



In-silico bonding schemes to encode chemical bonds involving sharing of electrons in molecular structures



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ABSTRACT

Encoding of covalent and coordinate covalent bonds in molecular structures using ground state valence electronic configuration is achieved. The bonding due to electron sharing in the molecular structures is described with five fundamental bonding categories viz. uPair–uPair, lPair–uPair, uPair–lPair, vPair–lPair, and lPair–lPair. The involvement of lone pair electrons and the vacant electron orbitals in chemical bonding are explained with bonding schemes namely “target vacant promotion”, “source vacant promotion”, “target pairing promotion”, “source pairing promotion”, “source cation promotion”, “source pairing double bond”, “target vacant occupation”, and “double pairing promotion” schemes. The bonding schemes are verified with a chemical structure editor. The bonding in the structures like ylides, PCl₅, SF₆, IF₇, N-Oxides, BF₄⁻, AlCl₄⁻ etc. are explained and encoded unambiguously. The encoding of bonding in the structures of various organic compounds, transition metals compounds, coordination complexes and metal carbonyls is accomplished.

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1. Introduction

The encoding of chemical bonding is a method of representing the chemical bonds between the atoms through computer based tools and techniques. The encoding enables the storage, retrieval, communication, and processing of the bonding information through electronic media. The bonding information in a format to be processed by computers are useful in developing valuable applications. In general a chemical bond is considered to be formed as a result of the sharing of a pair of electrons by two atoms [1–7]. The shared pair of electrons between the two atoms is the representation of a chemical bond. The sharing of the two electrons may be equal or unequal. In equal sharing, each atom contributes one electron for the bond formation. The bonding due to unequal sharing utilizes a lone pair of electrons from one atom and a vacant electron orbital on the other [1–7]. Accordingly the encoding of chemical bonding involves the encoding of electron environment of the atoms participating in the chemical bonding. Since the location of electrons are normally detailed in terms of electron orbitals,

the encoding of valence electrons is essentially a description of the respective electron orbitals surrounding the atom. As an electron orbital can hold a maximum of two electrons, the number of electrons present in an electron orbital imparts specific electron status to the electron orbital. There are four possible electron status situations which can be associated to an electron orbital. The presence of a single electron is signifying unshared or unpaired electron status of an electron orbital. A lone pair electron status is due to the presence of a pair of electrons in the electron orbital. The absence of electron is considered as vacant electron status of the electron orbital. A shared pair of electrons representing a chemical bond brings the bond pair electron status to the electron orbital. Pertaining to the chemical bonding, those electron orbitals which are involved in chemical bonding alone are significant. The electron orbitals participating in chemical bonding are known as valence electron orbitals. The electrons associated with the valence electron orbitals are called as valence electrons. Consequently, detailing of valence electron orbitals in terms of its electron status such as unpaired electron, lone pair electron, bond pair electron, and vacant electron is crucial to encode the bonding in chemical structures.

The chemical structures are encoded with several formats [8–15]. The widely used structure encoding formats are Connection Table [9] (CTab), Molfile [9], SMILES [10–12], InChI [13,14], and CML

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[15]. The CTab format is the oldest one and is still used with modifications. Molfile is one of the modified form of Connection Table representation of chemical structures. SMILES format is a simple notation based representation of chemical structures suitable for handling the chemical information with databases. InChI the IUPAC International Chemical Identifier is also a notation format of representing chemical structures. It is developed as a non-proprietary international standard to represent chemical structures. As the handling of chemical information in web media demanded the chemical structural information to be described in terms of markup languages, CML (Chemical Markup Language) evolved. In CML the structural information is described based on the Extensible Markup Language (XML) technology [16]. The XML framework allows the description of chemical information with domain specific XML elements along with necessary attributes to attach semantics. The structure description in these file formats are normally handled by chemical structure editors. The existing file formats are handled by few commercial, non-commercial and open source chemical structure editors [17–21]. A structure editor is a software tool to draw, edit, store and to retrieve the chemical structures in electronic media. Though there are several encoding formats available to describe the chemical structural information, the semantics associated with them are not sufficient enough to describe the electron environment of atoms. In the existing encoding systems, the detail of electron information is either absent or they are not explicit. The encoding of chemical bonding can be achieved by a format which can detail the valence electronic environment of atoms. One such format reported earlier [22–26] is capable of encoding the valence electron details of every atom in the chemical structures. In this system, the structural information is captured with XML elements along with appropriate attributes. The significant feature of the system is the capability to describe the electron information in terms of <electronLink> XML elements. The system treats each electronLink as a representation of an electron orbital associated with an atom. Accordingly the system allows the description of valence electron configuration of any atom with necessary and sufficient number of electronLinks.

