



A Theoretical Method for Calculating the Bond Integral Parameter for Atomic Orbitals

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Abstract: In molecular orbital theory, the bond integral parameter k is used to calculate the bond integral β for different molecular structures. The bond integral parameter k , which represents the ratio of bond integrals between two atoms of a diatomic molecule, is a function of the bond length. This parameter is usually obtained empirically; however, it will be shown that k can be determined analytically by utilizing the overlap integral S . k will be calculated for different atomic orbital combinations (ss, pp) of σ and π interactions as a function of bond length for a carbon-carbon diatomic molecule. The results, which are represented graphically, indicate that different atomic orbitals in different interactions can have the same, or very close to the same, k values. The graphs reveal some significant features for the different atomic orbital combinations with respect to magnitude and profile, as well as illustrate good agreement with experimental results, which validates the utilization of the overlap integral calculation method for the determination of the bond integral parameter k .

Keywords: Molecular Orbital Theory, Bond Integral, Overlap Integral, Atomic Orbitals, Carbon Dimer

1. Introduction

Molecular Orbital Theory (MOT) has been used extensively in physical, inorganic, and organic chemistry to predict physical properties of a single molecule, such as orbital energies, bond length, bond order, bond energies, bond delocalization energies, and electron densities [1, 2, 3]. An important parameter that has been employed in MOT and has been used extensively in the Hückel method for molecular systems containing different atoms is the bond integral parameter k . This parameter is considered to be a scaling factor for bond integral calculations.

The bond integral parameter k is very useful for large and complex molecular systems with many different types of atoms, such as DNA, and allows the general molecular orbital energy equation [1, 2, 3, 4] to be solved. One such application [4] pertains to the determination of the strength of the electronic coupling between two adjacent base pairs for a B-DNA molecule, where k values were only determined for $2p\sigma$ and $2p\pi$ atomic orbital pairs, which resulted in the calculation of 342 atomic orbital combinations. These k values were utilized in a 361 element energy matrix for the calculation of the molecular orbital wave function coefficients,

which were then used for the electronic coupling computation. What is new is a detailed analysis of k for different atomic orbital combinations and interactions resulting in a more comprehensive understanding of some important and interesting features, as well as a comparison between the calculated and empirical values of k for a carbon dimer.

By definition, the bond integral $\beta = k\beta_o$, where β is the measured interaction energy between two atomic orbitals (which is difficult to obtain empirically), and β_o represents a standard β defined at a specific bond length, such as the carbon-carbon bond distance in benzene (1.397Å). Now, β has been proposed [5] to also be proportional to the overlap integral S , which can be written as $\beta = S\beta_o/S_o$. The overlap integral S is a non-energy quantity [1], which can be determined theoretically, thus allowing for the calculation of k , where $k = S/S_o$, and S_o represents a standard overlap integral defined at a specific bond length. For this study, a homo-nuclear carbon dimer was considered, thus simplifying the calculations of the overlap integral S and the bond integral parameter k . The carbon dimer consists of two carbon atoms, where each carbon atom consists of a $1s$ orbital, $2s$ orbital, and

three $2p$ orbitals. Two sets of calculations were performed: 1) the overlap integral S values were calculated for s and p atomic orbitals at different energy levels and 2) the bond integral parameter k values were then calculated for the same types of atomic orbitals at different bond lengths. The data from the first set of calculations was used to verify the method. To verify the overlap integral S calculation method, principal quantum numbers $n=1, 2, 3$, and 5 were used for the σ interactions and $n=2, 3$, and 5 for the π interactions. The data from the second set of calculations was used to evaluate the k values. For the evaluation of the k values, the same principal quantum numbers were utilized. As mentioned earlier, the analysis of the resulting data revealed some significant features of the overlap integral S and bond integral parameter k as a function of bond distance.

