The Visual and Statistical Exploration of the Shared Electrons versus Transferred Electrons Scatterplot and Its Application in the Classification of Chemical Bond Types

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The Visual and Statistical Exploration of the Shared Electrons versus Transferred Electrons Scatterplot and Its Application in the Classification of Chemical Bond Types

Summary. The Shared electrons – Transferred electrons (*S-T*) scatterplot is a simple way to map chemical bonds and classify them, in which *S* and *T* represent the number of shared and transferred electrons per bond, respectively. In this paper, nature, structure and properties of the *S-T* scatterplot are studied, and its usability is tested. The literature on chemical bonds supports the natural need for extending the known forms of the *S-T* scatterplot to bonds with high (towards the maximum of 6) and low (towards zero) bond orders. For this purpose, an extensive search was performed in literature, and an *S-T* database with bond classification was generated. In total, 2,224 database entries were obtained for 20 bond types: metavalent, metallic, ionic, single covalent, resonant 1-2, double, resonant 2-3, triple, quadruple, quintuple, sextuple, hypervalent, hypovalent, π-complex, through-space, van der Waals, weak, hydrogen and the charge-transfer bond, and weak interaction. The resulting *S-T* scatterplot was analyzed graphically and statistically. A limiting curve was found to enclose the *S-T* space together with the coordinate axes. Because of its complexity, the *S-T* scatterplot has to be analyzed and used in parts, which are as follows: the central (typical bonds) and upper parts (single and multiple bonds), special bond types, and the weak bond types. Several pairs of neighbouring bond types (11) exhibit statistically significant or borderline significant diferences in terms of centroids distance, when tested with a two-dimensional Student test. Several bond types (14) have linear regression lines, out of which 8 have statistically significant or borderline significant slopes. The metallic, metavalent, single covalent, and ionic divalent and trivalent bonds have negative slopes. In other cases, mostly for multiple bond types, slopes are positive due to statistical and computational reasons. The *S-T* scatterplot may easily be used for a correct assignment of bond type to a new bond, as illustrated for examples from the test set. The *S-T* scatterplot is a continuum of bond types, which corroborates with the modern understanding of the chemical bond. The *S-T* scatterplot is useful for the chemical bond concept, and should therefore be studied further.

Keywords: chemistry teaching; chemical bond properties; computational chemistry; interatomic interactions; statistics; structural chemistry.

> „The root of wisdom — to whom
> has it been revealed? Her clever
> devices — who knows them?"
> (Sirach 1:6)

1. INTRODUCTION

In 2018, the concept of metavalent bond, a new bond type between the single covalent and the metallic bond, appeared together with a Shared electrons (*S*) – Transferred electrons (*T*) scatterplot (Wuttig *et al.*, 2018), or simply the *S-T* scatterplot. Since then, several publications about the *S-T* scatterplot as means for bond mapping have appeared (Raty *et al.*, 2019; Cheng *et al.* 2020; Kooi, Wuttig, 2020; Maier *et al.*, 2020; Guarneri *et al.*, 2021; Wuttig *et al.*, 2023; Zhang *et al.*, 2023; Wuttig *et al.*; 2024; Raty *et al.*, 2024). The *S-T* scatterplots contained a few hundred datapoints assigned to the single covalent, ionic, metallic, and metavalent bond, and a few datapoints belonging to the hypervalent, resonant (benzenic), and the van der Waals bond. These bond types exhibited rather good distinction in the *S-T* scatterplot; thus, the scatterplot showed to be useful in bond type assignment to new bonds. In a recent paper, the author of the present paper has constructed a new *S-T* plot based on available numerical data (less than two hundred) from literature in order to assign the correct bond type for potassium dimers in biomacromolecules (Kiralj, 2025).

The *S-T* scatterplot is a rectangular diagram, which represents an extension of triangular van Arkel-Ketalaar diagrams (Jensen, 1995; Leach, 2024). Chemical bonds in elements and binary compounds of van Arkel-Ketalaar diagrams are classified into three bond types: metallic, ionic, and covalent. Such diagrams are based on quantities similar to or related to electronegativity. Worth mentioning are some other classification schemes preceding the *S-T* scatterplot, based on quantum-chemical calculations, such as bond classification based on topological analysis of electron localization functions (Silvi, Savin, 1994), and bond classification based on quantities derived from topological charge and electron density (Mori-Sánchez, 2002).

A new research has appeared (Müller *et al.*, 2024), criticizing the *S-T* scatterplot and the concept of the metavalent bond, because of the inability of the authors to distinguish hypervalent from metavalent bonds well. This criticism and the previous experience with the *S-T* scatterplot have raised the question about the general usability and the nature of the *S-T* scatterplot, which could be verified by using a large dataset.

The other motivation for this study is the natural need to extend the *S-T* scatterplot to other bond types not yet studied, especially those with low and very low bond orders (weak bonds), as well as to those with high bond orders (multiple bonds). The *S-T* scatterplot shows all data in the same way, and all datapoints represent chemical bonds. This implies a verification of the concept of the chemical bond. That is why an online literature search on the definition and description of the chemical bond (at least at the university students' level) was made; it is presented in Tables 1 and 2. The 53 literature sources differ in responses to three basic questions about the chemical bond. The sources were graded for completeness and correctness of knowledge on the chemical bond with grades ranging from 2 to 5. Higher grade means a more reliable source. Literature possibly graded 1 was discarded: in cases when no clear or any description of the chemical bond was given, when it was defined inadequately as 'glue', 'bond' or 'connection' between atoms, and when it was avoided to say what the chemical bond was. Sources graded 5 have the best answers, which may be summarized in the following way: a chemical bond is a combination of interactions (consequences of fundamental physical forces) between charged and moving subatomic particles of atoms in question, ranging in energy from very weak to strong interactions, and causing the formation of any kind of substance. According to this definition, anything that holds atoms together is a chemical bond: classical bond types, weak bonds, very weak bonds, intermolecular and intramolecular interactions, weak interactions in all aggregation states, bonds in chemical reactions or other processes. The famous *Comprehensive Handbook of Chemical Bond Energies* (Luo, 2007) contains data for both strong, intermediate, and weak bonds, which may be called primary, mixed, or secondary chemical bonds, respectively (Callister, Rethwisch, 2018).

Table 1. Literature 1-29 overview of basic questions on the chemical bond, with grades (G)

No.	What is the chemical bond?	Between what is it?	What does it form?	G	Reference
1	attractive force (electrostatic, between opposite charges, ranges from 2 – 250 kcal/mole)	atoms	aggregate	5	Considine, 2005
2	attractive force which holds various constituents together	2 atoms, various constituents	compound	3	Gupta, 2020
3	force between 2 atoms/ 2 groups	2 atoms/ 2 groups	molecule	2	Sutcliffe, 1977
4	not observable/entity, effect of electrons-nuclei interactions	electrons and nuclei	matter	5	Koleżyński, 2011
5	interplaply between attraction of opposite charges, the repulsion of like charge, and the effect of kinetic energy of electrons	opposite/like charges	not specified	5	Atkins, de Paula, 2006
6	connecting electrons, they join atoms	atoms	compound	4	McMurry, Fay, 2004
7	strong forces/attraction that joins ≥ 2 atoms	2 atoms/2 ions	molecule, crystal	3	OpenStax College, 2015
8	force that holds atoms together	2 or more atoms	molecule	2	Chang, 2008
9	attraction (electromagnetic force) between opposite charges	atoms/opposite charges	not specified	4	Hsu et al., 2010
10	strong attractive force between certain atoms in a substance	atoms	substance	4	Ebbing, Gammon, 2009
11	strong attractive force that holds atoms together in molecule or crystal	atoms	molecule, crystall. salt	3	McGraw-Hill, 2003
12	strong attractive interaction bet. atoms	2 adjacent atoms	molecule	2	Brown et al., 2012
13	strong force/attraction between atoms in a molecule or crystal	atoms	molecule/ crystal	3	Daintith, 2008
14	force that holds atoms together	atoms	compound	3	Zumdahl, Zumdahl, 2007
15	forces that hold atoms together	atoms	molecule	2	Dunnning et al., 2023
16	force between 2 atoms/2 groups	2 atoms/2 groups	molecule	2	Rittner, Bailey, 2005
17	forces that hold atoms together	atoms	molecule	2	Gillespie, Popelier, 2001
18	attractive force between atoms	atoms	molecule	2	Carmen, 2009
19	interactions between subatomic particles	subatomic particles	not specified	5	Seifert, 2023

20	force between 2 atoms/2 groups	2 atoms/2 groups	molecule	2	IUPAC, 2006
21	attractive forces between particles	particles involved in the bond	not specified	4	Estévez-Tamayo, 2012
22	interaction between 2 atoms/2 groups	2 atoms/2 groups	molecule	2	Duarte, 2001
23	unifying forces acting on atoms	atoms	compound	3	Požar, 1980
24	force that holds atoms together (intramolecular, intermolecular)	atoms	molecule/ matter	4	Balaban, Zeljković, 2021
25	total force that holds atoms together	atoms	compound/ molecule	3	Orlin, 2010
26	connecting electrons, they hold nuclei together	nuclei	molecule	3	Clayden et al., 2012
27	force of attraction between atoms	atoms	nanomachine/ molecule	3	Brown, Holme, 2011
28	force that holds atoms together	atoms	compound	3	Silberberg, 2010
29	force that holds atoms together	atoms	compound	3	Moore, 2003

Table 2. Literature 30-53 overview of basic questions on the chemical bond, with grades (G)

No.	What is the chemical bond?	Between what is it?	What does it form?	G	Reference
30	force that holds substance components together	substance components	substance	4	Latscha et al., 2011
31	interaction between atoms, that holds atoms together	atoms	matter, molecule	4	Türk, 2011
32	interatomic interaction (electromagnetic, transforms outer electronic shells)	atoms and valence electrons	molecule, mol. comp., crystal	5	Byelorussian Encyclopedia, 2016
33	sum of electrical forces (internuclear repulsion, electrons-nuclei attraction)	atoms, nuclei and electrons	molecule, crystal	5	Əliyev, 2005
34	force that holds atoms together	atoms	substance	3	Pică *et al.*, 2007
35	electrostatic forces that act between particles, 2 atoms/2 groups	particles, 2 atoms/ 2 groups	substance, molecule	4	Langaas Bønes, 2022
36	electrical attraction between atoms, ions, or molecules	atoms, ions, molecules	substance	4	Inkilä, 2018
37	lasting attraction between atoms, ions, or molecules	atoms, ions, molecules	compound	3	Kumar, 2018
38	interaction between 2 atoms/2 groups	2 atoms/2 groups	molecule	2	Tőkés, 2002

