

■ Bonding Analysis

Covalent Bonding and Charge Shift Bonds: Comment on “The Carbon–Nitrogen Bonds in Ammonium Compounds Are Charge Shift Bonds”

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Abstract: The paper by Gershoni-Poranne and Chen (R. Gershoni-Poranne, P. Chen, *Chem. Eur. J.* **2017**, *23*, 4659) gives an incorrect definition of covalent bonding. Furthermore,

the assignment of so-called charge shift bonds in ammonium compounds has no physical foundation and is conceptually redundant.

The publication by Gershoni-Poranne and Chen^[1] suggests that the C–N bonds in protonated and methylated ammonium compounds are so-called charge shift (CS) bonds, which are “a third type of chemical bond^[2] in addition to the traditionally recognized covalent and ionic bonds.” The CS character of a bond is estimated by the calculated energy differences of isodesmic reactions between Hartree–Fock (HF) and correlated MO calculations. It is postulated that “the identification of the charge shift bonds....affects understanding of their role in organocatalysis, in which the C–N bonds are stretched”.

We think that the presentation of the CS bond and further statements about covalent bonding in the paper give a misleading understanding of the nature of the chemical bond. There is confusion between the *description* and the *explanation* of chemical bonding, which is due to an uncritical use of the electron-pair bonding model of Lewis^[3] and its adoption into quantum chemistry by Pauling.^[4] There is also a misinterpretation of some mathematical terms that are generated in the calculation of the molecular electronic structure and the physical mechanism that leads to a chemical bond.

The authors state in the introduction “In covalent bonds, the bond energy stems mainly from the spin-pairing energy between atoms”. This widely spread belief that electron pairing is the driving force of covalent bonding is not correct. The term “covalent bond” was coined along with the octet rule by Langmuir^[5] in 1919 as a follow up of the suggestion made by Lewis in 1916 that electron pairs should be considered the basis of a chemical bond;^[3a] however, the suggestion was meant as a

model, not as physical explanation. At that time there was no physical law that correctly described the strong attraction between neutral atoms that give rise to a chemical bond. The electron-pair of Lewis came as a model for molecular structures and reactivities that was in the course of time constantly improved and modified by the input of experimental facts like a neural network. It is amazingly successful and unsurpassed for the description of chemical phenomena until today, more than a century after it was suggested. However, it is *not* a physical explanation for covalent bonding. Lewis was aware of it in his epochal paper where he suggested “Electric forces between particles which are very close together do not obey the simple law of inverse squares which holds at greater distances”.^[3a] This is a remarkable statement that goes in the right direction, but Lewis could not foresee the eventual answer in terms of quantum chemical postulates that was provided by physics for calculating electrical forces between atoms.

The physical explanation for covalent bonding was finally given by Heitler and London in their ground breaking paper in 1927, in which they used the newly developed quantum theory of Heisenberg and Schrödinger for calculating the potential energy curves of H₂ and He₂.^[6] The essence of their finding was expressed with the words (original in German, translated by the author): “.....crucial for the understanding of the feasible behavior between two neutral atoms is a characteristic quantum mechanical vibration phenomenon....”. The conclusion of their work is that covalent bonding is a quantum mechanical effect, which arises from the mixing (interference) of the wave functions of atoms or fragments that leads, after occupation by electrons, to attractive or repulsive interactions depending on the symmetry of the new wave function. Ruedenberg has shown that the energy lowering due to covalent bonding comes from the decrease of the kinetic energy of the electrons in the interatomic basin.^[7] The overall increase of the kinetic energy and lowering of the potential energy, which is requested by the virial theorem,^[8] is due to the contraction of the remaining electronic charge at the nuclei that encounter stronger attraction.^[9]

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Thus, covalent bonding does *not* require two electrons for a chemical bond, it can develop already with only one electron. The bond energy of covalent bonds does not stem from the spin-pairing energy between atoms. A striking example are the covalent bonds in Li_2 and Li_2^+ , in which the removal of one electron from the bonding orbital in Li_2 raises the bond dissociation energy from $D_e = 24.6 \text{ kcal mol}^{-1}$ in the neutral molecule to $D_e = 33.2 \text{ kcal mol}^{-1}$ in the covalent bond of the cation.^[10] The frequent occurrence of two-electrons bonds is due to the Pauli principle,^[11] which allows a maximum of two spin-paired electrons in a spatial orbital.^[12] The Pauli principle is a fundamental postulate of quantum theory, which strongly determines molecular structures and energies, but it is *not* the origin of covalent bonding. The frequently made statement that covalent bonding comes from electron-sharing may arise from the great success of the electron-pair bonding model of Lewis,^[3] but the *description* of a chemical bond must not be confused with the physical *explanation* of covalent bonding.^[13]

