



SIGNIFICANCE OF COVALENT BONDING AND ORBITAL OVERLAP

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ABSTRACT

The energy decomposition analysis (EDA) method was used in order to explore the chemical bonds that exist between the diatomic molecules $\text{Li}_2\text{-F}_2$ and $\text{Na}_2\text{-Cl}_2$ at a number of different bond dimensions. For the purpose of carrying out this investigation, calculations based on density functional theory were carried out at the BP86/TZ2P level. The phrase "interatomic interactions" may be used to refer to three distinct types of interactions from various atomic interactions. Pauli repulsion (DEPauli), attractive orbital interactions (DEorb), and quasiclassical electrostatic interactions (DEelstat) are a few examples of the interactions that fall under this category. In order to compare the energy terms and orbital overlaps, an analysis is carried out utilising a large number of different interatomic distances. The computation, analysis, and reporting of the quasiclassical electrostatic interactions between two electrons in the 1s, 2s, 2p(s), and 2p(p) orbitals are carried out. In spite of the fact that it nearly always achieves its greatest value at distances that are obviously less than the length of the equilibrium bond, it has been established that the most significant overlap of the s valence orbitals does not alter the equilibrium distances of the covalent bonds. This is the case despite the fact that it makes the most significant overlap.

Keywords : *Covalent , Bonding , Orbital , Overlap*

INTRODUCTION

The present understanding of chemical bonding takes into consideration two fundamental theories of chemical bonds: ionic interactions and covalent bonding. Both of these ideas are considered to be fundamental. It is generally agreed that these two ideas are most important. The vast majority of individuals are of the opinion that these two ideas are the most important. The chemical link might be explained by any one of these explanations, making them all equally plausible. In the process of teaching the concept of ionic bonding, it is nearly always necessary to bring up the traditional electrostatic interactions that take place between point charges. When defining covalent bonding, it is often used to refer to attractive orbital interactions between doubly occupied and unoccupied orbitals (also known as donor-acceptor bonds) or partially filled orbitals (also known as electron-sharing bonds). Both of these types of interactions are referred to as "donor-acceptor bonds." The two types of interactions that are being discussed here are examples of covalent bonding, which are unique from one another. In neither of the two



hypotheses that attempt to explain bonding is the concept of repulsion between electrons that have the same spin taken into consideration. However, when the orbital overlap is significantly increased, the Pauli repulsion becomes more powerful than the electrostatic repulsion. Within the context of the interatomic interactions that occur at relatively close distances between the internuclear nuclei, electrostatic repulsion is the dominant driving force. This is the unique circumstance that brings about the occurrence of it. The valence shell electron pair repulsion (VSEPR) scheme is an example of a bonding model that only takes into account Pauli repulsion in order to make predictions about the geometry of molecules using any relevant information. Despite the fact that we disagree with a significant number of the assertions that have been made about the VSEPR model, we acknowledge that Pauli repulsion is an essential energy word for knowing the process of chemical bonding. After doing a substantial amount of study over the course of the last several years, we have come to the realisation that Pauli repulsion has a considerable impact on the binding energies and molecular geometries of molecules.

Concept for grouping chemical bonding orbital interactions

When it comes to classifying chemical bonds, one of the most important concepts to comprehend is the split of orbital interactions into s, p, and d contributions. Relationships between these contributions and single (s) or multiple (p) bonding are often discussed. Through his investigation on the chemical bonding that occurs in ethylene, HJckel was able to get an understanding of the difference between s and p forms of bonding. His study into the chemical bonding in benzene, which he discovered to be very essential, was built on this information, which served as the basis for his vital investigation. As it turns out, this understanding was the foundation upon which HJckel's study was built. The ground state of oxygen with three S g was the subject of a previous theoretical investigation that Lennard-Jones conducted, which served as the foundation for this work. Even though Pauling was adamantly opposed to the idea that ethylene has two unique types of carbon-carbon bonds, this discovery opened the way for a more in-depth understanding of many of the bonds that are present in compounds that come under the major category. There are a number of characteristics that distinguish the two bonds from one another. One of these characteristics is the manner in which the s and p orbitals of two atoms or pieces E overlap with one another as a function of the internuclear distance difference. In order to convey this information, the symbol $r(E E)$, which stands for the internuclear distance, is used. As demonstrated in Figure 1a, the majority of chemistry textbooks have an illustration that demonstrates how to differentiate between s and p bonding conditions. In spite of the fact that it does not have a name, the particular model orbital that is being deliberated over is a hybridised s orbital that is spx.

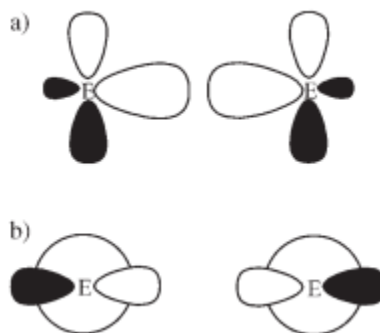


Figure 1.. A graphic representation of the bonding overlap between two spx hybrid orbitals may be seen in (a). b) Schematic representation of the overlap in bonding between the s and p(s) orbitals.

The maximal intensity and creation of a covalent bond between two atoms is achieved by the overlap and interaction of p(p) orbitals.

