atoms	0.0006	0.0006

Sigma overlap to tertiary #7 (overlap 3_{rd} #7)
    3 tertiary atoms are at opposite corners at 6.165 Å
    cos(angle)=0.8167
	0.0000	

Total tertiary overlap #7 for 3 atoms		0.0001
Total Overlap		**0.9997**

VII. RESULTS

Some results from the application of the methods described herein are presented in Tables VI, VII and VIII. Table IX provides a description of the components of the C_2 calculation. Table X is a detailed description of the components of the CH_4 calculation.

Bond lengths are generally accurate to 0.005Å and bond energies to a few percent. Except for a few bonds to hydrogen, the bond length results are independent of the bond energy results. Of these results, only for H_2 is the bond length determined by a maximum in the bond length versus bond energy curve. Otherwise the bond length is found at the point where overlap becomes 1.0 (and fraction_bonding becomes 0.5) as the bond length is decreased.

Aside from the character of the original atomic orbital, bond lengths are impacted only by core orthogonalization and the selected orbital scale factor. Finding the optimum parameters for the core orthogonalization, using the analytical procedures described above, particularly for C through F, is not difficult. Bond lengths are not sensitive to small changes from the optimal orthogonalization parameters although care must be taken in the core orthogonalization to assure accurate bond energies. Orbital scale factors are generally easy to establish as the energy required to compress an atomic orbital rises rapidly with the factor. The factors used are shown in the results tables for comparison purposes. Consistent with the data in Table I, the factors are larger for lighter elements. Orbital scale factors for poly-coordinate atoms are larger than those of di-atomics because the energy to compress the orbital is spread among several bonds.

Bond energies are sensitive to the magnitude of the s*top* value. Care has been taken to use the same s*top* value in different compounds in which the atom shows a similar electronic structure. The s*top* values used for each bond are shown in the results tables for comparison purposes.

The results tables provide the bonding and not bonding configurations of the bonding atoms. In these tables $2sp_0$ indicates an opposing orbital and $2sp$ is a hybrid orbital made by adding a small amount of 2p to a 2s orbital. The z axis is taken as the bond axis. Notice that in O_2 and O_2^-, the bonding configurations include two $2p_z$. One of these is reconfigured as $2p_\perp$ (or more precisely, $2p_\pi$ since there is pi bonding here) in the not bonding configuration. In CH3 and graphite, one of the C atom's 2s orbitals is promoted to $2p_\perp$ when any of the central C atom's 3 bonds is not bonding [(1.0-0.5 0.5 0.5)=0.875] to meet the orthogonality requirement. In graphite, this promotion allows pi bonding when the C atoms on both sides of the bond are not

bonding (0.875 0.875). In graphite pi bonding is reduced by the extent of simultaneous pi bonding to other Cs.

Hybridization of the bonding orbitals on central atoms in poly-atomics is different from that in di-atomic molecules or terminal atoms. The hybridization of bonding orbitals on atoms that are not in the terminal position is determined via the availability of s character. In three-coordinate CH_3 (D_{3h} symmetry) and graphite, the square of the central C bonding orbital s coefficient, $fs_b fs_b$, is 0.667. The s character in the bonding orbital cannot be oversubscribed, so 3 fraction_bonding $fs_b fs_b$ must be less than or equal to 1.0 and, since fraction_bonding=0.5, $fs_b fs_b$=0.667. The s character in a bonding orbital is maximized because this leads to a lessor orbital overlap and a shorter bond. Following the same logic, four-coordinate atoms or pseudo four-coordinate central atoms (those which have a combination of four lone pairs and bonds) have $fs_b fs_b$=0.5. Diamond and methane have four-coordinate central atoms and have T_d symmetry. Water and ammonia are pseudo four-coordinate. Two-coordinate atoms such as CO_2 have $fs_b fs_b$= 0.75. In the two-coordinate case, the s character of the central atom's orbital is limited because, when both sides are not bonding, 0.25 of the time, $fs_b fs_b$ must equal 0.5.