39	combined forces that hold atoms or molecules together (electrostatic, between electrons and nuclei)	atoms, ions, molecules, nuclei and electrons	aggregate	5	Tikhonov *et al.*, 2013
40	bonding and anti-bonding electrostatic forces on nuclei, exerted by electrons	electrons and nuclei	substance	5	Chaquin *et al.*, 2014
41	interaction between atoms, ions or molecules, at a distance to form and stabilize an aggregate/ substance	atoms, ions, molecules	aggregate, substance	5	Callaerts, Dehon, 2019
42	attractive force between ≥ 2 atoms (electrostatic, forms new particles – stable at least for some time)	atoms	molecule, compound	4	SET Group, 2004
43	interaction that holds atoms together	atoms	not specified	3	Sidorov *et al.*, 2014
44	nuclei-electrons interaction, (electrostatic forces, attraction balances repulsion)	atoms, nuclei and electrons	not specified	5	Korovin, 1998
45	interaction caused by overlap of electron clouds of bonding particles	electron clouds, bonding particles	molecule, crystal, etc.	5	Ugay, 1997
46	all interactions between atoms that ensure a stable compound (electrostatic, electrons-nuclei)	atoms, electrons and nuclei	two- or polyatomic compound	4	Levitin *et al.*, 2002
47	set of forces and various types of interactions on atoms and groups	atoms, groups	molecule, ion, radical	3	Popkov, Berlyand, 2011
48	force connecting atoms in molecule	atoms	molecule	2	Arstanbekova, 2017
49	interaction between atoms of the same/different elements due to forces that hold them together (stable state)	atoms	not specified	4	Toshpulatov, Raxmatullaev, 2005
50	forces between atoms	atoms, ions	molecules	2	Isxakova, 2020
51	interaction between atoms	atoms	chem. species	3	Balzani *et al.*, 2021
52	combined magnetic forces induced by spin and rotation of nuclei and electrons of two atoms	atoms, nuclei and electrons	not specified	5	Zhonglin, 2022
53	specific interaction between particles	particles	not specified	3	Cídlová *et al.*, 2018

This generalized concept of the chemical bond is the basis of the present paper: several types of interactions are considered bonds between two atoms. Complicated bonds connecting more than three atoms are not treated as a whole bonding unit, but instead, its fragments (atom pairs) are included in the study. Extensive literature search for data to obtain variables *T* and *S* and bond type assignment is performed, and an *S-T* database of considerable size is built. The database is then used to generate the *S-T* scatterplot, which is analyzed graphically and statistically to have more insight into the nature of the *S-T* scatterplot and bond types. Finally, it is illustrated how the *S-T* scatterplot can easily be useful in the correct bond type assignment to a chemical bond.

2. METHODS

2.1. The shared electrons – transferred electrons database formation

A database for chemical bonds of several bond types (the *S-T* database) was generated from literature by searching for three quantities: 1) the number of shared electrons (*S*) between two atoms in a bond; 2) the number of transferred electrons (*T*) from one to the other atom of the bond; and 3) the information about the chemical bond type. Other necessary data were: chemical elements in the bond, substance formula or name, aggregation state, and calculation method. Item 3) was either taken from literature or assigned in this paper, based on bond types of similar cases and chemical knowledge. Items 1) and 2) were from literature whenever possible, in textual, tabular, or pictorial form – from supporting information to published articles. *T* was not used as the number of transferred electrons divided by the oxidation number. In other cases, when *S* and/or *T* were not available, they were calculated using other data. *S* was simply obtained by multiplying the bond order with 2, and *T* was used as reported or calculated charge transfer for the bond in question. For all bonds between two chemically and symmetrically equivalent atoms, only the bond order was necessary, and due to no charge transfer, *T* was set to zero. When it was not the case with *T*, then it was deduced from partial atomic charges: it was first calculated for terminal bonds as charge transfer, then for neighbouring bonds, and so on for other bonds, whenever possible.

When there was no bond order, but charge transfer or partial atomic charges were available, a more complicated procedure of bond length – bond order relationship was carried out to estimate bond orders, for example for π-complex bonds in organometallic compounds, for charge-transfer bonds, and for resonant bonds in some aromatic systems. The procedure started with the collection of atomic radii for the elements in the bond in question: van der Waals radius, molecular single bond covalent radius, molecular double bond covalent radius, and molecular triple bond covalent radius (when available), all from the online database *Webelements.com* (Winter, M. Sheffield, 2024: https://www.webelements.com/). Then, the radii were summed to obtain bond lengths for the van der Waals bond, single, double, and the triple covalent bond, to which bond orders 0, 1, 2, and 3 were assigned. This small data matrix of bond lengths (dependent variable) and bond orders (independent variable) was used to obtain a polynomial regression curve of the second or third order by employing the online software *Polynomial Regression Data Fit* (Lutus, P. Beaverton, OR, 2023: https://arachnoid.com/polysolve/). In the following step, the bond length for the actual bond was measured using molecular graphics software *Mercury 3.6* (Cambridge Crystallographic Data Centre. Cambridge, 2015) on a relevant structure retrieved from the online *Access Structures service of the Cambridge Structural Database* and *Inorganic Crystal Structure Database* (Cambridge Crystallographic Data Centre. Cambridge, 2024: https://www.ccdc.cam.ac.uk/structures/). Finally, the bond order of the actual bond was determined from the polynomial regression relationship and converted to *S*. The bond order was determined in the inverse sense, *i.e.*, the bond lengths were calculated for many values of the bond order in an iterative manner until the bond length closest to the measured bond length was reached, below the difference of 0.001 Å.

Other special cases to obtain *S* and *T* were for hydrogen bonds, and when published, structural data had to be transformed using certain chemical knowledge (application of the known bond length – bond order relationships, simple determination of bond orders from resonance structures, rescaling bond orders based on more correct aromatic structures, etc.). Hydrogen bonds are a special case, because two structures had to be known, one before and the other after the hydrogen bond has been established. The difference in partial atomic charges on the hydrogen atom in question is equal to the charge transfer, and the value of the hydrogen bond order ought to be known in the publication. The *Scilab 5.5.2* software (Scilab Enterprises, S. A. S.; Versailles, 2015) was used for various simple calculations whenever it was necessary to obtain *S* and *T* values from other quantities.

2.2. Visual inspections of the shared electrons – transferred electrons scatterplot

The visual inspection of the whole *S-T* scatterplot and its characteristic regions for the main bond types, single and multiple covalent bonds, special bonds, and weak bond types was performed by using the *Scilab 5.5.2* software (Scilab Enterprises, S. A. S.; Versailles, 2015). The farthermost datapoints served for the construction of the limiting curve, a third-order polynomial regression curve, employing the online software the *Polynomial Regression Data Fit* online software (Lutus, P. Beaverton, OR, 2023: https://arachnoid.com/polysolve/) and reproducing it at high-quality graphics made by the *Scilab 5.5.2* software.

2.3. Student test for differences between neighbouring chemical bond types

A chemical bond type in the *S-T* scatterplot can be understood as a two-dimensional distribution of datapoints assigned to this bond type. The distinction of two neighbouring bond types in the *S-T* scatterplot can be assessed by carrying out a two-dimensional *t*-test, during which it is checked whether the centroids of the bond types belong to the same distribution (null hypothesis). For this purpose, a two-dimensional *t*-test was established. Two groups of datapoints, belonging to bond type 1 and bond type 2, have centroids with coordinates $(\overline{T}_1, \overline{S}_1)$ and $(\overline{T}_2, \overline{S}_2)$, respectively, with errors (standard deviations) $s(\overline{T}_1)$ and $s(\overline{S}_1)$ for the first, and $s(\overline{T}_2)$ and $s(\overline{S}_2)$ for the second centroid. The two-dimensional Euclidean distance between the centroids is:

$$D = \sqrt{(\bar{T}_1 - \bar{T}_2)^2 + (\bar{S}_1 - \bar{S}_2)^2}$$

In general, for a single function of *n* variables, $y = f(x_1, x_2, x_3, \ldots, x_n)$, the variance is given as a summation of variances for all pairs of the variables (Shmueli, 2008):

$$s^2(y) = \sum_{i=1}^{n} \sum_{j \geq i}^{n} \frac{\partial y}{\partial x_i} \frac{\partial y}{\partial x_j} \mathrm{cov}(x_i, x_j)$$

Using this expression and knowing that $s^2(x_i) = \mathrm{cov}(x_i, x_i)$, and that $\mathrm{cov}(x_i, x_j) = 0$ when variables are mutually independent, one obtains the general expression for $s^2(D)$:

$$s^2(D) = \left(\frac{\partial D}{\partial \bar{T}_1}\right)^2 s^2(\bar{T}_1) + \left(\frac{\partial D}{\partial \bar{T}_2}\right)^2 s^2(\bar{T}_2) + \left(\frac{\partial D}{\partial \bar{S}_1}\right)^2 s^2(\bar{S}_1) + \left(\frac{\partial D}{\partial \bar{S}_2}\right)^2 s^2(\bar{S}_2)$$

$$+ \frac{\partial D}{\partial \bar{T}_1} \frac{\partial D}{\partial \bar{S}_1} \mathrm{cov}(\bar{T}_1, \bar{S}_1) + \frac{\partial D}{\partial \bar{T}_2} \frac{\partial D}{\partial \bar{S}_2} \mathrm{cov}(\bar{T}_2, \bar{S}_2)$$

where the covariance terms are

$$\mathrm{cov}(T_1, S_1) = \frac{\sum_i (T_{1i} - \bar{T}_1)(S_{1i} - \bar{S}_1)}{n_1 - 1}$$

$$\mathrm{cov}(T_2, S_2) = \frac{\sum_i (T_{2i} - \bar{T}_2)(S_{2i} - \bar{S}_2)}{n_2 - 1}$$

and T_{1i} and S_{1i} are the i-th values of T_1 and S_1, and T_{2i} and S_{2i} are the i-th values of T_2 and S_2. The final expression for $s^2(D)$ is

$$s^2(D) = \left(\frac{\bar{T}_1 - \bar{T}_2}{D}\right)^2 [s^2(\bar{T}_1) + s^2(\bar{T}_2)] + \left(\frac{\bar{S}_1 - \bar{S}_2}{D}\right)^2 [s^2(\bar{S}_1) + s^2(\bar{S}_2)]$$

$$+ \frac{(\bar{T}_1 - \bar{T}_2)(\bar{S}_1 - \bar{S}_2)}{D^2}[\mathrm{cov}(T_1, S_1) + \mathrm{cov}(T_2, S_2)]$$