When comparing elements E and E, it is important to note that there is a greater distance between the beginning of the s bonding pattern and the beginning of the p bonding pattern than there is between the two elements immediately linked together. The reason for this is that the spx-hybridized s atomic orbitals (AOs), which are oriented along the internuclear axis, begin to overlap sooner than the p orbitals, which are orthogonal to the s bonding. This is the reason why this occurs. This is what precipitated the current predicament. This is the cause of the current predicament that we find ourselves in. This is the reason why we are in the predicament that we are in at the moment. In this study, it is shown that the s orbital overlap, which is denoted by the symbol S(s), reaches its highest point at a certain distance $r(E E)$, and then begins to diminish as the distance between the orbitals decreases. It is possible that this is due to the fact that the bigger lobes of the spx hybrids are now less likely to intersect than they were in the beginning. However, this is of more significance due to the fact that the bigger lobes of the other atom begin to overlap with the smaller lobes of the opposite sign as they get closer to the nodal surface at the rear of the other atom. With this new development, it is essential to take it into consideration. Destructive interference is the term used to describe the process that immediately follows, which ultimately results in the cancellation out of overlap. Because of this, the s(sp_x) overlap and associated bonding that occurs between two atoms or bits of molecules is at its maximum when they are in close proximity to one another. Something takes place whenever the value of $r(E E)$ is greater than zero, regardless of the value. As the distance between the two places decreases, the accompanying s bonding and the s overlap both become less significant.

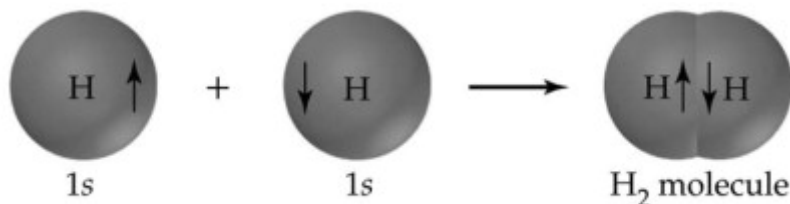


Figure. 2 Two s orbitals combine to generate a σ bond.

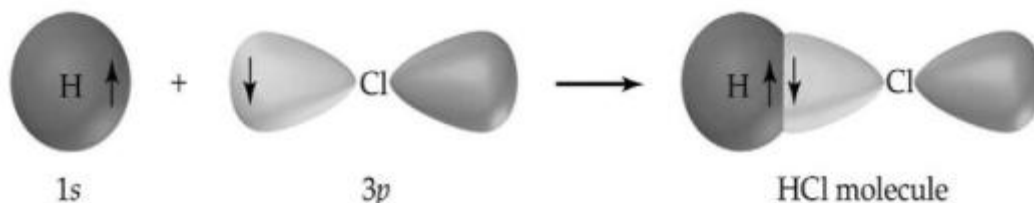


Figure. 3 Furthermore, a σ bond forms between an orbital in s and a p orbital.

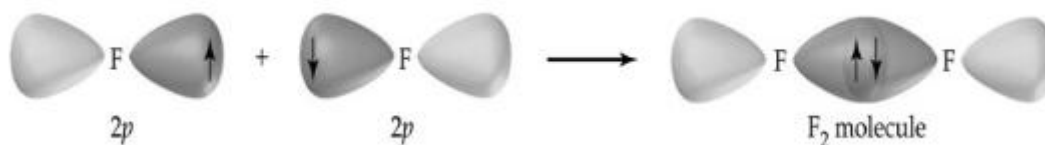


Figure 4 Two p orbitals parallel to their internuclear axis also create a σ link.

As can be shown in Figure 3-4, the formation of a sigma (σ) bond takes place when electrons are transferred from one s orbital to another within the confines of a single covalent binding relationship. For the purpose of describing this phenomenon, the phrase "electron sharing" is used. The kind of bonding known as "sigma bonds," which are formed as a consequence of covalent chemical linkages, is widely regarded to be the most powerful type of bonding. One other situation that has the potential to result in the formation of sigma bonds is the transfer of two electrons between two p orbitals that are parallel to the internuclear axis (Figure 3-4). One alternative is the formation of sigma bonds, which may take place, for example, between a s orbital and a p orbital. In this case, the situation is different. As can be shown in Figure 3-5, which is displayed above, in order to establish a pi (π) bond, it is necessary to transfer two electrons between two p orbitals that are perpendicular to the internuclear axis. As a matter of common knowledge, it is widely accepted that the initial bond in double and triple bonds is one of the bonds that constitute a σ bond.

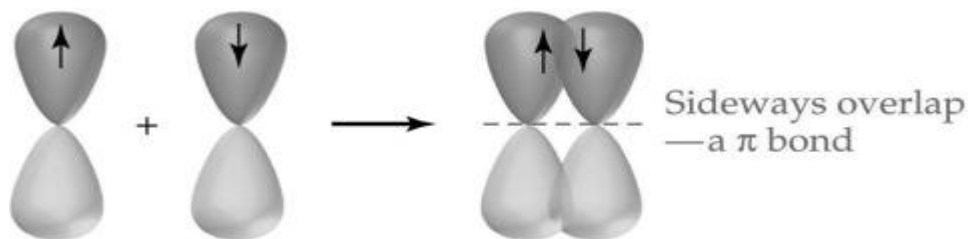


Figure 5 A π bond is formed by a double p orbital that is parallel to the internuclear axis.

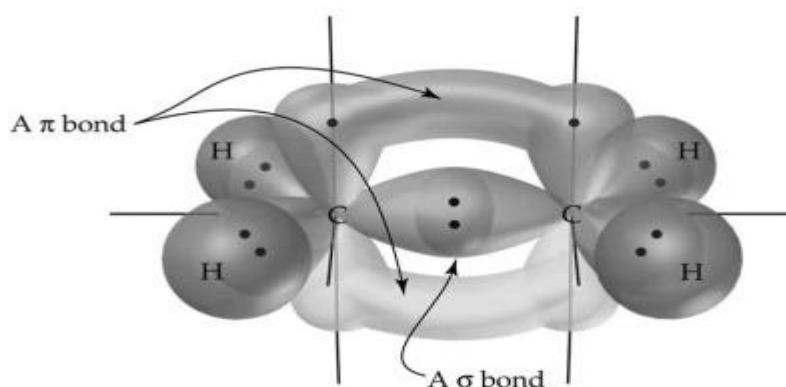


Figure 6 A double bond is made up of two bonds: one on the first bond and one on the second. The diagram provides a detailed explanation of why a double bond cannot spin on itself.