There are two types of chemical bonding that are traditionally distinguished in chemistry, both originating from electrostatic forces. One is ionic bonding, which may classically be understood as the attraction between atoms that carry opposite electric charges q . The concept can be taken over to quantum theory by using the quasi-classical charge distribution^[14] of the atomic charges rather than point charges for calculating the interatomic interactions. Purely ionic bonds exist only in solids, in which charged atoms are well separated from each other and in which the overlap between the atomic wave functions is negligible. The lowering of the potential energy due to static Coulombic attraction between opposite charges is the physical basis of ionic bonding. The second type of chemical bonding is the covalent bond, in which the lowering of the kinetic energy of the bonding electrons provides the interatomic stabilization.^[15] Covalent bonding and ionic bonding are associated with a different physical mechanism of chemical bonding—but what are charge-shift bonds?

In order to grasp the meaning of the CSB^[2] one must consider the basic approaches of molecular orbital (MO) and valence bond (VB) theory for calculating the electronic structure and energy of a molecule. In MO theory, one begins with the linear combination of the atomic orbitals λ_{ar} , which give the delocalized molecular orbitals φ_i .^[16] The occupation of the energetically lowest lying MOs leads, through multiplicative steps, to the Hartree–Fock (HF) determinant Φ^0 as the reference term for the wave function. The total wave function for the electronic ground state Ψ_0 may then be expressed as linear combination of Φ^0 and the electronically excited HF functions Φ^n , in which n denotes the number of excited electrons in the HF term [Eq. (1); c = expansion coefficients].

$$\Psi_0^{\text{MO}} = c_0 \Phi^0 + \sum c_1 \Phi^1 + \sum c_2 \Phi^2 + \sum c_3 \Phi^3 + \dots \quad (1)$$

When the expansion of Equation (1) includes all possible excitations of the electrons, the wave function Ψ_0^{MO} spans the complete Hilbert space of the ground state that is given by the basis functions. The associated energy E_0^{MO} is correct

within the basis set limit and neglecting relativistic effects [Eq. (2)].

$$E_0^{\text{MO}} = E^0 + E^1 + E^2 + E^3 + \dots \quad (2)$$

The Hartree–Fock energy E^0 usually covers about 99% of the total energy E^0 . The other energy terms E^m ($m > 0$), which come from the mixing of electronically excited configurations, are corrections that are due to the individual correlation of the electrons, which is averaged in the HF approximation. The largest contribution to the correlation energy is provided by the term $\langle \Phi^0 | r^{-1}_{0,2} | \Phi^2 \rangle$, which comes from the combination of the HF reference function Φ^0 with the doubly excited configurations Φ^2 . It is important for the present topic to emphasize that the contribution of correlation energy does *not* suggest the appearance of electronically excited states, even when the calculations involve wave functions of excited configurations. They are purely mathematically derived expressions that improve the description of the interelectronic repulsion in MO calculations.

Although the HF energy E^0 typically provides about 99% of the total energy E_0 , it is often a poor approximation for calculating energy differences ΔE . This holds, for example, for bond dissociation energies (BDEs) D_e , which are usually too small when the correlation energy is neglected. A prominent case is the BDE of F_2 , which is even unbound at the HF level. Table 1

Table 1. Calculated bond dissociation energies D_e [kcal mol^{-1}] with MO and VB methods using large basis sets.

	HF	MO ^[a] Corr.	HF + Corr.	HL	VB ^[b] RE	HL + RE	Exptl ^[c]
H_2	83.9	25.5	109.4	95.8	9.2	105.0	109.5
F_2	−27.0	65.2	38.2	−28.4	62.2	33.8	38.2

[a] Calculated at CCSD(T)/aug-cc-pV5Z. [b] Reference [2c]. [c] Reference [10a].

shows that the D_e value for difluorine at the HF level even when using a large basis set remains negative when correlation energy is not considered. The crucial contribution of correlation energy to the BDE does not mean that the nature of the fluorine–fluorine bond is different from the bond in H_2 , for which the HF calculation gives a reasonable but too small estimate of the BDE. Both molecules have covalent bonds that arise from the mixing of the atomic wave functions and the occupation of the resulting molecular orbitals. The difference between H_2 and F_2 is only that MO calculations request correlation energy already for a qualitatively correct BDE of difluorine. This is, because the electron–electron interactions between the larger number of electrons at the fluorine atoms at short distances are poorly described at the HF level.