The next concern in developing a system to encode the chemical bonding is the order of electron placement in the valence electron orbitals and the sequence of the valence electron orbitals itself. The order $1s < 2s < 2p < 3s < 3p < 4s < 3d$ is useful for the placement of valence electrons to describe bonding in atoms of *s*-block and *p*-block elements up to atomic number 20. The same order of orbital filling can be extended to other atoms of *s*-block and *p*-block elements for the purpose of chemical bonding. In the case of transition metals the outermost electrons are placed in the same order but for the bonding purpose the (n) *s* electrons are used first followed by the (n-1) *d* electrons. Further, the sequence of (n-1) *d*, (n) *s*, (n) *p*, and (n) *d* is required to describe the structures of some coordination complexes. As there is no single ordering of electron orbitals [27–29] which is correct and common for all the atoms, the decision on the order of valence electron orbitals for *in-silico* chemical bonding becomes a concern. Another issue in encoding the chemical bonding is the consideration excited state or ground state configuration. There is a common practice to explain the maximum valence state of an atom by assuming the atom as undergoing prior excitation. In this excited situation an electron from a lone pair is considered to be promoted into an available vacant orbital resulting in two orbitals with unpaired electron status. However, there are variant views about the involvement of lone pair electrons in the

bond formation [30–32]. In the structures of PCl_5 , SF_6 , IF_7 , etc. the lone pairs are used for the formation of two single bonds. Whereas, in the structures of sulfuric acid, perchloric acid, etc. the lone pairs lead to the formation of double bonds. In the structures of ylides [33], the excited state electronic configuration of carbon atom is not suitable for describing the bonding. While the excited state configuration is needed for describing the chemical bonding in several situation, the same is not suitable for detailing the bonding in some other situations. There are examples like the formation of N-Oxides in which the lone pair electron of nitrogen atom leads to the formation of a single bond with charges. Anomaly also can be indicated in the structures of transition metal atoms. The electronic configuration of **Cu** is considered as the one in which the 3*d* orbitals are fully filled, leaving the 4*s* orbital as half filled. This state of electronic configuration is not suitable for explaining the structure and paramagnetic nature of CuO [34]. Accordingly there is a need for a common basis of valence electron arrangement to describe the chemical bonding generically.

A detailed study to fix the fundamental basis for encoding the chemical bonding reveals that the ground state electronic configuration is found to be serving the purpose. A general way to describe the structures in terms of chemical bonding is to consider a central atom, X which is linked to one or more peripheral atoms, Y. In the present study the central atom is treated as a target atom and the peripheral atoms as source in forming the chemical bonds. Accordingly, starting from the atom of first element in the Periodic Table, every atom is considered as target for bonding. The known chemical structures of target atoms are compared with respect to their electronic environment before and after bonding with suitable source atoms. It is observed that the *in-silico* chemical bonding can be accomplished with the details of ground state valence electronic environment of the target and source atoms. The lone pair electron status and the vacant electron status of electron orbitals are playing very crucial role in this encoding system. The probable bonding schemes are proposed to explain the involvement of lone pair and vacant orbitals of both target and source atoms in chemical bonding. This approach explains the bonding in anomalous structures properly. The bonding in chemical structures created with this approach are compared with the bonding in known structures and found to be correct. The approach may form as a basis to mimic real time bonding in future.

2. Fundamental XML data

The fundamental requirement for encoding a chemical bond between two atoms is the description of the corresponding valence electrons of the respective atoms. It is a process of encoding the valence electron orbitals with the semantics of electron status such as unpaired electron orbital, bond paired electron orbital, lone pair electron orbital, and empty electron orbital. Accordingly, the basic description of atoms along with the details of their valence electrons is encoded into an XML document. The XML document is used as the basis to construct the chemical structures by the structure editor ChemEd [24]. In the XML document, the atoms are represented with <atomFragment> and the valence electron orbitals with appropriate number of <electronLink> XML elements. The XML representation of ground state electronic configuration of carbon and sulfur atom fragments are presented in the following code snippets:

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