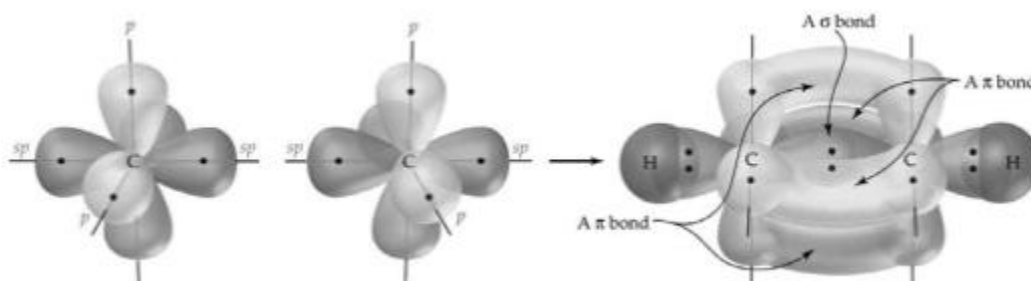


Figure. 7 A triple bond consists of two σ bonds at the end and one σ bond at the beginning.

Dual-imaging probe for magnetic resonance and fluorescence imaging

In comparison to the other conceivable interactions that might take place between molecules, the half-life of covalent connections between them is much longer. The carboimide chemistry technique is the one that is used the most often in the field of covalent bonding in order to manufacture the surface of C-dots. In this mode of action, two examples of catalyst combinations

that are often employed are N-hydroxysuccinimide (NHS) and ethyl (dimethylaminopropyl) carbodiimide (EDC). Both of these compounds are referred to as ketones. As a consequence of the high concentration of amino and carboxyl groups that may be present in biomolecules, this phenomenon takes place. Conjugating quinoline derivative and cyclic DTPA dianhydride (cDTPAA), which serve as selective zinc probe and Gd³⁺ chelation ligands, respectively, onto the surface of amino-terminated C-dots was accomplished in our previous work by the utilisation of carbodiimide chemistry and EDC/NHS catalysis. In order to do this, the combination of the two compounds proved to be beneficial. C-dots have the potential to behave as a zinc-selective receptor whenever they are functionalized with quinoline derivatives, as seen in Figure 5.5A. This is due to the fact that there is a possibility that the fluorescence at 350 nm will undergo an excitation shift from blue to green when zinc ions are activated. Chelation with Gd³⁺ for a further period of time makes it possible to carry out the synthesis of C-dots that are functionalized with Gd-DTPA. In the future, these C-dots might be used for magnetic resonance imaging as well as fluorescence imaging if they are effectively conditioned to serve as a dual-imaging probe.

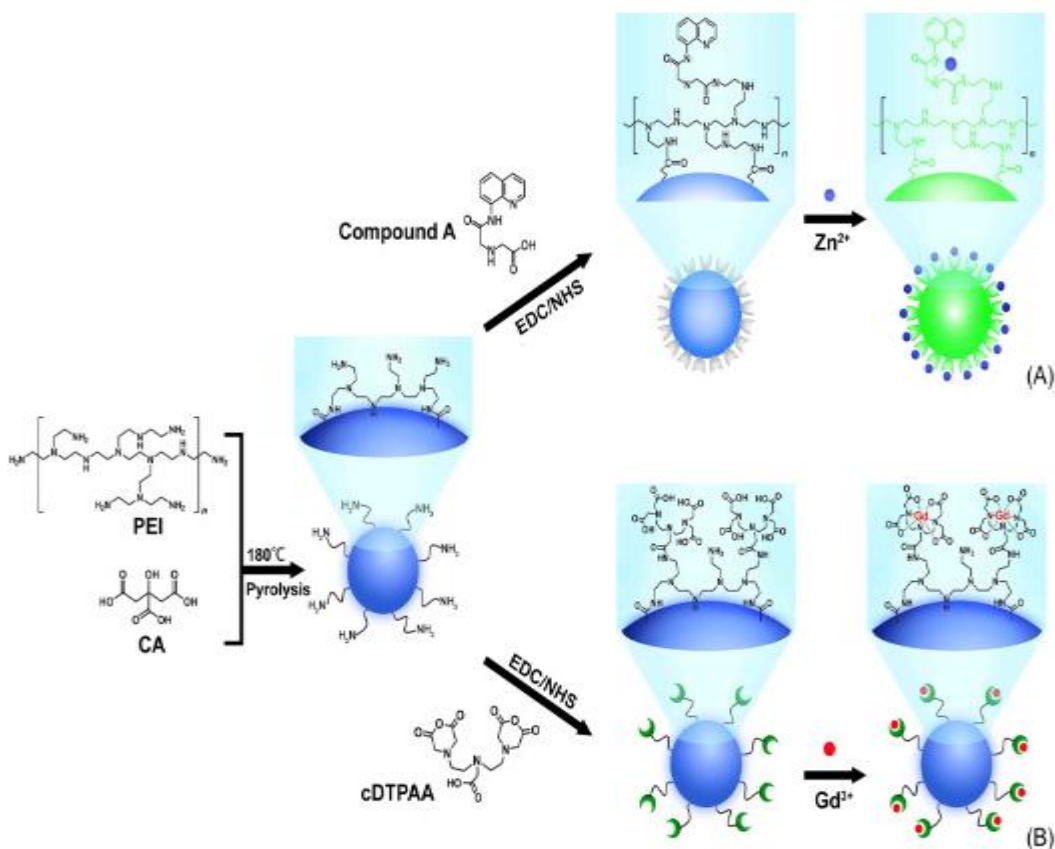


Fig. 8 Carbodiimide chemistry was used to synthesise the DTPA-functionalized C-dots (B) and the quinoline-derivative-functionalized C-dots (A).