The VB method also presents an expansion of the wave function Ψ_0^{VB} , but the individual terms are constructed and assembled in a different way.^[17] There are several variants of VB theory, but the starting point is similar for all of them. The VB

wave function Ψ_0^{VB} is expressed as the sum of two-center product functions ($\lambda_a\lambda_b$) as it was done by Heitler and London in their original work.^[6] The occupation by two electrons gives rise to the spin-coupled covalent term ($\lambda_a-\lambda_b$) ("Heitler–London" term HL) and to the ionic terms ($\lambda_a|-\lambda_b^+$) and ($\lambda_a^+ \lambda_b|^-$). The basic VB expansion, which includes all possible products in the molecule, can be given by the simplified form shown in Equation (3).

$$\Psi_0^{\text{VB}} = \Sigma c_1(\lambda_a-\lambda_b) + \Sigma c_2(\lambda_a|-\lambda_b^+) + \Sigma c_3(\lambda_a^+ \lambda_b|^-) \quad (3)$$

Mathematically, MO theory rests on the product of sums, while VB theory is based on the sum of products. Both methods converge to the same result if all terms are considered and thus, they are essentially equivalent approaches toward the correct wave function. Coding the MO terms into computer programs leads to faster algorithms than the VB approach. This is the reason why quantum chemical methods that strive for numerical accuracy are mostly based on MO theory, because much larger molecules can be calculated with high precision than with the VB method. The VB method is more closely associated with the electron-pair model of Lewis, which is the reason that Pauling favored it over the MO method. It is tempting to directly correlate the terms of Equation (3) and the numerical results of VB calculations with the bonding model of covalent and ionic bonding, which makes the VB approach seductively appealing for chemists. Alternative methods that use the total electron density have been developed like the NBO (natural bond orbital) procedure, which extract the Lewis bonding model from MO calculations.^[18] It must be realized that the individual numbers of the VB terms and the NBO(MO) calculations refer to a chemical model, but not to physical reality. There is a danger to identify the results with the physical mechanism of the chemical bond. Valence bond theory is a quantum theoretical method that must not be confused with the electron-pair model of Gilbert Lewis.^[19]

The calculation of the BDE with the VB method considers the energetically lowest lying structure (HL or ionic) of Equation (3) as major term. The weight of the two terms characterizes the bond as more covalent or more ionic, which is a useful method for connecting accurate quantum chemical calculations with a bonding model. The VB calculation of D_e is then improved by mixing covalent and ionic VB structures. The mixing contributions yield the resonance energy (RE) in accordance with the term resonance that was introduced by Pauling.^[4] It describes the correct wave function as mixing of various "resonating" VB structures, which has become a common model for describing the bonding situation in molecules. The RE plays a similar role for improving the reference energy of VB calculations as the correlation energy does in MO calculations. The two approaches for calculating D_e by MO and VB theory are given in Equations (4) and (5).

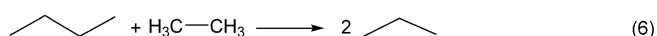
$$D_e(\text{MO}) = D_e(\text{HF}) + D_e(\text{Corr.}) \quad (4)$$

$$D_e(\text{VB}) = D_e(\text{major}) + D_e(\text{RE}) \quad (5)$$

Table 1 shows that the BDE of F_2 that is calculated using the major (HL) term of the VB expansion is equally wrong ($D_e = -28.4 \text{ kcal mol}^{-1}$) as the result of the MO calculation at the HF level ($D_e = -27.0 \text{ kcal mol}^{-1}$). The numerically similar values do not mean that the VB(HL) and MO(HF) levels are equivalent; the results for other molecules may be quite different. Accurate values are obtained with the MO method when correlation energy is included and when the RE term is considered in the VB calculation. The correlation energy and the RE term are both mathematical corrections to the MO(HF) and VB(HL) methods for calculating the electronic structure of molecules.

Here is where charge-shift bonding now comes into play. Whereas correlation energy has never been claimed to indicate a novel sort of bonding, the advocates of the CSB directly identify the mixing of the VB terms in Equation (3) with a new type of chemical bond.^[2] The occurrence of the RE term as dominating contribution for the BDE of F_2 and some other bonds like OH–OH led them propose that there are actually three types of chemical bonds, namely covalent bonds, ionic bonds and charge-shift bonds (CSBs) which leads to a "new landscape of electron-pair bonding".^[2d] The name CSB stems from the RE term in which the HL structure and the ionic structures in Equation (3) mix, which is formally associated with a shift of an electron from one VB structure to the other. This is a misinterpretation of the mathematical terms that occur in the VB expansion. The assignment of a third bond type is not justified, because the interatomic interactions in F_2 follow the same mechanism as in H_2 .^[7d,20] The leading terms of the VB expansion [Eq. (3)] may be associated with covalent and ionic bonding, but that does not mean that each term indicates a different type of bond. The mathematical description of the molecule with a particular method (VB) is mistakenly used as criterion for the physical mechanism and classification of a chemical bond. The bonding in F_2 arises from covalent interactions like in H_2 , and the particular difficulties of quantum chemical methods for calculating the BDE are not related to the nature of the bond. This is clearly recognized by MO theory, for which the particular electronic structure of F_2 is recognized as an electron correlation problem, but not as a new type of bond. Further molecules with CSBs have been reported in the past, in which the accurate calculation of the BDE with VB methods exhibits large contributions by the RE term.^[21] It has been shown that the RE term of VB calculations can be extracted from MO calculations by suitable reformulation of the wave function, which is not surprising when one considers the basic equivalence of the two methods.^[22] However, this does not mean that the CSB as physically meaningful bonding concept is also found in the MO method.