2. Theory

2.1. Analytical Calculations

Before the bond integral parameter k is discussed, a review of the one-electron overlap integral method is required. In general, the one-electron overlap integral is defined [1] as

$$S_{a,b} = \int \psi_a^* \psi_b d\nu, \quad (1)$$

where ψ_i represents the wave function (atomic orbital) for atom i , ψ_i^* the conjugate of ψ_i , and $d\nu$ the volume element. Equation (1) represents the total overlap between two atomic orbitals because the integration is performed over all space. $S_{a,b}$ can be expressed as

$$S_{a,b} = \lim_{\delta\nu \rightarrow 0} \sum \psi_a^* \psi_b \delta\nu, \quad (2)$$

where (2) represents the basic definition of the definite

$$S(n_a p \sigma, n_b p \sigma; p, t) = (3/2) N_a N_b (R/2)^{m_a + m_b + 1} \int_{-1}^1 \int_{-1}^1 (\xi + \eta)^{m_a - 2} (\xi - \eta)^{m_b - 2} (\xi^2 \eta^2 - 1) (\xi^2 - \eta^2) e^{-p(\xi + \eta)} d\eta d\xi,$$

$$S(n_a p \pi, n_b p \pi; p, t) = (3/4) N_a N_b (R/2)^{m_a + m_b + 1} \int_{-1}^1 \int_{-1}^1 (\xi + \eta)^{m_a - 2} (\xi - \eta)^{m_b - 2} (\xi^2 - 1)(1 - \eta^2)(\xi^2 - \eta^2) e^{-p(\xi + \eta)} d\eta d\xi, \quad (3)$$

where $N_a = \left[\frac{(2\alpha)^{2m+1}}{4\pi(2m)!} \right]^{1/2}$, $N_b = \left[\frac{(2\beta)^{2n+1}}{4\pi(2n)!} \right]^{1/2}$, α and β are

defined as constants from exponential functions that are used in describing Slater-type atomic orbitals,

$m_a = n_a - \delta$, $m_b = n_b - \delta$, n_a and n_b represents the quantum numbers for atoms a and b , δ is a constant having a value of 0 for $n=1, 2, 3$ and 1 for $n=5$, R is the internuclear distance, ξ and η are spheroidal coordinates, where $\xi = (r_a + r_b)/R$ and

$\eta = (r_a - r_b)/R$, r_a and r_b are distances of an electron from atoms a and b ,

$$p \equiv \frac{1}{2}(\mu_a + \mu_b)R/a_H, \quad t \equiv (\mu_a - \mu_b)/(\mu_a + \mu_b)$$

and μ_a and μ_b are Slater values that are listed in Table 1 (for the calculation of these values refer to the Appendix).

integral in (1). The summation is over $\sum \psi_a^* \psi_b \delta\nu = \psi_{a1}^* \psi_{b1} \delta\nu + \psi_{a1}^* \psi_{b2} \delta\nu + \dots$ and $\delta\nu$ is the change in the spherical volume.

An atomic orbital is a mathematical function that describes the wave-like behavior of a single electron in an atom [6]. This function can be used to calculate the probability of finding any electron of an atom in any specific region around its nucleus. The term also may refer to the physical region or space where the electron can be calculated to be present, as defined by the particular mathematical form of the orbital [7]. The atomic orbitals that will be considered in this study are Slater-type and are designated as s and p orbitals. Examples of s and p orbitals for σ and π interactions are illustrated in Fig. 1.

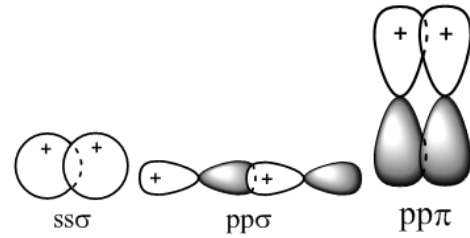


Figure 1. Three types of $1s$ and $2p$ orbital interactions for diatomic molecules.

The notation used in Fig. 1 describes the two atomic orbitals involved and the interaction between them. As an example, the notation $ss\sigma$ symbolizes two s orbitals in a σ interaction. The σ interaction involving s and p orbitals is not considered in this study. The equations for S for all Slater-type atomic orbital pairs consisting of ns , $np\sigma$ and $np\pi$ atomic orbitals for $n=1, 2, 3$, and 5 have been formulated [8].