Bis(dithiocarbamato)copper (II) is functionalized using amino acids and carbon disulfide.

Besides the formation of covalent connections with carboxyl groups, amino groups are also capable of quickly conjugating into isothiocyanate, sulfonyl chloride, and carbon disulfide groups. This section provides a few examples of things that fall within this category. The findings of Diac's research indicate that the conjugation of rhodamine B (RhB) isothiocyanate onto the surface of the C-dot via the interaction of amino and isothiocyanate groups has the potential to be used in the development of photovoltaic devices and FRET-based sensing platforms (Fig. 5.6A). Yes, in point of fact it is. It is possible that the functionalization of bis(dithiocarbamato)copper (II) on the surface of C-dots will occur as a consequence of the interaction between amino and carbon disulfide groups. It is possible for you to do this by making use of the interaction. Figure 5.6B illustrates a typical fluorescence "turn-on" reaction that occurs when the C-dots that are formed are exposed to Hg^{2+} during the experiment. To be honest, it is correct. A dual-emitting nanoprobe was created by Ye and colleagues by the use of covalent bonds to attach a europium complex (BHHCT-Eu $^{3+}$) to the surface of the C-dot. This nanoprobe was designed for the ratiometric detection of Cu $^{2+}$ in aquatic environments. This was accomplished via the involvement of the interaction between the amino and sulfonyl chloride groups. The purpose of carrying out this procedure was to create a nanoprobe that emitted light at two different wavelengths. To be honest, it is correct. Furthermore, it has been shown that surface engineering C-dots has the potential to successfully build a C-dot-based platform that is capable of PDMA for bioimaging and serum-resistant gene transfer. In order to do this, surface-initiated atom transfer radical polymerization, often known as ATRP, is used. This result has been shown by efficacious experiments. Through the use of N,N'-carbonyldiimidazole activation as a catalyst, it is feasible to transform amino-terminated C-dots into Br-terminated C-dots. This alteration is brought about as a consequence of the interaction between 2-bromoisobutyric acid and surface amino groups respectively. After that, the Br-terminated C-dots are mixed with a number of additional components, including sodium chloride, 2-(dimethylamino) ethyl methacrylate (DMAEMA), pentamethy ldiethy lenetriamine (PMDETA), and other components, in a solution of degassed ethanol. Immediately after the completion of that step, the combination is left to react at room temperature for a period of three hours. After that, the mixture is combined with MPDSAH, and it is allowed to react for a further twenty-four hours at room temperature. The C-dots that are functionalized by PDMA are produced as a result of this procedure.

OBJECTIVES OF THE STUDY

1. To investigate the usage of amino acids and carbon disulfide in functionalizing bis (dithiocarbamato)copper (II).
 2. Researching dual-imaging probes for magnetic resonance imaging and fluorescence
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METHODS

The application of the generalised gradient approximation (GGA) to density functional theory (DFT) resulted in an increase in the bond lengths of the diatomic molecules. The collaboration between the Perdew correlation functional and the Becke exchange functional (BP86) was the driving force behind the realisation of this possibility. For the purpose of computing the SCF, the non-contracted Slater-type orbitals (STOs) were used via the utilisation of basis functions. Additionally, in order to improve the triple-z quality of the basis sets, two different sets of polarisation functions are used. The functions 2p and 3d are associated with hydrogen, while the functions 3d and 4 f are associated with the other atoms present in the universe. When it comes to these sets, both of these functions are present. In the case of core electrons, which are represented by the numbers 1s for atoms in the second period and 1s2s2p for atoms in the third period, it was shown that the frozen-core approximation is the one that must be used. The BP86/TZ2P sign is the one that is used to represent this particular theoretical level. Furthermore, in order to get the intended outcomes of matching the densities of the molecules and perfectly mirroring the Coulomb and exchange potentials in each SCF cycle, an extra set of s, p, d, f, and g STOs was used. This was done in order to achieve the required results. This was used in order to get the intended results. It was done in this manner in order to achieve the desired level of homogeneity. For the purpose of assisting with the calculations on the computer, the ADF programming tool was used.

Ziegler and Rauk, in collaboration with Morokuma, developed a novel approach to energy decomposition, which was then used to the investigation of the interactions between separate atomic particles. Bonding studies are primarily concerned with the instantaneous interaction energy DE_{int} of a bond A B between two fragments A and B in the prescribed electronic reference state and in the frozen geometry of AB. This is the centre of attention for bonding research. The research is mostly focused on this aspect. AB's frozen geometry is used to represent this energy in terms of its frozen geometry. The bonding process is broken down into its component parts by the energy that is being discussed. The difference in energy that exists between the E2 and E atoms while they are in this state is referred to as DE_{int} , which is also referred to as the electronic reference state or the electronic ground state. In the next section of this article, you will have the opportunity to learn more about this aspect of the present state of things for diatomic molecules. In order to offer further details, the interaction energy is composed of three primary components that are related to one another.

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$



$$\Delta E(= -D_e) = \Delta E_{\text{int}} + \Delta E_{\text{prep}}$$

DEprep=0 and DEint=De are the findings that were discovered for the E2 molecules. This is due to the fact that the atomic fragments that were used in our calculations were in the electronic ground state. The reason for this is because the ground state of the atomic components does not exist. It is possible that this may be explained by the fact that the atomic components are in a state of balance. It is rather surprising that EDAs have the capacity to generate bonds with a stability of a few kcal/mol per unpaired electron. These bonds may be formed utilising open-shell fragments. Their failure to remember to take into consideration the spin polarisation that is present inside the segments is the reason for this observation. It is the limitations that technology has imposed on us that are directly responsible for these restraints. Furthermore, it is of the utmost importance to stress that the spin-polarization error DEcorr was taken into consideration at each and every step of the bond energy adjustment procedure. This is evident from the data that is shown in the tables. Within the literature, you may be able to obtain further information on the EDA.