Consistent with the traditional view, NH_3 and H_2O have one and two traditional sp^3 orbitals containing lone (non-bonding) pairs of electrons respectively. The bond axes in these molecules are bent inward relative to the electronic axes to make the lone pair(s) orthogonal to the H 1s bonding orbital. The calculated bond angles reflect the requisite bending.

Dipole moments, μ, have been calculated for NO, NH_3 and H_2O. Dipole moments are very sensitive to the electronic structure of the molecule. The calculated values are in good agreement with the observed values.

Table VI. Results for Some Di-Atomics Which Exhibit No Resonance

Molecule	$D_e{}^a$ or $D_0{}^b$/eV	Bond Length/Å	Configurations[c,d,e,f] (C to O $1s^2$ omitted)	Bonds	stop/ eV
H_2	observed 4.75 calculated 4.67	observed 0.741 calculated 0.754	H 1s(polarized w/p_z) H $fs_b \cdot fs_b$=0.992 $fact_{1s}$=1.15 $fact_{2pz}$=3.5	σ	n/a
C_2	observed 6.3 calculated 6.51	observed 1.2425 calculated 1.243	bonding C $2sp^2 2p_\pi^2$ not bonding $2sp_o 2sp 2p_\pi^2$ $fact_{2s,2p}$=1.035	2 σ (dual) $fs_b fs_b$=0.957 2 π	6.55 (unpaired)
N_2	9.91 calculated 9.80	1.0977 calculated 1.100	bonding $2s^2 2p_z 2p_\pi^2$ not bonding $2sp_o 2s 2p_z 2p_\pi^2$ $fact_{2s,2p}$=1.015	2 σ (dual) 2 π	12.40
BN	observed 3.92 ±0.08 calculated 4.00	observed 1.281 calculated 1.281	bonding B $2s^2 2p_z$ not bonding B $2sp_o 2s 2p_z$ bonding N $2s^2 2p_z 2p_\perp^2$ not bonding N $2sp_o 2s 2p_z 2p_\perp^2$ $fact_{2s,2p}$(B,N)=1.04,1.015	2 σ (dual) no π	B 6.55 N 12.40

Molecule	D_e^a or D_0^b/eV	Bond Length/Å	Configurations[c,d,e,f] (C to O $1s^2$ omitted)	Bonds	s*t*op/ eV
CN	observed 7.78 ±0.03 calculated 7.67	observed 1.172 calculated 1.169	bonding C $2sp^2 2p_\pi^2$ bonding N $2s^2 2p_z 2p_\pi^2$ not bonding C $2sp_o 2sp 2p_\pi^2$ not bonding N $2sp_o 2s 2p_z 2p_\pi^2$ $fact_{2s,2p}(C,N)=1.035,1.01$	2 σ (dual) C $fs_b fs_b = 0.953$ 2 π	C 6.55 (unpaired) N 12.40
NO	observed 6.56 calculated 6.42 ($\mu_{calc}=0.133$ D $\mu_{expt}=0.159$ D)	observed 1.1506 calculated 1.154	bonding N $2s^2 2p_z 2p_\pi^2$ bonding O $2s^2 2p_z^2 2p_\pi^3$ not bonding N $2sp_o 2s 2p_z 2p_\pi^2$ not bonding O $2sp_o 2s 2p_z 2p_\pi^2 2p_{\pi a}$ $fact_{2s,2p}(N,O)=1.02,1.02$	2 σ (dual) 2 π	N 12.40 O 16.60

[a] Homonuclear di-atomics. D_e is the equilibrium dissociation energy which is slightly larger than the molecular ground-state-dissociation energy D_0. Observed data are from Ira N. Levine, *Quantum Chemistry 7th edition*, pp 373, Pearson (2014) and/or John P. Lowe, *Quantum Chemistry 2nd edition*, pp 224, Academic Press (1993).
[b] Heteronuclear di-atomics. Observed D_0 data are from W.M. Hayes, Editor in Chief, *CRC Handbook of Chemistry and Physics*, Section 9, CRC Press (2014).
[c] fact is the orbital scale factor.
[d] 2sp is a hybrid orbital made by adding a small amount of 2p to the existing 2s orbital.
[e] $2sp_o$ is a hybrid opposing orbital formed to meet the valence orthogonalization requirement.
[f] $2p_{\pi a}$ is $2p_\pi$ made orthogonal to opposite 2p.