The most general equations, which were derived from (1), that describe the overlap integral S are

Table 1. Slater μ - values for valence shell ns, np AOs (Milliken *et al* 1949).

H	1.00	C ⁻	1.45	O ⁻	2.10	Na	0.733	S	1.817
Li	0.65	C	1.625	O	2.275	Mg	0.95	Cl	2.033
Be	0.975	C ⁺	1.80	O ⁺	2.45	Al	1.167	Br	2.054
B ⁻	1.125	N	1.95	F	2.60	Si	1.383	I	1.90
B	1.30	N ⁺	2.125			P	1.60		

The integrals in (3) can be evaluated by utilizing the following mathematical relation [9] for $t=0$ (identical atomic orbitals):

$$A_k(p) \equiv \int_1^\infty \xi^k e^{-p\xi} d\xi = e^{-p} \sum_{\mu=1}^{k+1} [k! / p^\mu (k - \mu + 1)!]. \quad (4)$$

For the first set of computations, the following equations are

utilized.

$$S(1s,1s) = (6)^{-1} p^3 [3A_2 - A_0], \quad (5)$$

$$S(2s,2s) = (360)^{-1} p^5 [15A_4 - 10A_2 + 3A_0], \quad (6)$$

$$S(3s,3s) = (25,200)^{-1} p^7 [35A_6 - 35A_4 + 21A_2 - 5A_0], \quad (7)$$

$$S(2p\sigma,2p\sigma) = (120)^{-1} p^5 [5A_4 - 18A_2 + 5A_0], \quad (8)$$

$$S(3p\sigma,3p\sigma) = (25,200)^{-1} p^7 [35A_6 - 147A_4 + 85A_2 - 21A_0], \quad (9)$$

$$S(5p\sigma,5p\sigma) = (4,233,600)^{-1} p^9 [105A_8 - 504A_6 + 450A_4 - 224A_2 + 45A_0], \quad (10)$$

$$S(2p\pi,2p\pi) = (120)^{-1} p^5 [5A_4 - 6A_2 + A_0], \quad (11)$$

$$S(3p\pi,3p\pi) = (25,200)^{-1} p^7 [35A_6 - 49A_4 + 17A_2 - 3A_0], \quad (12)$$

$$S(5p\pi,5p\pi) = (4,233,600)^{-1} p^9 [105A_8 - 168A_6 + 90A_4 - 32A_2 + 5A_0]. \quad (13)$$

With the ability to determine values for S , the k values can therefore be obtained. For the second set of computations, a simple equation is applied,

$$k = S / S_0, \quad (14)$$

where S is obtained from (5) - (13), and S_0 is the S value at a specific bond length d_0 , defined below; for this work, the bond length of a carbon dimer was used.

An accurate bond length for the carbon dimer was obtained from its rotational constant B [10] using the following equation

$$d_0 = (h / 8\pi^2 \gamma c B)^{1/2}, \quad (15)$$

where h represents Planck's constant (in J-sec), γ the reduced mass (in atomic mass units), and c the speed of light (in cm/s). From the reported value of the rotational constant (1.820053 cm^{-1}), d_0 was found to be 1.24246 \AA , which was employed in the calculations for the results and discussion section.

2.2. Empirical Calculations

In order to compare the empirical values of k with the calculated values, the empirical values were obtained by using the celebrated empirical Morse potential function [11] with a shifting parameter to calculate the interaction energy between two atoms

$$V(r) = D_e [1 - e^{-\alpha(r-r_e)}]^2 - C, \quad (16)$$

where the bond dissociation energy $D_e = \omega_e^2 / 4\omega_e r_e$, ω_e and

$\omega_e r_e$ represent vibrational constants, r_e the equilibrium distance, C a constant for shifting the reference line from zero to the continuum's edge, and $\alpha = 1.2177 \times 10^7 \omega_e (\gamma / D_e)^{1/2}$. Because D_e and α are determined from the experimental values of ω_e and $\omega_e r_e$, the values of $V(r)$ can easily be obtained. Therefore, the bond integral parameter can be calculated empirically as $k = V(r) / V(r_e)$.