In conclusion, we will talk about our opinions on the estimated energies, which are shown to two decimal places. The reason for this is not because the numbers that come after the decimal point will have any kind of chemical significance; rather, it is because the objective is to guarantee that the data can be reproduced precisely.

RESULTS AND DISCUSSION

Interactions between two electrons: For the remainder of this article, it will be helpful to investigate the interactions that take place between two electrons relative to their distance. These interactions are denoted by the symbol r_{12} , and they are a function of the distance between the electrons. On the left-hand side of Figure 2, you will see a representation of the process by which three curves for electron-electron (e-e) opposition are generated. Curves like this are the result of the process being carried out. Coulomb's law is a mathematical formula that describes the electrostatic interaction that takes place between two point charges that are equivalent to one another. The figures that are shown in the dotted curve are obtained by utilising Coulomb's law.

$$\Delta E_{\text{elstat}}(\text{classical}) = q_1 q_2 / r_{12}$$

When the value of r is equal to zero, it is well known that the repulsion that exists between two point charges acts in a manner that closes to being infinite. A representation of the behaviour that was seen in the observations is provided by the graph. Using the correct equation, which accurately portrays the repulsion that takes place between two electrons, results in the formation

of the second dotted curve. In order to offer a sufficient description of the wave function, this equation makes use of a wave function c rather than a point charge q on the wave function. The calculation was carried out with the help of a hydrogen AO that had a temporal resolution of one second, and the value of x was maintained at 1.0. Using equation (4a) in conjunction with the wave function c , it is feasible to compute the charge density ρ , which may be accomplished by combining the two equations. The quasiclassical repulsion that takes place between two electrons may be described by using equation (4b), which can be found here. In this equation, the symbols t_1 and t_2 represent the coordinates of electrons 1 and 2, respectively. There are two electrons in this equation.

$$\rho = |\chi|^2$$

$$\Delta E_{\text{elstat}} = \int \rho_1 \rho_2 / r_{12} d\tau_1 d\tau_2$$

Despite the fact that equations (3) and (4b) are not identical to one another, the repulsive curves that they produce are extremely dissimilar from one another in two separate ways. Whenever r is equal to zero, the repulsion that results in a limiting value may be found by using equation (4b), which provides the value. One of the various types that are available, this is only one of them. The behaviour may be explained by two different ideas: the bonding models of MO theory and classical electrostatics, which requires two electrons with opposing spins to occupy the same spatial orbital. Both of these theories are distinct from one another. An explanation for the phenomena may be derived from any of these two possibilities. This propensity is thought to be caused by these two ideas, according to the theory offered below.

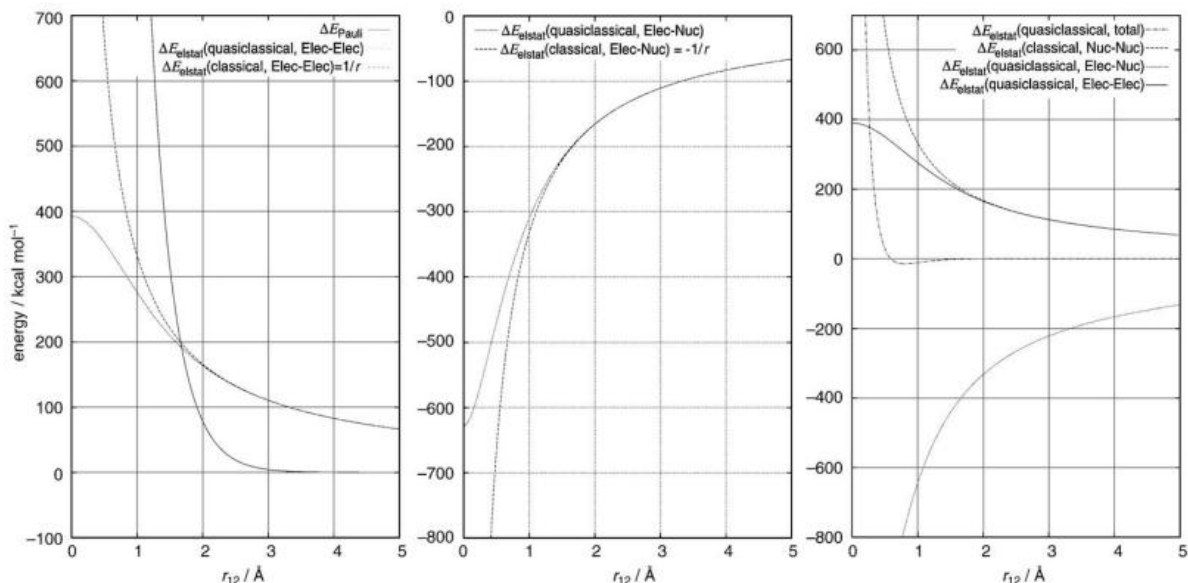


Figure 9. found the connection between the interaction energy and the distance (r_{12}) between two charged particles. Left: Repulsive interactions between two electrons calculated classically $DE_{elstat}(classical)=q_1q_2/r_{12}$ (dashed line); exchange repulsion between two electrons with the same spin in 1s orbitals DE_{Pauli} (solid line); quasiclassical repulsion between two electrons in 1s orbitals $DE_{elstat}=s_{11}12/r_{12}dt_1dt_2$ (dotted line). The quasiclassical attraction between a proton and an electron in a 1s orbital is shown by the equation $DE_{elstat}=q_1s_{12}/r_{12}dt_2$ (dotted line). Conversely, the equation $DE_{elstat}(classical)=q_1q_2/r_{12}$ (dashed line) represents the classical attraction between a proton and an electron. The total of the previously described attractive and repulsive quasiclassical interactions in H_2 would be an appropriate statement.