Table VII. Results for Some Di-Atomics Which Exhibit a Full Pi Resonance

Molecule	D_e^a/eV	Bond Length/Å	Configurations[b,c,d,e] ($1s^2$ omitted)	Bonds	s*t*op/ eV
B_2	observed 3.1 calculated 3.21	observed 1.590 calculated 1.582	bonding B $2sp^2 2p_\pi$ bonding B+ $2sp^2$ bonding B- $2sp^2 2p_\pi^2$ not bonding B+,B,B- $2sp_o 2sp 2p_\pi^{0,1,2}$ $fact_{2s,2p}=1.035$	2 σ (dual) $fs_b fs_b = 0.953$ $\pi_{resonance}$	4.35 (unpaired)
C_2^+	observed 5.3 calculated 5.22	observed 1.301 calculated 1.301	bonding C $2sp^2 2p_\pi^2$ bonding C+ $2sp^2 2p_\pi$ not bonding $2sp_o 2sp 2p_\pi^{1.2}$ $fact_{2s,2p}(C,C+)=1.08$	2 σ (dual) $fs_b fs_b = 0.915$ $\pi_{resonance}$	C 6.55 (unpaired) C+ 4.35 (unpaired)
O_2	observed 5.21 calculated 5.25	observed 1.2074 calculated 1.208	bonding O+,O,O- $2s^2 2p_z^2 2p_\pi^{1,2,3}$ not bonding O+,O,O- $2sp_o 2s 2p_z 2p_\pi^{2,2,2} 2p_{\pi a}^{0,1,2}$ $fact_{2s,2p}=1.0225$	2 σ (dual) $fs_b fs_b = 0.40$ 2 $\pi_{resonance}$ plus π plus π when both sides s⇒p	16.60

Molecule	D_e^a/eV	Bond Length/Å	Configurations[b,c,d,e] (1s² omitted)	Bonds	stop/eV
O_2^-	observed 4.14 calculated 4.11	observed 1.32 calculated 1.28	bonding O,O- $2s^2 2p_z^2 2p_\pi^{2,2} 2p_{\pi a}^{0,1}$ not bonding O,O- $2sp_o 2s 2p_z 2p_\pi^{2,2} 2p_{\pi a}^{1,2}$ $fact_{2s,2p}(O,O-)=0.965$	2 σ (dual) $fs_b fs_b=0.46$ $\pi_{resonance}$ plus 2 π	O 16.60 O- 16.60
F_2	observed 1.66 calculated 1.74	observed 1.412 calculated 1.418	bonding F $2s^2 2p_z^2 2p_\pi^2 2p_{\pi a}$ not bonding F $2sp_o 2s 2p_z 2sp_a 2p_\pi^2 2p_{\pi a}$ $fact_{2s,2p}=1.01$	2 σ (parallel) fraction_bond=0.25 for each of two σ 2 $\pi_{resonance}$ plus 2π	n/a

[a] D_e is the equilibrium dissociation energy. Observed data are from Ira N. Levine, *Quantum Chemistry 7th edition*, pp 373, Pearson (2014) and/or John P. Lowe, *Quantum Chemistry 2nd edition*, pp 224, Academic Press (1993).
[b] fact is the orbital scale factor.
[c] 2sp is a hybrid orbital made by adding a small amount of 2p to the existing 2s orbital.
[d] $2sp_o$ is a hybrid opposing orbital formed to meet the valence orthogonalization requirement.
[e] $2p_{\pi a}$ is $2p_\pi$ made orthogonal to opposite 2p.

