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Covalent Bonding: The Role of Exchange Effects

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Abstract

It is stressed that the two-center exchange energy components lead to a significant lowering of the total molecular energy because of exclusion of self-repulsion, and this is inevitable for covalent bond formation. The success of the two-center bond order index relies on the fact that it gives a qualitative estimate of this important phenomenon.

Keywords
Covalent bonding, Electron self-repulison, Bond order, Point-charge approximation, H_2^+ ion, H_2.

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In a recent paper[1] Bacskay and Nordholm performed a number of calculations of H_2^+ and essentially re-iterated and extended the classical results of Ruedenberg[2−4] concerning the complex role of kinetic energy in formation of chemical bonds. The results seem to be completely in line with the summary given in the textbook[5] of the present author: "The problem was investigated in much detail by Ruedenberg on simple examples like H_2^+. He considered the bond formation as being formally divided into consecutive steps: the first step is a *promotion* with a contraction of the valence orbitals. This leads to a lowering of the potential energy (the electrons in average are closer to the nuclei) but the kinetic energy increases *more* than this potential energy lowering. (This increase of the kinetic energy is an obvious consequence of the uncertainty relation.) Then the delocalization permits a kinetic energy lowering *with respect to the promoted state*; this decrease in the kinetic energy is inevitable to provide the possibility of conserving the lower potential energy that has been a result of the promotion. However, in the final account the bond formation is connected with a decrease of the potential energy and increase of the kinetic energy in accord with the virial theorem." (The last remark refers to the minimum on the potential energy curve, as the virial theorem is directly applicable only in points where the energy is stationary.)

The importance of the subject, however, deserves repeated attempts to give a proper physical interpretation of the chemical bond formation. In particular, it is desirable to connect the concept of delocalization appearing in the considerations like those of Ruedenberg or Bacskay and Nordholm with the concept of bond order (multiplicity) and the powerful picture of Lewis electron pairs which are fundamental in chemist's thinking. For that reason, it is desirable to consider *a different* simple *decomposition of the energy*, first for the same H_2^+ model, then for the general case, too.

As the internuclear distance increases, the energy of H_2^+ quickly tends to that of a free hydrogen atom (-1/2 atomic units), as the system dissociates into a hydrogen atom and a free proton. (The energy of a free proton is zero by definition, and it interacts with a *neutral* H atom.) However, owing to the symmetry of the system, the wave function of H_2^+ becomes the sum of wave functions corresponding the electron to be "here" or "there"; the energy of such a linear combination for sufficiently large distances equals that of either degenerate localized state. As we are dealing with a single electron system, this linear combination results in an electron orbital *delocalized* between the two atoms.

For such a wave function each hydrogen atom bears, on average, a positive charge 1/2. And from a global electrostatic point of view that means a rather significant repulsive interaction of $1/(4R_{AB})$ between the atoms, where R_{AB} is the interatomic distance. This electrostatic interaction decays rather slowly

with the distance. At the distances about or over 5 atomic units practically no interactions count except the electrostatic interactions of point charges; the repulsion of $1/(4R_{AB})$ would constitute 0.05 atomic units at R_{AB}=5 a.u. and 0.025 atomic units at R_{AB}=10 a.u. These are quite considerable numbers on the chemical scale: over 30 and 15 kcal/mol, respectively. But nothing similar can be seen on the actual H_2^+ potential curve – see Fig. 1. Why? Obviously there is an effect compensating this electrostatic repulsion. Understanding its nature is instructive for getting a deeper insight into the role of delocalization in chemical bonding.

If one has a proton and a H atom, then there are two global electrostatic effects which just cancel each other: an internuclear repulsion $1/R_{AB}$ and an electron-nuclear attraction $-1/R_{AB}$. In the delocalized case the global electrostatic effect formally contains – besides the terms present also in the $p + $ H case – an electron-electron repulsion that exactly equals the problematic $1/(4R_{AB})$ term. But we have in our system only a *single electron*, and the electron does not interact with itself in the non-relativistic quantum theory. So the global electrostatic effect should be corrected for the *self-interaction* of the electron. After this correction is done, we get zero electrostatic interaction, and the resulting potential energy curve will be determined by other factors—namely the behaviour of the potential and kinetic energies, as discussed in Refs. 1–5.

Nonetheless, the self-interaction correction discussed is in intimate connection with the concept of chemical bonding. To see this, we turn to the energy partitioning scheme discussed in Ref. 6. The expressions given there refer to the single determinant (Hartree-Fock) case. However, the Hartree-Fock level is sufficient for understanding the qualitative aspects of bonding: electron correlation usually influences the numbers but not the chemical picture.

In that energy decomposition the leading two-center contribution is the "electrostatic interaction in the point charge approximation". It represents a sum of two terms: one describes the electrostatic interaction of the resulting atomic point charges, another reflects the *interatomic exchange*. Now, it is known that in Hartree-Fock theory exchange includes the self-repulsion of electrons and that they cannot be separated out from each other conceptually, because self-repulsion alone would not be unitary invariant.