Having now the Euclidean distance between the two centroids and the corresponding estimated error, the t-parameter was simply calculated as

$$t = \frac{D}{s(D)}$$

There is certain collinearity between T_1 and S_1, and between T_2 and S_2 and hence, the degrees of freedom used was

$$df = n_1 + n_2 - 2$$

Several pairs of neighbouring bond types were tested. The p-value in each test was calculated for one-tailed hypothesis and at significance level $\alpha = 0.05$, employing the online calculator *P Value from T Score Calculator* (Stangroom, J. Social Science Statistics; Toronto, ON, 2024: https://www.socscistatistics.com/pvalues/tdistribution.aspx).

2.4. Liner regressions for chemical bond types

The visual inspection of all bond types with regard to possible regression, linear regression analysis, and plotting regression lines was performed by using the *Scilab 5.5.2* software (Scilab Enterprises, S. A. S.; Versailles, 2015), according to a previously published procedure (Kiralj, 2024). The F-test for linear regression models was carried out employing the online software *P-Value from F-Ratio Calculator (ANOVA)* (Stangroom, J. Social Science Statistics; Toronto, ON, 2024: https://www.socscistatistics.com/pvalues/fdistribution.aspx). The two-tailed t-test for statistical significance of all regression coefficients was carried out by using the *P Value Calculator* at GraphPad online software (GraphPad Software, Inc.; La Jolla, CA, 2024: https://www.graphpad.com/quickcalcs/pValue1/). The acceptable significance level in all regression analyses was $\alpha = 0.05$.

2.5. Testing the usability of the shared electrons – transferred electrons scatterplot

A dataset for external test was formed from literature that was not used in building the *S-T* database. Simple data for selected bonds, such as bond orders and partial atomic charges, were used to determine the *S*- and *T*-values. Parts of the *S*-*T* scatterplot, previously defined in visual analysis of the *S*-*T* database, were solely utilized in the visual identification of bond types for the testing data. The final deduction of the correct bond type was aided by chemical formulas and chemical knowledge about the substances in question.

3. RESULTS AND DISCUSSION

3.1. Description of the shared electrons *versus* transferred electrons scatterplot

The final chemical bonds database with *S*, *T* and bond classification values comprised 2,224 entries from 207 literature sources. The entries refer to both chemical bonds in various substances (in the crystalline and glass states, and in the gas phase) and calculation methods to obtain *S*, *T* or other quantities from which *S* and *T* can be derived. In other words, some bonds had more than one set of the *S* and *T* values, and even the classification status. In several cases, data for the „average" bond representing very similar bonds in ternary or quaternary intermetallic compounds were given. The database is presented in Figure 1, and in Tables 3 and 4.

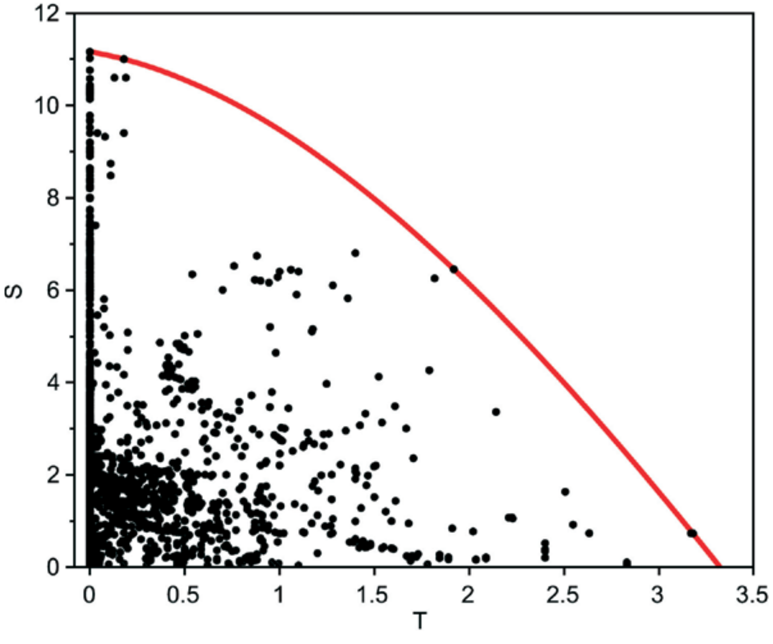

Figure 1. The shared electrons (*S*) *versus* transferred electrons (*T*) scatterplot for all chemical bond types, with the limiting parabola (red, $S = 11.16 - 0.6983\,T - 1.0733\,T^2 + 0.08189\,T^3$).

A limiting cubic parabola (Figure 1), based on four terminal datapoints, was constructed as a current limit for chemical bonds in the shared electrons – transferred electrons (*S*-*T*) scatterplot. Therefore, the boundaries of the *S*-*T* space for all chemical bonds are the *S*- and *T*-axis, and the limiting parabola. The *S*-*T* scatterplot has datapoints that are not uniformly distributed, but are more concentrated on the *S*-axis and in the region close to the origin. There are some gaps, empty parts of the scatterplot close to the curve, and in the region for $S > 7$. There are irregularities in the datapoint distribution because of insufficient data due to some tendencies noticed about research papers. First, there are no sufficient studies yet to cover the *S*-*T* space for high *S* values and for *S*- and *T*-values close to the limiting curve. Secondly, there are several modern research articles dealing with substances that would cover these vacant regions of the *S*-*T* scatterplot, but calculation procedures and corresponding analyses are not complete (no relevant information about bond orders and atomic charges or charge transfer for all bonds in a molecule or crystal). This is the reason why a large number of bonds with $T = 0$ (two chemically and symmetrically equivalent atoms) could enter the database only provided they had bond orders. Such entries, together with bonds in pure metals and homodinuclear molecules and ions, make nearly a half of the database (48.43% entries).

Table 3. Basic statistics[a] for the chemical bond types: typical and multiple chemical bonds

Chemical bond type	*N*	*N*%	*M*(*T*)	*s*(*T*)	*V*(*T*)%	*M*(*S*)	*s*(*S*)	*V*(*S*)%
Metavalent bond	265	11.92	0.29	0.30	105.17	1.01	0.20	20.16
Metallic bond (pure metals, alloys, intermetallic compounds)	140	6.29	0.21	0.53	157.68	0.53	0.25	47.44
Ionic bond (ionic compounds, intermetalllic compounds, some organic compounds)	94	4.23	1.27	0.64	50.85	0.28	0.20	71.55
Formal single covalent bond	651	29.27	0.26	0.40	151.54	1.75	0.34	19.35
Resonant 1-2 bond (between formal single and double covalent bond)	298	13.40	0.14	0.30	213.26	2.73	0.46	16.99
Formal double covalent bond	142	6.38	0.23	0.42	183.04	3.52	0.59	16.84
Resonant 2-3 bond (between formal double and triple covalent bond)	62	2.79	0.36	0.27	76.60	4.63	0.34	7.42

Formal triple covalent bond	85	3.82	0.10	0.35	349.73	5.18	1.03	19.83
Formal quadruple covalent bond	96	4.32	0.14	0.35	249.62	6.12	1.43	23.30
Formal quintuple covalent bond	28	1.26	0.02	0.05	242.90	7.75	1.49	19.23
Formal sextuple covalent bond	37	1.66	0.01	0.05	345.87	9.79	0.97	9.90
COMPLETE DATABASE	2,224	100.00	0.25	0.42	172.18	2.19	1.99	91.03

[a]Statistical parameters: *N* – number of entries (absolute frequency), *N*% – database fraction (relative frequency, in %); *M(T)*, *s(T)*, and *V(T)*% – mean, standard deviation and coefficient of variation (in %) of *T* (number of transferred electrons), respectively; *M(S)*, *s(S)*, and *V(S)*% – mean, standard deviation and coefficient of variation (in %) of *S* (number of shared electrons), respectively.

Table 4. Basic statistics[a] for the chemical bond types: non-typical and non-multiple chemical bonds

Chemical bond type	*N*	*N*%	*M*(*T*)	*s*(*T*)	*V*(*T*)%	*M*(*S*)	*s*(*S*)	*V*(*S*)%
Hypervalent covalent bond	7	0.31	0.91	0.83	91.26	1.86	0.46	24.68
Hypovalent covalent bond	65	2.92	0.22	0.45	202.48	1.26	0.71	55.97
π-Complex bond (metal-π-system bond)	9	0.40	0.01	0.02	153.40	0.59	0.12	20.27
Through-space bond	29	1.30	0.091	0.03	254.43	0.42	0.47	110.93
Van der Waals bond	42	1.89	0	0	–	0.06	0.06	98.09
Weak interaction (unspecified)	102	4.59	0.05	0.12	251.57	0.16	0.14	89.76
Weak bond (unspecified)	58	2.61	0.21	0.26	125.05	0.44	0.14	32.72
Hydrogen bond	8	0.36	0.17	0.23	138.96	0.20	0.07	36.10
Charge-transfer bond	6	0.27	0.05	0.01	9.68	0.22	0.03	11.92
COMPLETE DATABASE	2,224	100.00	0.25	0.42	172.18	2.19	1.99	91.03

[a]Statistical parameters: *N* – number of entries (absolute frequency), *N*% – database fraction (relative frequency, in %); *M(T)*, *s(T)*, and *V(T)*% – mean, standard deviation and coefficient of variation (in %) of *T* (number of transferred electrons), respectively; *M(S)*, *s(S)*, and *V(S)*% – mean, standard deviation and coefficient of variation (in %) of *S* (number of shared electrons), respectively.