3. Results and Discussion

For the first set of calculations, the overlap integral S at different energy levels (principal quantum numbers) is depicted in Figs. 2 & 3. Figure 2 reveals two sets of curves defined by the general trend of S as a function of bond distance. The first set, which represents two s orbitals with a σ interaction for $n=1,2$, and 3, has a maximum at $d=0 \text{ \AA}$ and a minimum at $d \rightarrow \infty \text{ \AA}$. The second set shown in Fig. 2, which represents two p orbitals with a σ interaction, for $n=2,3$, and 5 (no p orbitals exist for $n=1$) also has a maximum at $d=0 \text{ \AA}$ and S approaches zero as d extends to infinity. However, each curve in the second set of data also contains a local minimum at a specific distance that is dependent on n . The minima occur at a negative value of S , where the total overlap is dominated by the negative terms in (2). The first set of curves in Fig. 2 shows that the magnitude of S is largest for $n=3$ for all distances greater than zero. Similarly, the second set of curves in Fig. 2 also illustrates this same trend. This trend is predominately due to an increase in the size of the atomic orbitals as n increases. Furthermore, the position of the minima in the second set of curves shifts to larger distances as n increases, which is consistent with the trend noted above. Each minimum in the second set of curves represents a distance where there is an optimum overlap between the two p orbitals oriented along their bond axis. The slopes of all the curves in Figs. 2 and 3 are indicative of the changes in size and shape of the orbitals. The maximum and minimum variation in the overlap integrals correspond to the orbital interactions $2p2p\sigma$ and $3s3s\sigma$, respectively.

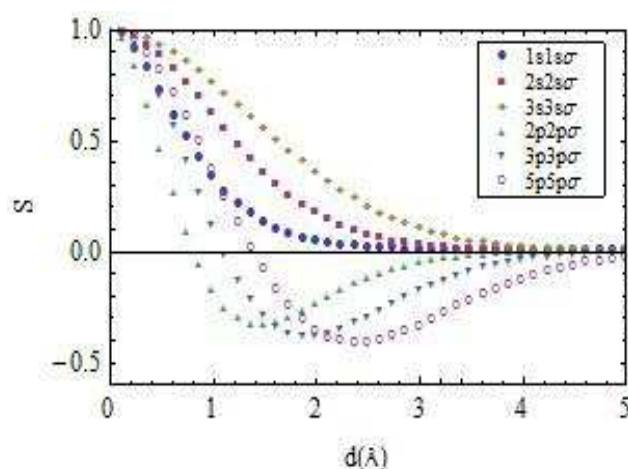


Figure 2. Overlap integral versus distance for a σ interaction (color version online).

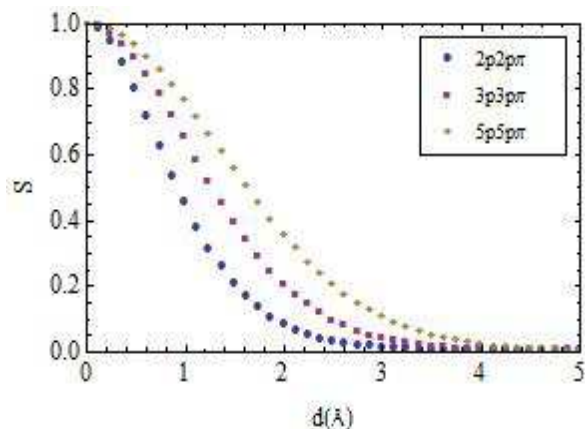


Figure 3. Overlap integral versus distance for a π interaction (color version online).

The curves in Fig. 3 represent two p orbitals in a π interaction for $n = 2, 3, \text{ and } 5$. They are similar to the first set of curves in Fig. 2 but with slightly different slopes, which is due to the difference in the shape and size of the orbitals (Fig. 1). These curves also exhibit the same trend (largest S value for the largest n value) as before, indicating a larger overlap value (magnitude) for a corresponding fixed distance as n increases.