Table VIII. Some Poly-atomics

Molecule	$D_0^{a,b}$/eV μ/D	Bond Length[c]/Å ∠[c]/°	Configurations[d] (1s² omitted)	Bonds	stop/eV
CH/CH₃ (methyl)	observed 4.22 calculated 4.25	observed 1.076 calculated 1.080	all bonding C (0.125) $2s^2 2p_z 2p_\perp$ otherwise $2s 2p_z 2p_\perp^2$ $fact_{2s,2p}(C)=1.05$ $fact_{1s}(H)=1.08$	σ C $fs_b fs_b=0.6667$ H polarized H $fs_b \cdot fs_b=0.977$	6.95
CO/CO₂	observed 8.33 calculated 8.33	observed 1.160 calculated 1.160	both bonding C,C+ $2s^2 2p_z 2p_\pi^{1,0}$ any not bonding C,C+ $2s 2p_z 2p_\pi^{2,1}$ bonding O,O- $2s^2 2p_z^2 2p_\pi^{1,2} 2p_{\pi a}^{1,1}$ not bonding O,O- $2s 2p_z 2sp_o 2p_\pi^{2,3} 2p_{\pi a}^{1,1}$ $fact_{2s,2p}(C,C+)=1.03,1.11$ $fact_{2s,2p}(O,O-)=1.01,0.93$	σ (dual when opposite bonding i.e. s⇏p_π) C $fs_b fs_b=0.75$ $\pi_{resonance}$ [O-C+O,OCO,OC+O-] π bond (reduced for coincident π) when s⇒p_π (i.e. one/both not sigma bonding)	C 7.50 C+ 5.05 O 16.60 O- 16.60
CH/CH₄ (methane)	observed 4.30 calculated 4.32	observed 1.087 calculated 1.104	C $2s 2p_z 2p_\perp^2$ $fact_{2s,2p}(C)=1.05$ $fact_{1s}(H)=1.13$	σ C $fs_b fs_b=0.5$ H polarized H $fs_b fs_b=0.984$	6.55

Molecule	D_0[a,b]/eV μ/D	Bond Length[c]/Å $\angle^c$ /°	Configurations[d] ($1s^2$ omitted)	Bonds	$stop$/eV
NH/NH$_3$ (ammonia)	observed 4.05 μ_{expt} =1.471 calculated 4.16 μ_{calc} =1.47	observed 1.012 $\angle$HNH= 106.7 calculated 1.023 $\angle$HNH= 106.8	N $2s2p_z$ $2p_\perp^{2+0.5}2sp_o^{0.5}$ $fact_{2s,2p}(N)=1.01$ $fact_{1s}(H)=1.17$	σ N $fs_b fs_b=0.565$ ($fs_b fs_b$ is nominally 0.5 axes bent to meet orthogonality) H polarized H $fs_b fs_b=0.958$	12.40
OH/OH$_2$ (water)	observed 4.79 μ_{expt}=1.854 calculated 4.79 μ_{calc}=1.83	observed 0.9575 $\angle$HOH= 104.5 calculated 0.923 $\angle$HOH= 104.5	O $2s^{1+0.25}2p_z$ $2p_\perp^{3+0.25}2sp_o^{0.5}$ $fact_{2s,2p}(O)=1.01$ $fact_{1s}(H)=1.16$	σ O $fs_b fs_b=0.66$ ($fs_b fs_b$ is nominally 0.5 axes bent to meet orthogonality) H polarized H $fs_b fs_b=0.92$	16.60
CC/ C$_3$CCC$_3$ (diamond)	observed 3.70 calculated 3.71	observed 1.544 calculated 1.541	$2s2p_z2p_\perp^2$ $fs_b fs_b=0.5$ 2s is promoted to 2p (s⇒p) completely $fact_{2s,2p}(C)=1.055$	σ C $fs_b \times fs_b=0.5$	6.55
CC/ C$_2$CCC$_2$ (graphite)	observed 4.95 calculated in-plane 4.79	observed 1.421 calculated 1.421	all bonding (0.125) $2s^22p_z2p_\perp$ any not bonding(0.875) $2s2p_z2p_\perp2p_\pi$ $fact_{2s,2p}(C)=1.055$	σ $fs_b fs_b=0.667$ partial dual σ when s⇏p (all bonding) on both sides π when s⇒p on both sides. (0.875 0.875) π bonding is reduced by coincident π bonding to other Cs	7.50