When it comes to the shapes of the curves that lie between curves one and two M, there is still more differentiation that has to be done. The mass of those bonds is represented by this mathematical figure, which displays the equilibrium for chemical bonds that are composed mostly of lighter atoms. The classical repulsion that takes place between two point charges at about 2 M may be replaced by electrostatic repulsion, which is more powerful than the classical repulsion that can be predicted by using equation (4b). Electrostatic repulsion can be employed in these situations. On top of that, the two curves that are generated by Equations (3) and (4b) are almost similar throughout the very long distances r for which they are applied. Despite the vast distances that separate them, this is in fact the situation. For this purpose, it is vital to have a comprehensive understanding of the electrostatic interactions that take place inside molecules and between two neutral atoms.



When two neutral atoms come into touch with one another electrostatically (without taking into consideration the possibility of orbital mixing), there is a possibility that they will experience a weak attraction or even repulsion towards the neutral atoms. There is a widespread misunderstanding that occurs rather often. There is a widespread misconception that orbital interactions are required for the formation of chemical bonds. This is one of the most common misconceptions. This idea is not supported by the facts for any reason! It has been shown in the past that equation (4b) for the electron-electron interaction is highly appealing when seen within the context of the classical electrostatic interaction that occurs between two neutral atoms at equilibrium distance. Because it provides an explanation for the manner in which electrons interact with one another, this is the reason. Two researchers, Hirshfeld and Rzotkiewicz in 1974 and Spackman and Maslen in 1986, demonstrated that this is really the case. In the context of atoms, this rule is exclusively applicable to a single kind of atom, namely the H₂ atom. "Quasiclassical" is the term that is used to describe the interaction that is estimated since the electron density that is employed in Equation (4b) originates from a quantum chemical calculation. DEelstat is necessary for the formation of particularly attractive nonpolar bonds, which may be present in a wide variety of diatomic and larger molecules, according to research that was conducted not too long ago. These connections are present in a wide variety of distinct molecules. Among the examples of covalent bonding in molecules that are often seen are the ones that have been shown above. Kutzelnigg, Bickelhaupt, and Baerends presented a mathematical justification for the findings as soon as the results were found. This justification was placed within the framework of the phenomenon's explanation that was mathematically based.

When it comes to the chemical bonding region seen in Figure 2 (left), the actual electron-electron repulsion is lower than the value that is predicted by Equation (3), which is derived from the point-charge approximation. When it comes to atom-to-atom electrostatic interactions, the significance of the fact that there are substantial repercussions cannot be stressed. Instead, if the point-charge approximation were to be applied to the remaining components, the net electrostatic interaction between neutral atoms would become more favourable. This would be the case because the net electrostatic interaction would be more advantageous. According to Equation (3), the actual electron-electron repulsion at equilibrium distance is less than what is predicted by the equation. This is what precipitated the current predicament. The reason for this is because while discussing the nuclear–nuclear repulsion mechanism, chemical interactions could tend to neglect the possibility of the nuclei expanding their spatial dimensions. The nuclei are able to repel one another as a consequence of this conclusion.

It is of the utmost importance to investigate the attraction that exists between nuclei and electrons in terms of their interaction. Located in the centre of Figure 2 are the curves that illustrate the electrostatic attraction that exists between two point charges that have opposite signs. The computation of these curves was accomplished by the use of a mix of classical and

quasiclassical analytical methods. The words "positive point charge" (q_1) and "negative charge" (q_2) are used to refer to the positive and negative charges that are associated with a single electron in a 1s hydrogen orbital, respectively..

$$\Delta E_{\text{elstat}} = -q_1 \int \rho_2 / r_{12} d\tau_2$$

The DEPauli curve, which can be seen as the third curve on the left side of Figure 2, was meticulously created in order to provide a clear illustration of the exact interactions that take place between two electrons that have the same spin. According to the Pauli postulate of quantum theory, it is impossible for two electrons that are functioning with the same spin to occupy the same position at the same time. Regarding the hypothesis, this was one of the needs that was included in the list of requirements. The interactions that take place between two electrons that are spinning in the same direction, on the other hand, cannot be accurately described by Equation (4b), which simply shows electrostatic repulsion. In order to fulfil the requirements of the Pauli postulate, the wave function of the product of two electrons must be antisymmetric with respect to the coordinate transformation. Figure 2 (left) illustrates how little of an impact the antisymmetrization of the product wave function c_1c_2 has on the energy when it is applied to larger interelectronic distances. At about three in the morning, DEPauli makes his first appearance in public. When the distance between two molecules is equal to r , practically all molecules are strongly attracted to one another. A strong attraction exists between molecules. Within the bonding range of 1-2 M, the Pauli term DEPauli is the most important term that is responsible for producing repulsive interactions. This occurs as a consequence of the reason that was discussed before. Hydrogen and other two-electron systems, on the other hand, are considered to be of very low significance.