An important note is that the first set of curves in Fig. 2 and the curves in Fig. 3 have only positive overlap values because all the product terms are positive. On the other hand, the second set of curves in Fig. 2 have both positive and negative values, indicating that the product terms may be a mixture of positive and negative values. Another important note is that in Fig. 2, for the second set of curves, the total overlap has a value of zero at specific distances. This suggests that no bonding between the p orbitals can occur at these distances due to the cancellation of the individual positive and negative contributions.

The trends that have been revealed in Figs. 2 & 3, with respect to the radial distribution function, are in agreement with published literature [12, 13]. In other words, for s orbitals in a σ interaction or p orbitals in a π interaction, as the energy level increases so does the orbital size, resulting in a larger overlap between the orbitals. However, as depicted in Fig. 2, for p orbitals in a σ interaction this is true only for distances less than those of the local minima.

Because a carbon dimer was considered for the calculation of the k values, only the $1s1s\sigma$, $2s2s\sigma$, $2p2p\sigma$ and $2p2p\pi$ orbital interactions will be utilized in this discussion.

For the second set of calculations, which pertain to the evaluation of the k values for the same types of atomic orbitals at different bond lengths, Fig. 4 depicts similar profiles for the orbital interactions $1s1s\sigma$, $2s2s\sigma$, $2p2p\pi$ when compared to Figs. 2 & 3. However, the $2p2p\sigma$ orbital interaction profile is approximately an inverse of that in Fig. 2. The reason for this discrepancy is because the orbital interactions $1s1s\sigma$, $2s2s\sigma$, $2p2p\pi$ all have positive overlap integral values, whereas the orbital interaction $2p2p\sigma$ does not. The

inverse effect is a result of having a negative overlap integral value for $d = d_o = 1.24246 \text{ \AA}$, resulting in a negative S_o value. All four curves in Fig. 4 intersect at the same point, where $k = 1$ and $d = d_o$. This is expected because k represents the ratio of S/S_o and S_o was defined at d_o . The maximum and minimum variations in k occur for the orbital interactions $2p2p\sigma$ and $2s2s\sigma$ respectively. Note that the $1s1s\sigma$, $2s2s\sigma$, and $2p2p\pi$ orbital interactions have similar k values for $d \geq 1.24246 \text{ \AA}$, and that these k values are less than those for the $2p2p\sigma$ interactions. Hence, at these distances

$$\frac{S_{1s1s\sigma}}{S_o^{1s1s\sigma}} \approx \frac{S_{2s2s\sigma}}{S_o^{2s2s\sigma}} \approx \frac{S_{2p2p\pi}}{S_o^{2p2p\pi}} < \frac{S_{2p2p\sigma}}{S_o^{2p2p\sigma}}. \quad (17)$$

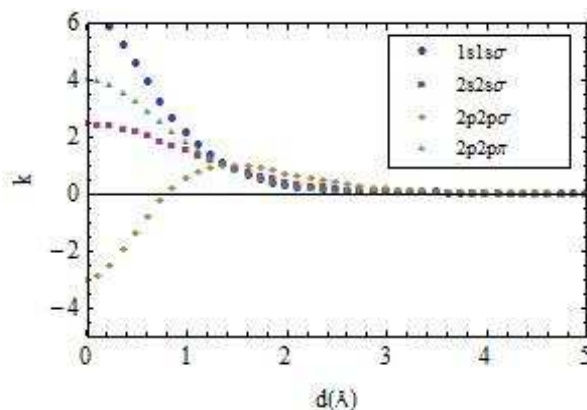


Figure 4. Bond integral parameter versus distance for σ and π interactions (color version online).

Therefore, for bond lengths less than d_o , the $1s1s\sigma$ interactions dominate, but at distances between d_o and 3.5 \AA , the $2p2p\sigma$ interactions prevail.