[a] D_0 is the molecular bond dissociation energy.
[b] Bond energies are from (or calculated from data) in W.M. Hayes, Editor in Chief, *CRC Handbook of Chemistry and Physics*, Section 5, CRC Press (2014).
[c] Structural data and dipole moment (μ) data are from W.M. Hayes, Editor in Chief, *CRC Handbook of Chemistry and Physics*, Section 9, CRC Press (2014).
[d] fact is the orbital scale factor.

Table IX. Components of the C$_2$ Calculation at 1.243 Å (Energy in electron volts)

The configuration of C in C$_2$ is $1s^22s^22p_{xy}^2$.

Component	Value	Energy (eV) Increment

Sigma overlap of one pair of orbitals (overlap $_{s\_s}$) (There are two pairs of 2s bonding orbitals)	0.7071	
Fraction_bonding $_{s\_s}$ fraction_bonding $_{s\_s}$ = (overlap $_{s\_s}$ /(1+ overlap $_{s\_s}$)	0.4142	
Simultaneous overlap of both pairs of orbitals (overlap $_{s-s/s-s}$) fraction_bonding $_{s\_s}$ fraction_bonding $_{s\_s}$ /((1- fraction_bonding $_{s\_s}$ fraction_bonding $_{s\_s}$)	0.2071	
Total overlap of both pairs (overlap) overlap = 2 overlap $_{s\_s}$ - 2 overlap $_{s-s/s-s}$	1.0000	
Fraction_bonding of both pairs fraction_bonding = (overlap/(1+ overlap)	0.5000	
Kinetic energy of bond of one sigma orbital pair (2 $KE_{bond\ s-s}$) $KE_{bond\ s-s}$ = Fraction_bonding (KE_{sl+sr}- KE_{sl} - KE_{sr})	5.9265	
Sigma bonding kinetic energy of both pairs (overlap/(1+overlap))/ (overlap $_{s\_s}$ /(1+ overlap $_{s\_s}$)) 2 $KE_{bond\ s-s}$	7.1539	7.1539
Kinetic energy of 2 pi bonds 4 KE_{bond_π}	4.2670	4.2670
Energy to make sigma pair 2s orthogonal to opposite $1s^2$ 2 (KE_ϕ - KE_ϕ) where ϕ is 2s made orthogonal, ϕ is 2s	-6.4001	
Energy to make 1st pair orthogonal to opposite $1s^2$ when not bonding 2 (KE_ϕ - KE_ϕ) (1- fraction_bonding)	-3.2001	-3.2001
Additional Energy to make 2nd pair orthogonal to opposite $1s^2$ when bonding and 2nd pair not bonding 2 (KE_ϕ - KE_ϕ) fraction_bonding (1- fraction_bonding $_{s\_s}$)	-1.8745	-1.8745
Nuclear-nuclear repulsion energy	-416.9974	-416.9974
Nuclear to opposite two 2s sigma orbitals energy When not bonding, (1-fraction_bonding), one 2s on each atom becomes an opposing orbital.	236.0087	236.0087
Nuclear to opposite 1s orbitals energy	277.9988	277.9988
Nuclear to opposite opposing orbitals energy Opposing orbitals occur only when not bonding, (1-fraction_bonding). The opposing orbital coefficients fp_o and fs_o are chosen to make the orbital orthogonal to the opposite bonding 2s orbital. fs_{or} overlap $_{s\_s\_n}$ - fp_{or} overlap $_{s\_pz\_n}$ = 0.0 The overlap $_{s\_s\_n}$ is the overlap of the (not core orthogonalized) 2s atomic orbitals.	50.4958	50.4958
Nuclear to opposite p_{xy} orbitals energy	249.6900	249.6900
Electron-electron repulsion energy	-392.2061	-392.2061
Energy to raise s to p 2 (1- (overlap/(1+overlap))) fp_o fp_o 6.55+ 2 (1- (overlap/(1+overlap))) fp_b fp_b 7.90+ 4 (overlap/(1+overlap)) fp_b fp_b 7.90	-4.50	-4.50

Energy for C atom compression (scale factor 1.035)	-0.33	-0.33	
Total		**6.51**	

Table X. Components of the CH₄ Calculation at 1.106 Å (Energy in electron volts)

The configuration of C in H_4C is $1s^2 2s 2p_z 2p_{xy}^2$.   CH₄ has a tetrahedral structure.