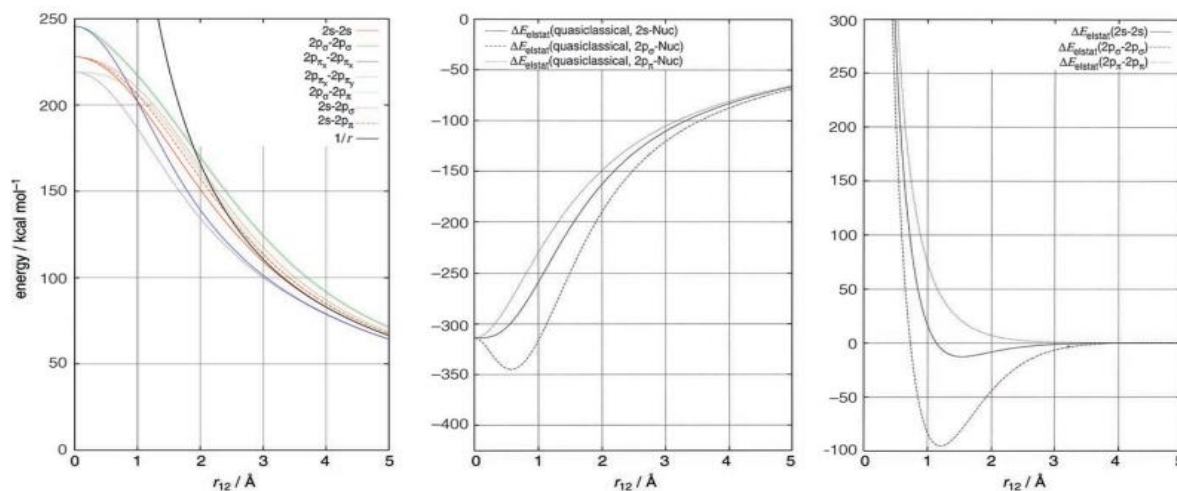


Figure 10. Calculated attraction and repulsion between two charged species, as shown in Figure 2 with the electron in either a 2s or 2p orbital. On the left, classical repulsion between two point charges $DE_{elstat} = \frac{q_1 q_2}{r_{12}}$ in orbitals represents the quasiclassical repulsion between two electrons; $DE_{elstat}(\text{classical}) = \frac{q_1 q_2}{r_{12}}$ (black entire line) Full lines in red, green, and blue indicate 2s–2s, 2p(s)–2p(s), 2p(p)–2p(p), dotted lines in green, blue indicate 2p(p)–2p'(p), dotted lines in red indicate 2s–2p(s), and dashed lines in red indicate 2s–2p(p). The quasiclassical attraction between the proton and electron is represented by the middle equation: $DE_{elstat} = \frac{q_1 s_{12}}{r_{12} dt^2}$ for N–2s (solid line); N–2p(s) (dashed line); and N–2p(p) (dotted line). Right: Total of the quasiclassical repulsive and attractive interactions of the two-electron diatomic molecule model, where $Z=+1$ denotes the nuclear point charges. The 2s (solid line), 2p(s) (dashed line), and 2p(p) (dotted line) orbitals contain the electrons.

Table 1. Energy partitioning analysis of first-row diatomics E2 (E=Li–F) in C2v at BP86/TZ2P (ZORA); energies in kcal/mol, distances r(E–E) in

	Li	Be	B	C	N	O	F
El. state	$1^1\Sigma_g^+$	$1^1\Sigma_g^+$	$3^1\Sigma_g^-$	$1^1\Sigma_g^+$	$1^1\Sigma_g^+$	$3^1\Sigma_g^-$	$1^1\Sigma_g^+$
ΔE_{int}	-20.71	-7.86	-74.67	-140.79	-240.23	-141.87	-52.87
ΔE_{Pauli}	1.76	41.62	135.00	252.20	802.37	464.93	146.07
$\Delta E_{elstat}^{[a]}$	-8.30 (36.9%)	-17.87 (36.1%)	-33.14 (15.8%)	-3.22 (0.8%)	-312.85 (30.0%)	-159.74 (26.3%)	-41.20 (20.7%)
$\Delta E_{orb}^{[a]}$	-14.17 (63.1%)	-31.62 (63.9%)	-176.53 (84.2%)	-389.77 (99.2%)	-729.76 (70.0%)	-447.07 (73.7%)	-157.75 (79.3%)
$\Delta E_{a1}^{[b]}(\sigma)$	-14.17	-31.62	-104.50 (59.2%)	-201.74 (51.8%)	-478.81 (65.6%)	-319.48 (71.5%)	-151.49 (96.0%)
$\Delta E_{a2}^{[b]}(\delta)$	0.00	0.00	0.00	0.00	0.00	0.0	0.00
$\Delta E_{b1}^{[b]}(\pi)$	0.00	0.00	-36.02 (20.4%)	-94.02 (24.1%)	-125.47 (17.2%)	-59.11 (13.2%)	-3.13 (2.0%)
$\Delta E_{b2}^{[b]}(\pi)$	0.00	0.00	-36.02 (20.4%)	-94.02 (24.1%)	-125.47 (17.2%)	-68.48 (15.3%)	-3.13 (2.0%)
$\Delta E_{corr}^{[c]}$	0.29	0.00	1.92	3.27	4.15	4.82	2.72
$D_e^{[d]}$	20.42 (24.62)	7.86 (2.28); 2.70 [calcd] ^[d]	72.75 (71.15)	137.52 (145.86)	236.08 (228.43)	137.05 (120.23)	50.15 (38.25)
$r(E-E)^{[e]}$	2.731 (2.673)	2.442 (2.45) ^[d]	1.617 (1.590)	1.253 (1.243)	1.102 (1.098)	1.224 (1.208)	1.420 (1.412)

Table 2. Energy partitioning study was carried out on several first-row dimers E2 and related species at BP86/TZ2P using specified pieces. energies in kcal/mol and distances in Å.

	$Li_2^{[a]}$ $1^1\Sigma_g^+$	$Li_2^{[a]}$ $1^1\Sigma_g^+$	Li_2^+ $2^2\Sigma_g^+$	Li_2^+ $2^2\Sigma_g^+$	Li_2^+ $2^2\Sigma_g^+$	Be_2 $1^1\Sigma_g^+$	Na_2 $1^1\Sigma_g^+$	Na_2 $1^1\Sigma_g^+$
Virtual space	only s orbitals in virtual space	no virtual orbitals	full	only s orbitals in virtual space	no virtual orbitals	only s orbitals in virtual space	only s orbitals in virtual space	no virtual orbitals
ΔE_{int}	-16.36	-14.60	-27.85	-14.91	-12.27	19.15	-15.18	-14.09
ΔE_{Pauli}	1.76	1.76	2.92	2.92	2.92	41.62	5.07	5.07
ΔE_{elstat}	-8.30	-8.30	+2.07	+2.07	+2.07	-17.87	-10.67	-10.67
ΔE_{orb}	-9.82	-8.06	-32.84	-19.89	-17.26	-4.60	-9.58	-8.49
$\Delta E_{a1}(\sigma)$	-9.82	-8.06	-32.84	-19.89	-17.26	-4.60	-9.58	-8.49
$\Delta E_{a2}(\delta)$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta E_{b1}(\pi)$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta E_{b2}(\pi)$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta E_{corr}^{[b]}$			0.14					
$D_e^{[d]}$			27.71(33.2)					
$r(E-E)^{[e]}$			3.1105					