Tables 3 and 4 present the *S-T* database in terms of chemical bond types with corresponding absolute and relative frequencies, (*S*, *T*) centroid coordinates with errors (standard deviations) and the coefficients of variation. There are 20 chemical bond types, divided into 11 more typical bond types (Table 3) and 9 more untypical bond types (Table 4). The more typical bond types are as follows: the metavalent, the metallic, the ionic, the formal single covalent, the resonant 1–2 (between formal single and double covalent bond), the formal double covalent, the resonant 2–3 (between formal double and triple covalent bond), the formal triple covalent, the formal quadruple covalent, the formal quintuple covalent, and the formal sextuple covalent bond. Under the term *formal* used in this paper for single and multiple covalent bonds, the formal (theoretically integer) bond order assignment is understood, which, in a certain extent, corresponds to calculated bond orders. The omission of this term in the further text relies on practical reasons. Metallic bonds were from pure metals, alloys, and intermetallic compounds, with a small electronegativity difference between the constitutive metals/metalloids. The metavalent bond is a relatively novel bond type (Raty *et al.*, 2019; Wuttig *et al.*, 2018; Wuttig *et al.*, 2023; Guarneri *et al*, 2021; Raty *et al.*, 2024), distinct from the single covalent, the ionic, and the metallic bonds, characterized as electron-deficient, soft, and longer bond. This bond type lies between the metallic and the formal single covalent bond.

The more untypical bond types studied in this paper are as follows: the hypervalent covalent, the hypovalent covalent, the π-complex (in metal-π-system complex), the through-space, the van der Waals, the weak (unspecified), the hydrogen and the charge-transfer bond, and the weak interaction (unspecified, weaker than the weak bond). The ionic bonds were always from the crystalline state of inorganic, intermetallic, or even organic substances. The through-space bonds comprised intermolecular bonds of type 1,3- or 1,4- bonds, or even between more distant atoms of the same molecule, but always with a possible orbital overlap. The charge-transfer bonds were between aromatic molecules in the mutually parallel position of their aromatic planes. The hypervalent bonds were covalent bonds in hypervalent species, such as ClF_3, XeF_2, SF_4, among many others (Noury *et al.*, 2002; Gillespie, Silvi, 2002; Müller *et al.*, 2024). The hypovalent bonds were mainly from boron compounds (Jacobsen, 2009). The weak bonds were those with *S*-values from around 0.7 to 0.3; below 0.3 were usually weak interactions, and above 0.7 metavalent bonds.

References No. 1, 19, 32, 39, 41, 45, and 52 (13% of all references), among the ones graded 5 (Tables 1 and 2), offer appropriate definitions for the chemical bond, generalized enough to involve attractive interatomic interactions of any strength, and at the same time, with sufficient details to emphasize that interactions are at subatomic level. These facts justify the extension of the literature forms of the *S-T* scatterplot (the metavalent, the single, the metallic, the ionic, and the van der Waals bonds) to other bonds with low and very low bond orders, as well as to multiple covalent bonds.

Bond types in this paper substantially vary in frequencies (Tables 3 and 4), from those having high frequencies, such as the formal single covalent (29%), the metavalent (12%), and the resonant 1-2 (13%) bond, to those with very low frequencies, such as the hypervalent (0.3%), the π-complex (0.4%), the hydrogen (0.4%), and the charge-transfer (0.3%) bond (Tables 2 and 3). These trends reflect the natural distribution of the bond types, and of the profiles of research papers dealing with the bonding analysis of various substances. However, when centroid coordinates are considered with their respective errors, some similarities and differences may be noticed between some bond types, however the tendencies are not clear, because the centroid coordinates and their respective errors are of the same order of magnitude (Tables 3 and 4). The coefficient of variation of T, $V(T)$% is non-existent for the van der Walls bond (all $T = 0$), it is small for the charge-transfer bond (10%), moderate for the ionic (51%) and resonant 2-3 bond (77%), and large for all other bond types (91–254%). This phenomenon has been caused less by insufficient data, and more by the natural distribution of bond types in terms of the T variable. Values of the coefficient of variation of S, $V(S)$%, are on average smaller than that of $V(S)$%, ranging from 10% to 111%. This means that the two-dimensional distribution of datapoints for a particular bond type is strip- or even triangle-shaped (Figure 2). The complete database has average $T = 0.25$ and $S = 2.19$, corresponding to a weakly polarized single covalent bond, with a large coefficient of variation in T (172%) and smaller in S (91%).

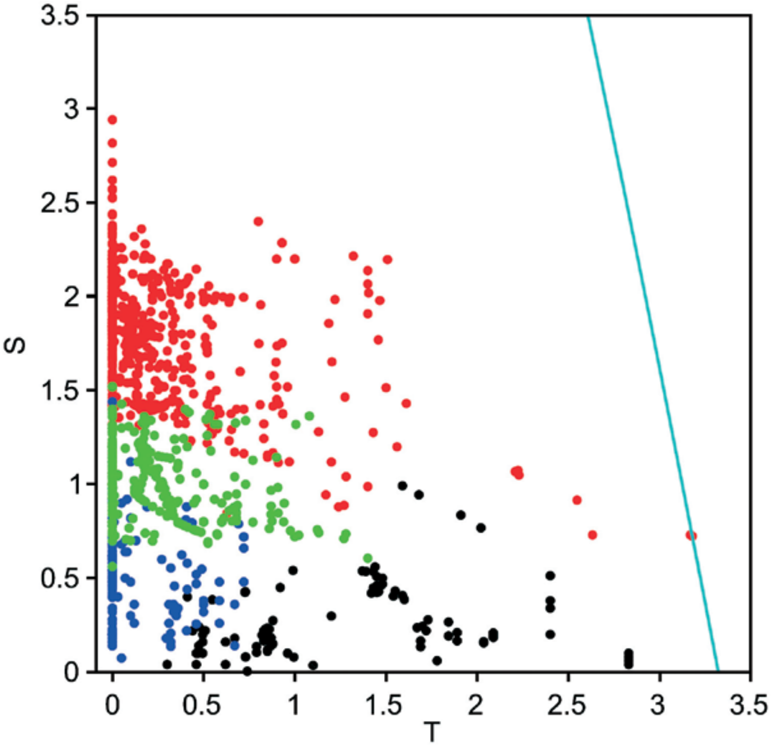

Figure 2. The shared electrons (S) *versus* transferred electrons (T) scatterplot for the main chemical bond types (ionic – black, metallic – blue, metavalent – green, formal single covalent – red), with the limiting parabola (cyan, $S = 11.16 - 0.6983\ T - 1.0733\ T^2 + 0.08189\ T^3$).

Figure 2 shows the essential, central part of the *S*-*T* scatterplot, with four basic bond types comprising 52% of database entries: the ionic, the metallic, the metavalent, and the single covalent bond, with the lower part of the limiting curve. Differences among these bond types are visible in their positions (see centroid coordinates in Table 3) and shapes of their two-dimensional distribution. The formal single covalent and the metavalent bond are spread as stripes inclined to the *T* axis; the metallic bond has a rhombus-like distribution; and the ionic bond seems to have a triangular distribution. The datapoints of the ionic bond form several groups, with an inclination similar to the one of the single covalent bond. These are monovalent, bivalent, trivalent, and other ionic bonds, corresponding to cation's formal charges 1+, 2+, 3+, and fractional charges, respectively. There are partial overlaps too, *i.e.*, the mixing regions of the neighbouring bond types, such as the single covalent-metavalent, the metavalent-metallic, and the metallic-ionic. It is reasonable that, for example, a formal single covalent bond is weak, and its bond order is smaller than the one of a stronger metavalent bond.

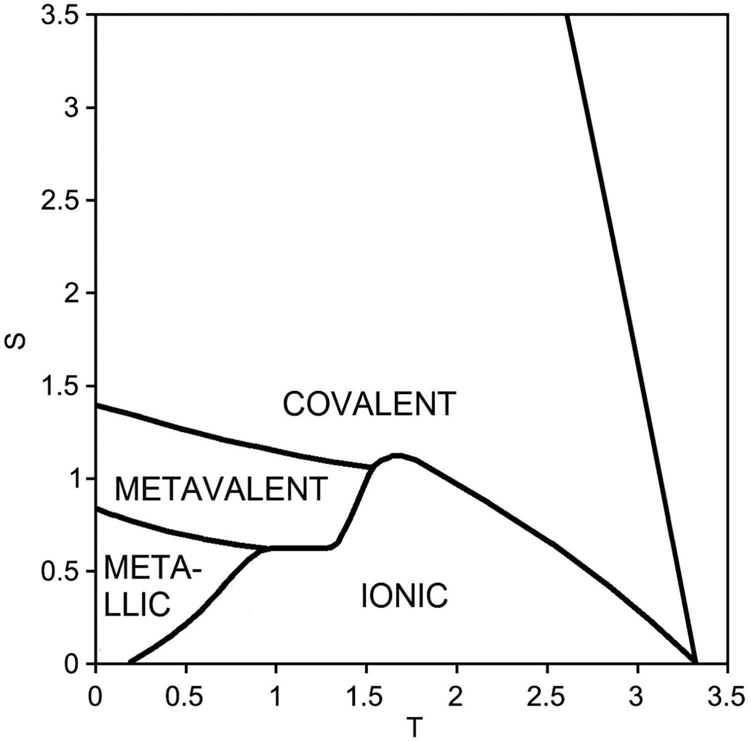

Figure 3. The shared electrons (*S*) *versus* transferred electrons (*T*) space for the main chemical bond types (ionic, metallic, metavalent, formal single covalent), with the limiting parabola ($S = 11.16 - 0.6983\,T - 1.0733\,T^2 + 0.08189\,T^3$).