Component	Value	Overlap change	Energy (eV) change
Primary H – C Bond			

Sigma overlap of primary orbitals (overlap$_{1st}$)
    overlap $_{1st}$ = 0.5 overlap $_{s-s}$ + 0.5 overlap $_{s-p}$
    fs_{br} = fp_{br} = 0.5
	0.8814	0.8814	

Fraction_bonding (fraction_bonding$_{1st}$) fraction_bonding$_{1st}$ = overlap$_{1st}$ /(1+ overlap$_{1st}$)	0.4685		
Kinetic energy of sigma orbital pair (2 KE$_{bond}$) KE$_{bond}$ = (1 /(1+ overlap$_{1st}$)) (fs$_{br}$ overlap $_{s-s}$ KE$_{net\ s-s}$+ fp$_{br}$ overlap $_{s-p}$ KE$_{net\ s-pz}$)	6.5892		6.5892
Energy to make H 1s orthogonal to opposite C $1s^2$ (KE$_{\phi'}$- KE$_{\phi}$) where ϕ' is H 1s made orthogonal, ϕ is H 1s	-9.2300		
Energy to make H 1s orthogonal to opposite $1s^2$ when not bonding KE$_{core\_ortho}$ = (KE$_{\phi'}$ - KE$_{\phi}$) (1- fraction_bonding$_{1st}$)	-4.6150		-4.6150
Nuclear-nuclear repulsion energy	-78.1189		-78.1189
C nuclear to H 1s energy	82.4697		82.4697
H nuclear to opposite two C 1s orbitals energy	26.0397		26.0397
H nuclear to opposite 2s orbital energy	12.6635		12.6635
H nuclear to opposite 2p$_z$ orbital energy	14.9262		14.9262
H nuclear to opposite two 2p$_{xy}$ orbital energy	22.8374		22.8374
H electron-C electron repulsions energy	-76.8004		-76.8004
Energy to compress/polarize H	-0.558		-0.558
Energy to raise C 2s to 2p	-1.63		-1.63
Energy to compress C orbitals (orbital scale factor = 1.05)	-0.08		-0.08
Total primary energy			3.723
Secondary H – H Bond			

Secondary H 1s – H 1s overlap (secondary overlap $_{s-s}$)	0.2605	

Secondary H – H sigma overlap along primary axis (overlap 2$_{nd}$)
    3 secondary atoms are at 1.8060 Å
    angle from bond axis is 35.265 degrees   cos(35.265)=0.8165
    overlap 2$_{nd}$ = 0.8165 0.8165 overlap $_{s-s}$
	0.1737	

Secondary fraction_bonding (fraction_bonding $_{2nd}$) fraction_bonding $_{2nd}$ = overlap $_{2nd}$ /(1+overlap $_{2nd}$)	0.1480	

First secondary fraction_bonding increment (fraction_bonding$_{2nd\_inc}$)
    fraction_bonding$_{2nd\_inc}$ = 0.5 (1- fraction_bonding $_{1st}$) fraction_bonding$_{2nd}$
    Secondary fraction_bonding is
       reduced by previous, coincident 1st order bonding.
       0.5 because secondary spans 2 primary
	0.0393	

First secondary overlap increment
  first secondary overlap =
          fraction_bonding$_{2nd\_inc}$/(1- fraction_bonding $_{2nd\_inc}$)
	0.0409	0.0409