Based on the information collected via the use of the EDA method, the Li_2^+ link that is associated with greater dependability has a single origin, which is the DEorb term. Both Li_2 and Li_2^+ will display Pauli repulsions that are essentially identical to one another, and Li_2^+ will even interact electrostatically with itself in a way that is repulsive. Therefore, Li_2^+ is one of the rare circumstances in which the normal electrostatic contact does not have any appeal at equilibrium distance. At this moment, H_2 is in the same predicament as before. Following that, the polarisation functions and the p valence AOs were removed from the equation in the course of an EDA reaction involving Li_2^+ . In spite of the fact that the DEorb term is still higher than in Li_2 , the results shown in Table 2 show that it reduces from 32.84 to 19.89 kcal/mol after the ablation of these orbitals. Due to the fact that the bulk of the enhanced binding in Li_2^+ is mediated by genuine orbital interactions, this data implies that this association is valid. The substantially lower lying 2s AOs of the cation are an example of one of these interactions. These AOs significantly increase bonding. Due to the fact that the association is much stronger, this is shown to be correct. By omitting the higher order (n)s orbitals ($n > 2$) of Li from the EDA of Li_2^+ , the findings that are shown in Table 2 provide more evidence in favour of this assertion. The results of the investigation revealed that the DEorb value was predicted to be 17.26 kcal/mol after these orbitals were removed. It is believed that a shift in the 2s orbital radius as a consequence of bond formation in Li_2^+ is responsible for the stability of 2.63 kcal/mol, which is larger than in Li_2 . This argument is supported by the fact that the discrepancy between the current result and the previous discovery (19.89 kcal/mol) shows that this modification could be the explanation for the stability. The significance of this becomes readily evident when one takes into account the fact that the present result is higher than the previous finding.

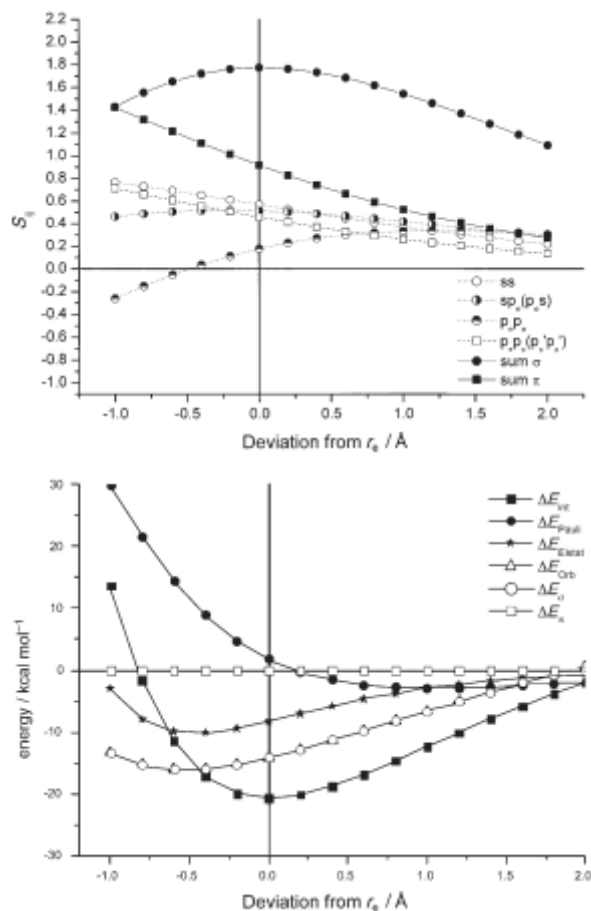


Figure 11. Above: Integrals of the 2s and 2p orbital overlap of Li2 dependent on the interatomic interaction. The bottom shows the computed Li2 EDA values as a function of interatomic distance. The reference value is 0.0, and the estimated equilibrium bond length is 2.731 M.

CONCLUSION

Because of this, it is currently impossible to provide an adequate characterisation of the equilibrium structure of a covalent bond between elements that are located in the second and higher rows of the periodic table. This is because the largest overlap of the s valence orbitals, which nearly always achieves its maximum value at a distance that is obviously less than the equilibrium bond length, does not in any way define the geometry of equilibrium. This is the reason why this is the case. This is what precipitated the current predicament. This is the cause of the current predicament that we find ourselves in. The formation of shorter bonds occurs not as a result of a lack of attractive interaction between electrons in valence orbitals but rather as a result of a considerable rise in Pauli repulsion between electrons in those systems. The creation of



shorter bonds may be attributed, in part, to this particular factor. It is the overlap of orbital surfaces that is responsible for determining the repulsive (DEPauli) and attractive (DEorb) interactions that occur between particles. On the other hand, in contrast to Pauli repulsion, attractive orbital interactions begin to take place at a larger distance. It's possible that the fact that the overlap between occupied orbitals and empty orbitals occurs earlier than the overlap between occupied orbitals might serve as a possible explanation for this phenomenon. This is due to the fact that the total impact of the two components is determined by the degree to which the valence orbitals are occupied throughout the reaction. One of the most significant aspects of covalent bonding that is often disregarded, despite the fact that it has the potential to be of great significance, is the quasiclassical electrostatic interaction.

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a saturated molecule which has a mirror plane always has p orbitals but it does not have a double bond.

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