Figure 3 represents rationalized distribution boundaries for the four bond types from Figure 2. The boundaries are mean curves of the mixing regions; they were drawn in a qualitative sense to facilitate the usage of the *S*-*T* scatterplot. It is clear now that the metallic bond goes deeply in between the metavalent and the ionic bond in the scatterplot. This is known as the region of „bad metals" (Wuttig *et al.*, 2023; Guarneri *et al.*, 2021; Raty *et al.*, 2024) – intermetallic compounds with non-typical metallic properties.

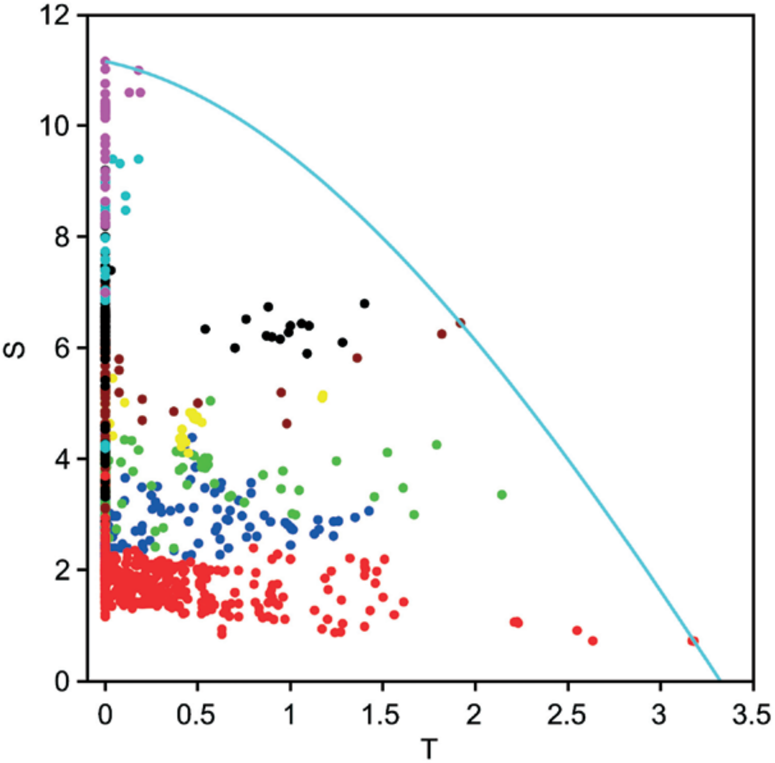

Figure 4. The shared electrons (*S*) *versus* transferred electrons (*T*) scatterplot for formal covalent bond types (single – red, resonant 1-2 – blue, double – green, resonant 2-3 – yellow, triple – brown, quadruple – black, quintuple – cyan, sextuple – magenta), with the limiting parabola (cyan, $S = 11.16 - 0.6983\ T - 1.0733\ T^2 + 0.08189\ T^3$).

Another very important part of the *S*-*T* scatterplot – the upper part – is the one containing the formal single and the formal multiple covalent bonds (double, triple, quadruple, quintuple, sextuple), including the resonant bonds 1–2 and 1–3 (Figure 4). The formal bond orders reach the maximum possible value of 6 (Roos *et al.*, 2007). The most of the bond types in Figure 4 – from the single to the quadruple – have stripe-shaped distributions, inclined to a certain extent to the *T*-axis or even parallel to it. The stripes make stacks along the *S*-axis. The distributions of the quintuple and sextuple bonds are not well defined; the main reason for it are insufficient data. Furthermore, the resonant bonds heavily overlap with the neighbouring bonds that have integer formal bond orders. The resonant bonds are very important bonds, in both organic and inorganic chemistry. It would hence be incorrect to classify them as formal single, double, or triple bonds in order to avoid overlaps. In fact, all the bond types above the resonant 1–2 bond have not many datapoints (28–142). Only the formal single covalent bond has a well-defined distribution; the resonant 1–2 bond has a pronounced overlap with the double bond; and all the other bond types either are not well defined or have overlaps, largely with the neighbouring bond types. Besides insufficient data, other possible reasons for this situation are as follows: 1) possible errors in bond type assignment; 2) natural causes – each bond type contains weak, moderate, and strong bonds; 3) some neighbouring bond types are too close in terms of bond orders (the resonant bonds with their neighbouring bond types).

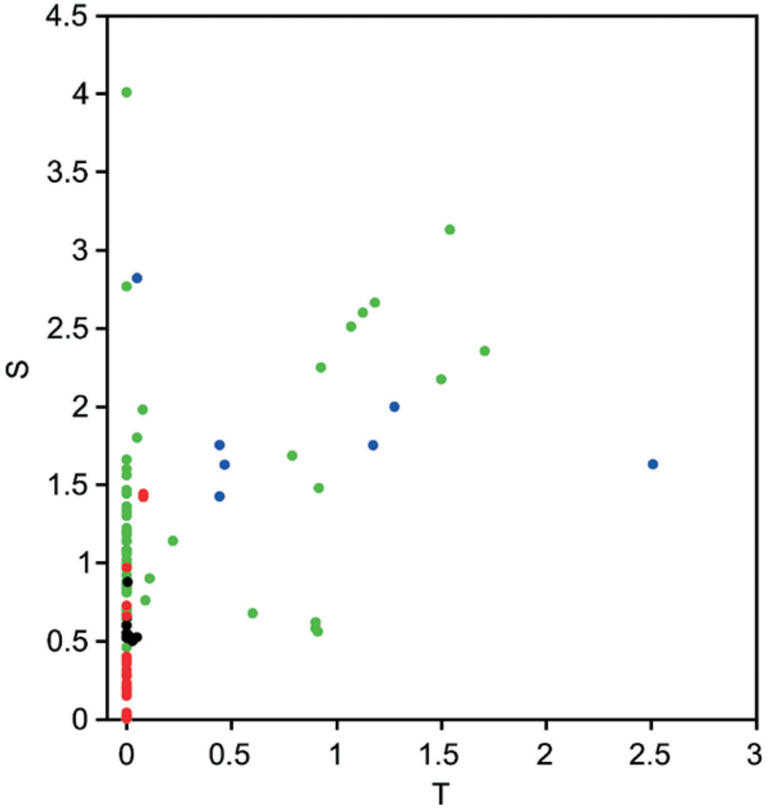

Figure 5. The shared electrons (*S*) *versus* transferred electrons (*T*) scatterplot for special bond types (hypervalent bond – blue, hypovalent bond – green, π-complex bond – black, through-space bond – red).

Figure 5 presents the part of the *S*-*T* scatterplot for four special bond types: the hypovalent, the hypervalent, the π-complex, and the through-space bonds. These bond types have a low number of datapoints (7–65), which are scattered in such a manner that no clear grouping tendency is visible. However, this set of special bond types is situated in the part of the *S*-*T* space characterized by $T < 3$ and $S < 4$. When compared, Figure 5 and Figure 2 show that there is a total overlap of the special bond types with the formal single covalent, the ionic, the metavalent, and the metallic bond. Hence, the two sets of bond types ought to be treated on separate plots.

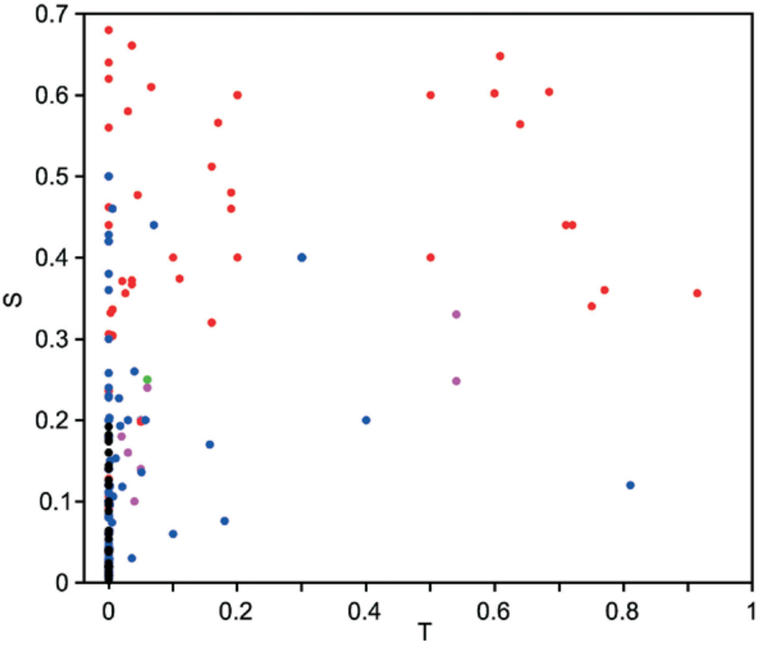

Figure 6. The shared electrons (*S*) *versus* transferred electrons (*T*) scatterplot for weak bond types (van der Waals bond – black, unspecified weak bond – red, unspecified weak interaction – blue, hydrogen bond – magenta, charge-transfer bond – green).

The other set of special bond types are the weak bond types (Figure 6): the van der Waals, the unspecified weak, the hydrogen, the charge-transfer bond, and the weak interaction. They have a low number of datapoints (6–106), which are irregularly spread in a relatively small part of the *S*-*T* space, close to the origin ($T < 1$, $S < 0.7$). The same space is common to the hypovalent, the π-complex, and the through-space bond (Figure 5), as well as to the ionic, the metallic, and the metavalent bond (Figure 2). This is the reason why the three sets of bond types ought to be studied separately, using three plots.

3.2. Statistical distinction of the chemical bond types

The two-dimensional *t*-test serves well as an aid in distinguishing the bond types in the *S-T* scatterplot (Figures 2–6). It may be expected that – if datapoints are too dispersed – the centroids for the two neighbouring bond types will have no distance statistically different from zero. Hence, the two-dimensional distributions will not be distinguished from each other. Tables 4 and 5 contain results of the *t*-test for several pairs of the neighbouring bond types, including the single – double covalent bond pair, and the pair of the two resonant bonds. The special and weak bond types, due to the low number of datapoints and pronounced dispersion, except for the weak bond, were not included in this distinction analysis.