The paper by Gershoni–Poranne and Chen^[1] now goes one step further and employs MO calculations for identifying CSBs. Based on earlier suggestions,^[23] they use the difference between the calculated HF energies and correlated MO (QCISD and MP4) energies for isodesmic reactions given in Equations (6) and (7) as a criterion for identifying the charge-shift (CS) character of a bond. VB calculations suggested that the central CC bond in [1.1.1] propellane is a CSB.^[21a] It was found that there is a correlation between the size of the RE term to



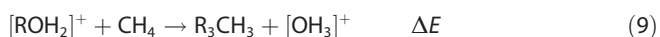
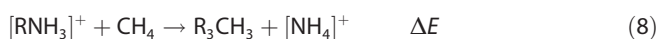
the BDE in VB calculations of chemical bonds and the correlation effect on isodesmic reactions.^[23]

Table 2 shows the data that were reported by Gershoni-Poranne and Chen^[1]. The reaction given in Equation (7) exhibits a

Table 2. Calculated reaction energies ΔE and reaction energy differences $\Delta\Delta E$ in kcal mol⁻¹ (using 6-311+G(d,p) basis sets) of the isodesmic reactions given in Equations (6) and (7) at the HF and correlated (QCISD) levels. Values are taken from reference [1].

Eq.	HF	ΔE QCISD	$\Delta\Delta E$ HF-QCISD
(6)	-0.075	-0.032	-0.043
(7)	-4.564	-2.465	-2.099

larger variation of the reaction energy from correlation contribution at QCISD/6-311+G(d,p)^[24] by -2.099 kcal mol⁻¹, which is taken as evidence that the central C-C bond in propellane is not a covalent bond. The authors then calculated the energies of isodesmic reactions given in Equations (8) and (9) of various ammonium compounds $[\text{RNH}_3]^+$ and protonated alcohols $[\text{ROH}_2]^+$.



The calculated ΔE values of the isodesmic reaction given in Equation (8) at correlated levels are between 1.50–3.54 kcal mol⁻¹ larger than the HF data. For the protonated alcohols the $\Delta\Delta E$ values of the reaction given in Equation (9) differ between HF and correlated MO methods by 3.43–7.09 kcal mol⁻¹. It is concluded that “all of the studied ammonium compounds indeed have significant CS character”. The authors plot the $\Delta\Delta E$ values of the MO calculations as a function of the %RE data that come from the VB calculations, which shows a nearly linear correlation. This is taken as evidence for using MO calculations as a proof of the CS character of the bonds. The authors go on and plot the total energies of the VB structures as a function of the C–N bond lengths. The curves suggest that the %RE and thus the CS character increases when the bonds become longer. They finally discuss the possible %RE character at a transition state of a reaction in which a C–N bond is partly broken. It is said that the bond may be expected to have approximately 70% CS character and that it seems possible that “CS character may modulate reactivity”. Experience has shown that bond breaking invokes larger contributions from correlation energy in MO calculations. The conclusion of the authors

is thus a trivial restatement of this finding for VB terms for which the increase of correlation contribution is dubbed as the appearance of more CSB. The statement in the title of the paper by Gershoni-Poranne and Chen may be expressed with MO theory as “the accurate calculation of the carbon–nitrogen bonds in ammonium compounds requests correlation energy”. The final sentence of the conclusion ends with the statement about the C–N bond in ammonium cations that “...the resonance energy...is the only bonding interaction”.

We think that Gershoni-Poranne and Chen mistakenly identify a mathematical expression with a physical interaction. The scenario that is suggested by their study for analysing chemical reactions such as organocatalysis leads to a pandemonium of numbers without giving any new physical insight. The practical value of identifying the CS character of a bond is dubious. Why should one carry out MO calculations of molecules and then identify the “CS character” of the bonds by isodesmic reactions, which have no physical relevance? The resonance energy is a mathematical term but not a bonding interaction. The division of chemical bonds in three types, covalent, ionic, CSB has no physical foundation and is conceptually redundant.

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Conflict of interest

The authors declare no conflict of interest.

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