Second secondary fraction_bonding reduced
    by previous fraction_bonding of both primary and 1st secondary.
    fraction_bonding $_{previous}$ = (overlap $_{1st}$+ 0.0409)/(1+overlap $_{1st}$+ 0.0409)
	0.4798	

Second secondary overlap increment
  second secondary overlap =
          fraction_bonding $_{previous}$ /(1- fraction_bonding $_{previous}$)
	0.0400	0.0400

Third secondary overlap increment	0.0392	0.0392
Kinetic energy of first H – H bond (KE$_{bond\_2nd}$) KE$_{bond\_2nd}$= fraction_bonding $_{2nd}$ (KE$_{sl+sr}$- KE$_{sl}$ - KE$_{sr}$)	0.3112	

First secondary kinetic energy increment (KE$_{bond\_2nd\_inc}$)
    KE$_{bond\_2nd\_inc}$ = (1- fraction_bonding $_{1st}$) KE$_{bond\_2nd}$
    Secondary KE$_{bond\_2nd}$ is reduced by previous, coincident
    1st order bonding.
	0.1654	0.1654

Second secondary kinetic energy increment (KE$_{bond\_2nd\_inc}$)	0.1586	0.1586
Third secondary kinetic energy increment (KE$_{bond\_2nd\_inc}$)	0.1524	0.1524
Single H nuclear-H nuclear repulsion energy	-7.9730	

Total nuclear-nuclear repulsion energy
    3 0.5 single nuclear-nuclear repulsion energy
    0.5 because spans two primary bonds
	-11.9595	-11.9595

Total H nuclear to opposite H 1s (1.5 single nuclear to opposite)	24.8811	24.8811
Total H 1s to H 1s electron - electron repulsion (1.5 single)	-12.7765	-12.7765
Total secondary energy		0.6215
Totals	**1.002**	**4.34**

VIII. OTHER RESULTS

The author has obtained results for many other molecules and lithium and beryllium metal. The additional results would require a discussion of sigma resonance, sigma/pi resonance, partial resonance, the impact of resonance on overlap, the calculation of fs_b fs_b for central atoms with bonds that are not identical (e.g. C in H_3CCH_3), additional discussion of secondary bonding, and other advanced topics which are beyond the scope of the present paper. The results presented herein are representative.

IX. CONCLUSIONS

The results presented herein support a model for the chemical bond which recognizes that the two electrons of the bonding pair are not completely identifiable, with respect to their source atom, when their orbitals overlap.

The method for the calculation of the chemical bond, presented here, provides reasonably good results, appears to be general, and is not computationally intensive (A run of six bond lengths takes a few seconds on a desktop PC.). Particularly notable is the discovery that, except for the H_2 case, the ratio overlap/ (1+ overlap) is 0.500 at the observed bond length. It is particularly hard to argue that this statistically sensible and computationally uncomplicated result is somehow fortuitous. It is also notable that the method described here is executed in terms understandable to the typical chemist (sigma bonds, pi bonds, hybrid orbitals, resonance, etc.).

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[1] C. A. Coulson, *Trans. Faraday Soc.,* **33**, 1479(1937).

[2] For an overview of MO and other methods see Ira N. Levine, *Quantum Chemistry 7th edition*, Pearson (2014) or John P. Lowe, Kirk A. Peterson, *Quantum Chemistry 3nd edition*, Elsevier Academic Press (2006).

[3] See, for example, Ira N. Levine, *Quantum Chemistry 7th edition*, pp 252, Pearson (2014).

[4] C.A. Coulson, *Valence 2nd editi*on, pp 91, Oxford University Press (1961).

[5] W.E. Duncanson and C.A. Coulson, Proc.Roy.Soc. (Edinburgh), **62**, 37 (1944).

[6] See, for example, W.M. Hayes, Editor-In-Chief, CRC *Handbook of Chemistry and Physics 95th Edition*, Section 10 pp 10-197, CRC Press (2014).

[7] See, for example, W.M. Hayes, Editor-In-Chief, CRC *Handbook of Chemistry and Physics 95th Edition*, Section 10 pp 10-147 CRC Press (2014).