Table 5. Comparative statistics[a] for pairs of neighbouring chemical bond types of lower bond order

Comparison	*N*	*D*	*s(D)*	*t*	*df*	*p*	α	*Difference*
Metavalent bond – Single covalent bond	916	0.74	0.40	1.86	914	0.032	0.05	visible
Metavalent bond – Ionic bond	359	1.22	0.59	2.06	357	0.020	0.05	visible
Metavalent bond – Metallic bond	405	0.50	0.32	1.58	403	0.058	0.10	almost visible
Metavalent bond – Weak bond	323	0.57	0.25	2.29	321	0.011	0.02	visible
Metallic bond – Ionic bond	234	1.16	0.66	1.75	232	0.041	0.05	visible
Metallic bond – Weak bond	152	1.07	0.69	1.56	150	0.061	0.10	almost visible
Ionic bond – Single covalent bond	745	1.78	0.55	3.25	743	0.0006	0.001	visible
Resonant 1-2 bond – Single covalent bond	949	0.99	0.58	1.73	947	0.042	0.05	visible
Double covalent bond – Single covalent bond	793	1.77	0.68	2.60	791	0.005	0.01	visible

[a] Statistical parameters: *N* – total number of entries, *D* – distance between the centroids, *s(D)* – standard deviation of *D*, *t* – Student's test statistic, *df* – degrees of freedom, *p* – probability for the null hypothesis, α – level of statistical significance, Difference – distinction status with respect to the obtained statistical significance.

Table 6. Comparative statistics[a] for pairs of neighbouring chemical bond types of higher bond order

Comparison	*N*	*D*	*s(D)*	*t*	*df*	*p*	α	*Difference*
Double covalent bond – Resonant 1-2 bond	440	0.79	0.75	1.05	438	0.147	0.20	not visible
Resonant 2-3 bond – Double covalent bond	204	1.66	0.69	2.63	202	0.052	0.10	almost visible

Resonant 2-3 bond – Resonant 1-2 bond	360	1.91	0.58	3.30	358	0.0005	0.001	visible
Triple covalent bond – Resonant 2-3 bond	147	0.60	0.99	0.61	145	0.271	0.30	not visible
Triple covalent bond – Double covalent bond	227	1.66	1.18	1.41	225	0.080	0.10	not visible
Quadruple covalent bond – Triple covalent bond	181	0.94	1.76	0.54	179	0.296	0.40	not visible
Quintuple covalent bond – Quadruple covalent bond	124	1.64	2.06	0.80	122	0.214	0.30	not visible
Sextuple covalent bond – Quintuple covalent bond	65	2.04	1.78	1.15	63	0.128	0.20	not visible

[a] Statistical parameters: *N* – total number of entries, *D* – distance between the centroids, *s(D)* – standard deviation of *D*, *t* – Student's test statistic, *df* – degrees of freedom, *p* – probability for the null hypothesis, α – level of statistical significance, Difference – distinction status with respect to the obtained statistical significance.

The total number of entries ranged from 65 to 949 (Tables 5 and 6). The values of *D* (the distance between centroids) are of the same order as the values of their standard deviation *s*(*D*), suggesting that it is necessary to carry out the *t*-test as a complement to the previous visual analysis of the *S*-*T* scatterplot. It has already been noticed that the centroid coordinates and their standard deviations are of the same order of magnitude (Tables 3 and 4); thus, high *t*-values should not be expected even when the degrees of freedom, *df*, is high. Indeed, the *t*-parameter varies from 0.6 to 2.1. Based on the *p*-values and the closest level of the statistical significance α, the following observations can be made: differences between the neighbouring bond types of the lower bond order (metallic, ionic, metavalent, single covalent, resonant 1-2) are well visible ($\alpha = 0.05$), even when including the metavalent bond – weak bond pair (Table 5). The metavalent – metallic difference is a borderline case of statistical significance at level $\alpha = 0.05$.

However, the differences are not well visible mainly for higher bond orders (Table 6), except for the pair of the two resonant bonds (statistically significant at $\alpha = 0.05$), and the pair double bond – resonant 2–3 bond (borderline significant at $\alpha = 0.05$). Such situation is mainly due to the lower number of entries and the pronounced mixing, as already noticed in Figure 4. The two resonant bond types, though not being neighbours, have theoretical difference in their mean bond orders of 2.5 – 1.5 = 1.0. Hence, the corresponding difference in *S* is 2.0, which is equal to theoretical differences between the neighbouring covalent bonds of higher bond orders. Therefore, the two resonant bonds are statistically different, which reinforces the importance of the correct classification of chemical bonds as the formal single, double, triple, resonant 1–2, and resonant 2–3 bonds in innumerous organic and inorganic substances.

3.3. Liner regression for chemical bond types

It has already been noticed that several bond types have stripe-shaped two-dimensional distributions (Figures 2, 3, and 4), so that the stripes extend mainly along the *T*-axis, and are somewhat inclined to it. Linear regression analysis for most chemical bond types is presented in Figure 7, and in Tables 7 and 8. Linear regression lines in Figure 7 are drawn for relatively well-defined two groups of the ionic bond (divalent and trivalent bond), the metavalent, the metallic, and the weak bond, the two resonant bonds, the formal single covalent bond, and all the formal multiple covalent bonds. Other bond types do not have enough data, they are too dispersed, and do not have a well-defined distribution, or they consist of subgroups with rather distinct behaviour. The ionic bond is a set of subgroups with different trends too; thus, the subgroups ought to be treated separately, not as a whole group.

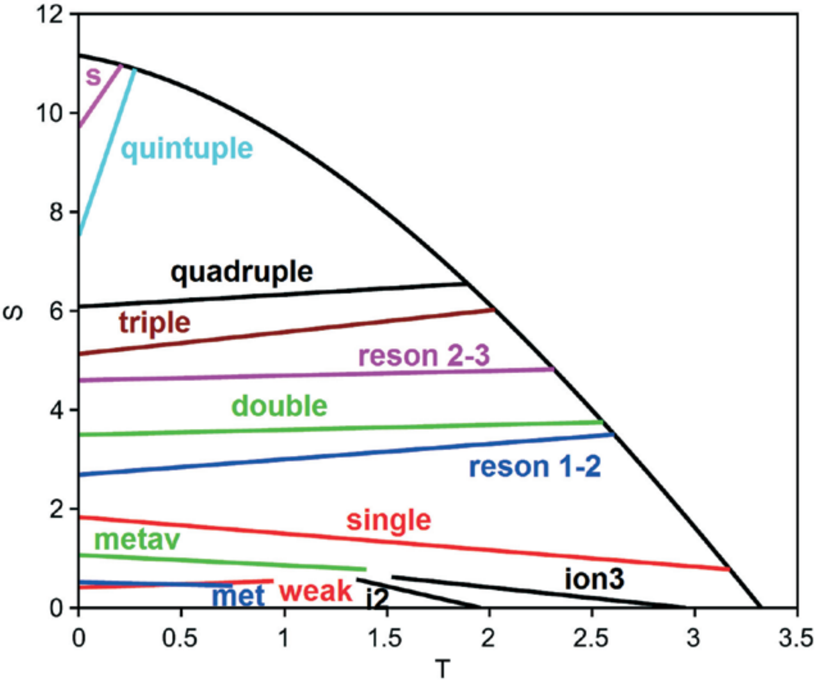

Figure 7. The shared electrons (*S*) *versus* transferred electrons (*T*) space for several chemical bond types is represented with corresponding regression lines, together with the limiting parabola (black, $S = 11.16 - 0.6983\ T - 1.0733\ T^2 + 0.08189\ T^3$): metallic (met, blue), weak (red), ionic divalent (i2, black), ionic trivalent (ion3, black), single covalent (red), resonant 1-2 (reson 1-2, blue), double covalent (green), resonant 2-3 (reson 2-3, magenta), triple (brown), quadruple (black), quintuple (cyan), sextuple (s, magenta). The corresponding linear regression coefficients are given in Tables 7 and 8.

Table 7. Statistics (*F*-test[a] and *t*-test[b]) for chemical bond types of lower bond order

Chemical bond type	*N*	*R*	*F*	*a*	*s(a)*	*t(a)*	*p(a)*	*b*	*s(b)*	*t(b)*	*p(b)*
Metavalent bond	265	0.309	27.8	1.066	0.016	65.00	<0.0001	-0.206	0.039	-5.27	<0.0001
Single covalent bond	651	0.392	118.0	1.833	0.015	125.49	<0.0001	-0.334	0.031	-10.86	<0.0001
Weak bond	58	0.249	3.7	0.410	0.024	17.34	<0.0001	0.135	0.070	1.92	0.059
Ionic bond	94	0.194	3.6	0.201	0.045	4.51	<0.0001	0.060	0.031	1.90	0.061
Ionic divalent bond	22	0.921	111.1	1.856	0.138	13.46	<0.0001	-0.949	0.090	-10.54	<0.0001
Ionic trivalent bond	21	0.569	9.1	1.281	0.319	4.01	0.001	-0.433	0.144	-3.02	0.007
Metallic bond	100	0.092	0.80	0.518	0.030	16.97	<0.0001	-0.094	0.102	-0.92	0.362

[a] *F*-test for linear models ($S = a + bT$): *F* – *F*-ratio, *R* – Pearson correlation coefficient. [b] Two *t*-tests for regression coefficients *a* and *b* of the regression model ($S = a + bT$): *s(a)* and *s(b)* are the estimated standard deviations of *a* and *b*, respectively; *t(a)* and *t(b)* are *t*-parameters for *a* and *b*, respectively; *p(a)* and *p(b)* are corresponding probabilities with respect to $\alpha = 0.05$.