It is also noteworthy that the orbital interaction $2p2p\sigma$ has a k value of zero for $d \approx 0.80 \text{ \AA}$, which is not true for the other curves. This corresponds to the overlap integral having a value of zero for the orbital interaction $2p2p\sigma$ as illustrated in Fig. 2. Therefore, at $d \approx 0.80 \text{ \AA}$, no σ bonding between $2p$ orbitals can occur, which implies that for any stacked conjugated molecular system, such as stacked benzene molecules or base pairs of a B-DNA molecule, there will be no charge transfer between the stacked molecules at this distance.

With regards to the empirical values of k , experimental values of the vibrational constants ω_e and $\omega_e r_e$ for an electronic state Σ_g^+ for C_2 [11, 14] and a C value of -7.6 eV were considered. As depicted in Fig. 5, the profiles of both the calculated and experimental curves are quite similar with both having the same maximum value, but at slightly different positions, and almost the same value at $d = 1.0 \text{ \AA}$ and approaching zero at $d \approx 4.8 \text{ \AA}$. Also indicated is the fact that the experimental values decrease somewhat more quickly as

compared to the calculated values. However, the close agreement between the two curves and the information presented earlier validates the utilization of the overlap integral calculation method for the determination of the bond integral parameter k .

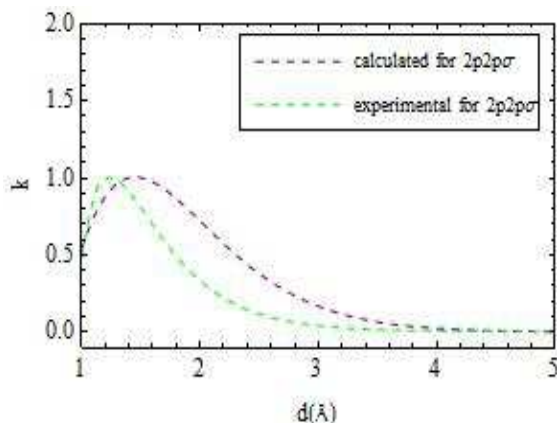


Figure 5. Bond integral parameter versus distance for σ interactions for calculated and experimental results (color version online).

4. Conclusion

In this paper it is shown that the analytical method for calculating the bond integral parameter by using the overlap integral is indeed a genuine approach. The results revealed that different atomic orbitals in different interactions can have almost the same, if not the same, k values. The important features of the different atomic orbital combinations with regard to magnitude and profile disclose the fact that for $npn\sigma$ interactions, where $n = 2, 3$, or 5 , no σ bonding will occur at specific distances. The validation of this method is supported by the close correlation between the analytical and empirical results.

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Appendix

A Slater μ -value represents the effective nuclear charge of an atom as defined by

$$\mu = Z_{\text{eff}} = Z - s,$$

where Z and s are the actual nuclear charge and screening constant, respectively. For determining μ , the electrons are divided into the following groups, each having a different screening constant:

$$1s; 2s, p; 3s, p; 3d; 4s, p; 4d; 4f; \text{ etc.}$$

The general equation for calculating the Slater μ -values is

$$\mu = [Z - 0.35(a-1) - 0.85b - 1.00c] / n_{\text{lastgroup}}, \quad (\text{A1})$$

where a is number of electrons in last group with principle quantum number $n_{\text{lastgroup}}$, b is number of electrons in the group with principle quantum number $n_{\text{lastgroup}} - 1$, and c is number of electrons in all groups with principle quantum number $n' < n_{\text{lastgroup}} - 1$ (for $n_{\text{lastgroup}} = 2 \Rightarrow n' = 0 \Rightarrow c = 0$).

To obtain the values shown in Table 1, only the $2s, p$ group needs to be considered. Therefore, (A1) becomes

$$\mu_{2sp} = [Z - 0.35(a-1) - 0.85b - 1.00(0)] / 2. \quad (\text{A2})$$

As an example, we consider a carbon atom, where $Z_{\text{carbon}} = 6$ and the electronic configuration is $1s^2 2s^2 2p^2$. Then, (A2) is written as

$$\mu_{2sp} = [6 - 0.35(4-1) - 0.85(2) - 1.00(0)] / 2 = 1.625.$$

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