Table 8. Statistics (*F*-test[a] and *t*-test[b]) for chemical bond types of higher bond order

Chemical bond type	*N*	*R*	*F*	*a*	*s(a)*	*t(a)*	*p(a)*	*b*	*s(b)*	*t(b)*	*p(b)*
Double covalent bond	142	0.071	0.7	3.496	0.057	61.57	<0.0001	0.100	0.118	0.85	0.398
Resonant 1-2 bond	298	0.201	12.5	2.689	0.029	92.21	<0.0001	0.312	0.088	3.54	0.001
Resonant 2-3 bond	62	0.076	0.3	4.596	0.073	63.37	<0.0001	0.096	0.162	0.59	0.557
Triple covalent bond	85	0.150	1.9	5.132	0.115	44.53	<0.0001	0.439	0.318	1.38	0.171
Quadruple covalent bond	96	0.061	0.3	6.086	0.157	38.65	<0.0001	0.245	0.417	0.59	0.558
Quintuple covalent bond	28	0.373	4.2	7.523	0.289	26.04	<0.0001	12.322	0.014	2.05	0.051
Sextuple covalent bond	37	0.291	3.2	9.712	0.161	60.26	<0.0001	6.040	3.355	1.80	0.081

[a] *F*-test for linear models ($S = a + bT$): *F* – *F*-ratio, *R* – Pearson correlation coefficient. [b] Two *t*-tests for regression coefficients *a* and *b* of the regression model ($S = a + bT$): *s(a)* and *s(b)* are the estimated standard deviations of *a* and *b*, respectively; *t(a)* and *t(b)* are *t*-parameters for *a* and *b*, respectively; *p(a)* and *p(b)* are corresponding probabilities with respect to $\alpha = 0.05$.

Intuitively speaking, the *S*-*T* relationship is a straight line with a negative slope: the bigger the charge transfer from one atom to the other in the bond, the smaller the bond order for the chemical bond. This is a measure of covalency (electron sharing), regardless of bond type. Such behaviour is visible in Figure 7 for the formal single covalent bond, the metavalent, the metallic, and the two ionic bonds. It is furthermore visible – although not as apparent – in the *S*-*T* scatterplots from literature (Raty *et al.*, 2019, p. 2), and in a recent previous study by the author of this paper (Kiralj, 2025), with much fewer datapoints. The weak bond type shows different inclination with respect to the *T*-axis, the cause of which may be of statistical (insufficient data) or chemical nature (distinct groups within the bond type, among others). Similarly, all bond types above the single bond have non-negative slopes, close to zero (double, resonant 2–3, and quadruple), small positive (resonant 1–2 and triple), and high positive slopes (quintuple and sextuple). Why this phenomenon: the bigger the charge transfer, the higher the bond order? In some cases, the reason is statistical due to insufficient data (especially for polar multiple bonds) or the existence of distinct datapoint groups within the same bond type, or even incorrect assignment of the bond types. On the other hand, similar behaviour of the seven covalent bond types cannot be merely coincidental. The other possible reason is methodological, *i.e.*, methods that are more sophisticated are necessary for calculations of the partition of valence electrons into shared, transferred, and non-shared electrons. Rare articles deal with bonding in polar multiple bonds. Observations in two studies on polar triple bonds (Hennico *et al.*, 1988; Qin *et al.*, 2024) provide a very sensible explanation: polar triple bonds possess three bonding electron pairs, which are however less delocalizable that the ones in non-polar triple bonds; therefore, the bond orders of polar triple bonds are smaller. This rationalization may be extended to all multiple and resonant bond types. Though the scope of this research does not include a more extensive discussion of possible chemical reasons, it would be a very interesting subject in future research.

Tables 7 and 8 present the linear regression analysis with the *F*-test and *t*-tests for bond types from Figure 7. Note that the *p*-value from the *F*-test of regression equations is equal to the *p*(*b*)-value from the *t*-test for the regression coefficient *b*. Statistically significant regression equations in the *F*-test and in all *t*-tests, *i.e.*, regression lines with statistically significant correlation coefficients *R* and regression coefficients *a* and *b*, are those for the metavalent, the formal single covalent, the ionic divalent, the ionic trivalent, and the resonant 1-2 bond type. The line for the weak bond is not statistically significant at $\alpha = 0.05$. The quintuple bond's line is a borderline case of statistical significance. All the other studied bond types have no statistically significant regression lines – either in the *F*-test or in the *t*-test for the regression coefficient *b*. The ionic bond type, when treated as a whole, has false positive *b*, which is statistically non-significant even at $\alpha = 0.05$. The regression lines for the ionic divalent and trivalent bonds have highly negative *b* values ($b < -0.4$). All bond types between the resonant 1–2 bond and the quintuple bond have low *R* values, tending towards being close to zero; hence, the corresponding *b* values are statistically not significant. In conclusion: a greater number of data, and more sophisticated methods or some corrections to present methods for calculation of *S* and *T* values are needed. This imperative does however not apply now for the assignment of bond type to a new bond using the *S*-*T* scatterplot, since all calculations are made in the same manner.

3.4. Application of the shared electrons – transferred electrons scatterplot

A small test dataset was formed from literature data (Bâldea, 2022; Pendás, Francisco, 2018; Zhao, Cheng, 2021; Pathak *et al.*, 2017; Gagliardi, Roos, 2003) for 12 chemical bonds belonging to 7 bond types (Table 9): bond orders λ and partial atomic charges, as the most common data available in literature. The amount of the shared electrons is simply $S = 2\lambda$, while the amount of the transferred electrons is $T = \Delta Q$, whereby ΔQ is the charge transfer for the bond in question. ΔQ may easily be determined from atomic charges for a terminal bond (as the absolute charge of the terminal atom), and for a bond between chemically and symmetrically equivalent atoms (in this case, $\Delta Q = 0$). Based on the chemical formula, one may assign bond type for some cases, but not always (Table 9). The *S*-*T* scatterplot should help in that, as illustrated by examples in Table 9. Figures 1–7 are variants of the *S*-*T* scatterplot, and all of them should be checked for bond types. Between two and five figures were used by placing the (*T*, *S*) bond coordinates onto plots mentally, without looking at chemical formulas or thinking about substance properties. In some cases, there were two or more bond types as solutions, with equal or different chances to be true. The final decision was made by rejecting less probable bond types, and by additionally checking the remnant bond candidate or two candidates with the chemical formula. For example, the O_2 molecule is always depicted with the double bond, and not a resonant 1–2 bond; the N-Na bond cannot be a metallic bond, but a weak bond. For cases when we do not know the bond type or the exact bond type, the *S*-*T* scatterplot is very useful: the Mg-Cl and Ca-Cl bonds come out as ionic divalent bonds, the Re-Re bonds are quadruple, and the Ne-Ne bond can only be a weak van der Waals bond, because Ne is a noble gas. Hence, the presented test for the *S*-*T* scatterplot illustrates its usefulness and easy usage. Of course, a special or a rare bond type, not included in this research, cannot be identified by the *S*-*T* scatterplot: a new extended research should be conducted.

Table 9. Test set of chemical bonds[a] with the bond type assignment[b] from formula and the *S-T* scatterplot

Substance (state)	Bond	λ	ΔQ	*T*	*S*	Formula	*S-T* scatterplot	Figures No.
$H_1–C_1≡C_2–C_3≡C_4–C_5≡C_6–H_2$ (g)	C_3-C_4	1.411	0	0	2.822	triple	resonant 1-2	2, 4, 7
$H_1–C_1≡C_2–C_3≡C_4–C_5≡C_6–H_2$ (g)	H_1-C_1	0.934	0.233	0.233	1.868	single	single	2, 3, 4, 7
Cl–C≡N (g)	Cl-C	1.067	0.118	0.118	2.134	single	single	2, 4, 7
N≡C–C≡N (g)	C-C	1.618	0	0	3.236	single	resonant 1-2 (single, double)	4, 7
Na–C≡N (g)	Na-C	0.214	0.618	0.618	0.428	single	metallic/weak (hypovalent, ionic)	2, 3, 5, 6
:C=N–F (g)	N-F	0.259	0.033	0.033	0.518	single	metallic/weak (hypovalent, π-comp., through-space, weak int.)	2, 3, 5, 6, 7
:C=N–Na (g)	N-Na	0.122	0.651	0.651	0.244	single	metallic/weak (hypovalent, π-complex, through-space)	2, 3, 5, 6, 7
Ne_2 (g)	Ne-Ne	0.034	0	0	0.068	?	vdW (through-space, weak int.)	5, 6
O_2 (g)	O-O	1.541	0	0	3.082	double	resonant 1-2/ double (single, hypervalent)	4, 5, 7
$Ca_2MgCl_6·H_2O$ (s)	Mg-Cl	0.369	1.672	1.672	0.738	ionic2	ionic divalent	2, 3, 7
$Ca_2MgCl_6·H_2O$ (s)	Ca-Cl	0.213	1.487	1.487	0.426	ionic2	ionic divalent	2, 3, 7
$Re_2Cl_8^{2-}$ (g)	Re-Re	3.200	0	0	6.400	?	quadruple	4, 7

[a] Bond parameters from literature (Bâldea, 2022; Pendás, Francisco, 2018; Zhao, Cheng, 2021; Pathak *et al.*, 2017; Gagliardi, Roos, 2003): λ – bond order (*S* = 2λ), ΔQ – charge transfer (ΔQ = *T*) calculated as the absolute atomic charge of the terminal atom (for a terminal bond) or of the metallic ion (for ionic compound), or taken as zero when bond atoms are chemically and symetrically equivalent. [b] Bond type assignments: Formula – based on chemical formula, *S-T* scatterplot – based on scatterplot variants (cited Figures) as highly probable (no brackets), less probable (within brackets), and the final solution (underlined) when the figures are combined with formula and chemical knowledge. Abbreviations: vdW – van der Waals, π-comp. – π-complex, ionic2 – ionic divalent, quadr. – quadruple.

In a previous paper (Kiralj, 2025), an *S-T* scatterplot was made using only 173 datapoints, in order to assign bond types to 8 entries for potassium-potassium bonds in biomacromolecular crystal structures. Similarly to testing the *S-T* scatterplot in this paper, it was easy to locate the potassium dimers in the bordering region of the formal single covalent and the metavalent bond. Recently, the usage of the *S-T* scatterplot was criticized for its inability to distinguish the hypervalent from the metavalent bonds (Müller *et al.*, 2024). This comparison has neglected a few factors of merit for an objective judgment of the problem addressed. First, the datasets for the bond types studied (single covalent, hypervalent, metavalent, ionic, and metavalent) were small; hence, natural mixing regions could not be identified. Secondly, instead of *T*, its derivative – *T* divided by formal charge – was used. Thirdly, there was no care about the calculation method for partial atomic charges – there are methods tending to overestimate or underestimate charges, thus one has to choose the most appropriate method to avoid extreme and unrealistic situations. Fourthly, instead of *S*, an analogue was used, whereby new tendencies were introduced into the scatterplot. This analogue of *S* was identified as not suitable when building the *S-T* database in the present paper. Fifthly, the *S-T* scatterplot showed three mixing regions made by ionic and single covalent bonds; this is not known in previous papers tackling the scatterplot. Sixthly, significant dispersion of the hypervalent bond in the *S-T* space was not detected as a natural feature of this bond type. Seventhly, known similarities between single covalent and hypervalent bonds (Gillespie, Silvi, 2002; Nouri *et al.*, 2002), which might suggest possible metavalent – hypervalent similarity, were not addressed. Therefore, the mentioned criticism should not be taken into account. In the present paper, as well as in the previous one (Kiralj, 2025), *T* was not normalized by oxidation state. If the normalization is performed, then the datapoints for all single and ionic bonds lie along the same line (Cheng *et al.* 2020; Kooi, Wuttig, 2020; Maier *et al.*, 2020; Guarneri *et al.*, 2021; Wuttig *et al.*, 2023; Zhang *et al.*, 2023; Wuttig *et al.*; 2024; Raty *et al.*, 2024); between the line and datapoints for metals, a gap is formed. When *T* is not normalized, the gap does not exist (Raty *et al.*, 2019; Kooi, Wuttig, 2020). Besides, how to normalize *T* for other special bonds, weak bonds and weak interactions, and the van der Waals bonds in order to have a natural continuity of the bond types in the scatterplot, and to include mixing regions and overlaps? The same problem arises with pure metals too, which always have $T = 0$, and the oxidation state zero. Hence, no division is possible.

The *S-T* scatterplot is a two-dimensional arrangement of various bond types in the *S-T* space. Chemical bonds are known to be multidimensional phenomena (Kiralj, 1999; Kiralj, Ferreira, 2002; Kiralj, Ferreira, 2003); it is therefore unrealistic to expect all bond types to be well-distinguished, with neither overlaps nor mixing regions in a two-dimensional scatterplot. In several articles (Raty *et al.*, 2019; Maier *et al.*, 2020; Cheng *et al.* 2020; Kooi, Wuttig, 2020), a third dimension was added to the *S-T* scatterplot: a physico-chemical property, an atomic or a bond feature. Better distinction was achieved for smaller sets of datapoints belonging to several bond types. Which property would be appropriate for differentiating the bond types when there are thousands of datapoints, as is the case of this paper? It is a matter of an extensive search in a potential future research.

The literature search on the chemical bond (Tables 1 and 2) fairly clearly shows diversity in its definition and description (see underlined items for the nature of the chemical bond), which reflects the differences in grades – the mean grade is 3.5, with standard deviation 1.1 and the significant coefficient of variation (31.6%). The grades have unimodal distribution: the fraction of grade 3 is 32.1%, whereas the other grades have the same fraction 22.6%. The 53 literature sources (Tables 1 and 2) are from 25 countries, and are writen in 20 languages; there was no perceived cultural or language influence on the chemical matter in question. Therefore, the situation regarding the understanding of the chemical bond is universal, with a significant fraction of sources (around 35%) which have the following definition in common: the chemical bond is an interaction at the atomic level and not the subatomic; it causes formation of molecules only, and possibly of crystals. This is the reason why the meaning of the term *chemical bond* has to be changed among chemists. The *S-T* scatterplot is one of the issues speaking in favour to this imperative.

4. CONCLUSION

The nature, properties, and usability of the Shared electrons – Transferred electrons (*S-T*) scatterplot were investigated by building and analyzing a large database with the amount of shared (*S*) and transferred (*T*) electrons, and bond type information. In total, 2,224 database entries were generated for 20 bond types, based on the data from literature: the metavalent, the metallic, the ionic, the formal single covalent, the resonant 1–2, the formal double covalent, the resonant 2–3, the formal triple covalent, the formal quadruple covalent, the formal quintuple covalent, the formal sextuple covalent, the hypervalent, the hypovalent, the π-complex, the through-space, the van der Waals, the weak, the hydrogen and the charge-transfer bond, and the weak interaction. Based on graphical and statistical analysis, as well as on an applicability test, the following conclusions about the *S-T* scatterplot may be summarized:

1) There is a limiting curve (an arc of a parabola), which, together with the *T*-axis and the *S*-axis, defines the real *S-T* space of currently known chemical bonds with available data.

2) The *S-T* scatterplot has to be analyzed and used in parts due to its complexity as a whole: the central part (the metavalent, the ionic, the metallic, and the single covalent bond), the upper part (all multiple covalent bonds, including the single bond), the four special bonds (the hypervalent, the hypovalent, the π-complex, and

the through-space bond), and the five weak bonds (the van der Waals, the weak, the hydrogen and the charge-transfer bond, and the weak interaction). This way overlaps are avoided, and it is easier to treat the mixing regions around the boundaries of certain bond types.

3) Pairs of neighbouring bond types with larger numbers of datapoints (in the central and upper parts, including the weak bond) in many cases (11 out of 17) show statistically significant differences at $\alpha = 0.05$ level in terms of centroid distance, as confirmed by the two-dimensional Student's test established in this paper. In other words, the tested bond types occupy distinct regions of the *S-T* scatterplot.

4) Regression lines have negative slopes for several bond types (the metallic, the metavalent, the single covalent, and the ionic divalent and trivalent bond) – as expected, and for other bond types with larger numbers of datapoints, the lines have positive slopes. Statistically significant or borderline significant slopes are for 8 out of 14 tested bond types. The positive slopes may be a consequence of insufficient data, the existence of distinct subgroups within the same bond type, the incorrect bond type assignment, or the low quality of calculation methods used in literature.

5) The *S-T* scatterplot may be easily used for the correct assignment of the bond type to a new bond, as was illustrated for diverse examples from the test set. In this way, the usefulness of the *S-T* scatterplot may be confirmed, and the criticism from recent literature refuted.

6) The *S-T* scatterplot represents a continuum of bond types, which are placed next to each other with or without a mixing region, and with or without an overlap. Inside the *S-T* space, no gap is expected for a much larger number of datapoints than could be provided in this paper. New bond types, not inspected in this paper, may be added to the *S-T* scatterplot in future research.

7) The literature search on the concept of the chemical bond has justified the extension of the known forms of the *S-T* scatterplot to chemical bonds with lower and very low bond orders, as well as to bonds with high bond orders (multiple bonds). On the other hand, the same search has clarified that a significant fraction of modern literature still demonstrates a very limited view on what a chemical bond is. *Chemical bond* should be extended to all interactions that hold atoms together, whereby diverse substances are formed.

Potential future research might focus on a larger database and the clarification of certain issues regarding the *S-T* scatterplot (mixing regions, negative slopes, special and weak bonds included in all analyses, introducing several other special bonds), as well as on the promotion of the universality of the term *chemical bond* in contemporary chemistry, especially in chemical education.

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Vizualno i statističko izučavanje dijagrama raspršenja *Dijeljeni elektroni* naspram *Preneseni elektroni* i njegova primjena za klasifikaciju tipa kemijske veze

Sažetak

Dijagram raspršenja *Dijeljeni elektroni – Preneseni elektroni (D-P)* jednostavan je način mapiranja i klasifikacije kemijskih veza gdje su *D* i *P* respektivno brojevi dijeljenih i prenesenih elektrona po vezi. U ovom radu proučavaju se priroda, struktura i svojstva dijagrama raspršenja *D-P*, te je testirana njegova primjenljivost. Pregled literature podupire prirodnu potrebu za proširenjem poznatih oblika dijagrama raspršenja *D-P* na veze s visokim (prema maksimumu 6) i s niskim (prema nuli) redovima veza. U tu svrhu načinjeno je ekstenzivno pretraživanje literature, te je stvorena baza podataka *D-P* s klasifikacijom veza. Ukupno su načinjena 2.224 unosa u bazu podataka za 20 tipova veza: metavalentnu, metalnu, ionsku, jednostruku kovalentnu, rezonantnu 1-2, dvostruku, rezonantnu 2-3, trostruku, četverostruku, peterostruku, šesterostruku, hipervalentnu, hipovalentnu, π-kompleksnu, kroz prostor, van der Waalsovu, slabu i vodikovu vezu te vezu s prijenosom naboja i slabu interakciju. Rezultirajući dijagram raspršenja *D-P* analiziran je grafički i statistički. Pronađena je granična krivulja, koja s koordinatnim osima zatvara prostor *D-P*. Zbog svoje složenosti, dijagram raspršenja *D-P* treba se analizirati i upotrebljavati u dijelovima, a to su: središnji (tipične veze) i gornji dio (jednostruka veza i višestruke veze), tipovi posebnih veza te tipovi slabih veza. Mnogi parovi susjednih tipova veza (11), kada su testirani dvodimenzionalnim Studentovim testom, pokazuju statički značajne ili granično značajne razlike u smislu udaljenosti centroida. Mnogi tipovi veza (14) imaju pravce linearne regresije, od kojih osam ima statistički značajne ili granično značajne nagibe. Metalna, metavalentna, jednostruka kovalentna, ionska divalentna i trivalentna veza imaju negativne nagibe. U drugim slučajevima, najviše kod tipova višestrukih veza, nagibi su pozitivni zbog statističkih i računalnih razloga. Dijagram raspršenja *D-P* može se lako primijeniti za određivanje tipa veze za novu vezu, kao što je to pokazano na primjerima testnog skupa. Dijagram raspršenja *D-P* jest kontinuum tipova veza, što se slaže s modernim shvaćanjima kemijske veze. Dijagram raspršenja *D-P* koristan je za koncept kemijske veze, te se treba dalje proučavati.

Ključne riječi: međuatomske interakcije; poučavanje kemije; računalna kemija; strukturna kemija; statistika; svojstva kemijske veze.

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