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The expressions in Ref. 6 are given in terms of spin-orbitals; turning to the spatial orbitals, the two-center exchange contribution in the point-charge approximation can be re-written as

$$
\begin{aligned}
E_{AB}^{exch.point} &= \epsilon_{AB}^{exch.point} + \epsilon_{BA}^{exch.point} \\
&= -\frac{1}{R_{AB}} \sum_{\mu \in A} \sum_{\nu \in B} \left[(\mathbf{P}^{\alpha}\mathbf{S})_{\mu\nu}(\mathbf{P}^{\alpha}\mathbf{S})_{\nu\mu} + (\mathbf{P}^{\beta}\mathbf{S})_{\mu\nu}(\mathbf{P}^{\beta}\mathbf{S})_{\nu\mu} \right] \quad (1) \\
&= -\frac{1}{2R_{AB}} \sum_{\mu \in A} \sum_{\nu \in B} \left[(\mathbf{D}\mathbf{S})_{\mu\nu}(\mathbf{D}\mathbf{S})_{\nu\mu} + (\mathbf{P}^{s}\mathbf{S})_{\mu\nu}(\mathbf{P}^{s}\mathbf{S})_{\nu\mu} \right]
\end{aligned}
$$

Here R_{AB} is the internuclear distance between atoms A and B, $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$ are the usual "density matrices" for spins α and β, respectively, $\mathbf{S}$ is the overlap matrix of the atomic orbitals, $\mathbf{D}$ is the "total density matrix" and $\mathbf{P}^{s}$ the spin-density matrix. All matrices are expressed in the basis of atomic orbitals.

Now, comparing with the definition[7,8] of the *bond order index*, B_{AB} we see that[9]

$$
E_{AB}^{exch.point} = -\frac{1}{2R_{AB}} B_{AB} \quad (2)
$$

As the bond order B_{AB} for H_2^+ is exactly $1/2$, this result is completely in agreement with the self-interaction term $-1/(4R_{AB})$ discussed above.

Table 1 contains some selected energy values for the H_2^+ system calculated by using cc-pVTZ basis set. As could be expected, the point-charge approximation is good at larger internuclear distances, but not at the equilibrium one; there the reduced overall electrostatic repulsion reflects the stabilizing effect of the charge accumulation between the nuclei.

Now, if we add one more electron, then there will be two electrons occupying the bonding molecular orbital, leading to one Lewis electron pair, and the bond order value becomes equal to one. The electron-electron self-interaction, reducing the total energy as compared with the crude electrostatics, would also be twice as large at the same distance R_{AB} – but the increase of bonding interactions reduces R_{AB}, so the effect becomes larger. Note that in this case there are no resulting atomic charges, so the exclusion of the electron self-interaction gives an energy reduction with respect to the vanishing overall electrostatic interaction energy (at the level of point charge approximation), corresponding to the neutral situation.

However, it is also to be realized that in case with a doubly occupied bonding MO there is a price to be paid for the exchange (self-interaction) reduction of the electrostatic energy. That is connected with the appearance of the ionic terms in the wave functions, *i.e.,* those in which both electrons are

on the same atom. This gives rise to one-center electron-electron repulsion terms[11] which are absent for a single H atom. They may be very significant, but this effect is an inevitable consequence of electron delocalization. And electron delocalization is necessary in order that other terms usually discussed in connection with bond formation – like accumulation of charge in the bonding region, reduction of the kinetic energy as compared with the atomic promoted states *etc.*, – could contribute to the final energy. Thus the total binding energy is due to these terms as well as the exchange energy; while the appearance of the ionic terms reduces the energy of the chemical bonding. (Table 2 collects some illustrative numbers for the Hartree-Fock calculations performed for the H_2 molecule by using cc-pVTZ basis set.)

The effects of the charge accumulation *etc.*, are responsible for the fact that putting the electrons in the *antibonding* combination of the two hydrogenic orbitals leads to repulsive interaction and no chemical bonding — although the interatomic bond order and the exchange effects are independent of whether the bonding or the antibonding combination of the hydrogenic orbitals is occupied. This clearly puts some limits on the interpretative power of the bond order index, as it does not always permit to distinguish between bonding and antibonding situations. In practice, however, that may influence some non-bonded interactions, only.

It is interesting to follow what happens if further electrons are added to the system—assuming, of course the appropriate increase of the nuclear charges, too, so the overall neutrality of the system is maintained. The next interesting system is a helium dimer in which — to a good approximation — both the bonding and the antibonding combinations of the atomic *1s* orbitals are doubly occupied. In light of the above remark about the antibonding orbitals, at first sight one could expect that the exchange effects of both pairs of electrons will be added up. This is not, however, the case: they destroy the effect of each other. Both the practical calculations and a detailed analytical study[8] show, that such a pair of bonding and antibonding orbitals lead to zero bond order, thus to zero electrostatic exchange effect. This may be understood very easily without much calculation.

It is known that the single determinant wave functions are uniquely determined by the *subspace* of the occupied orbitals, which means that one can use instead of the original orbitals any their linear combinations, as far as they are linearly independent and thus span the original occupied subspace. (This may change only the normalization of the many-electron wave function, but that has no physical significance.) In particular, the original atomic orbitals of which the bonding and antibonding MO-s are built also represent appropriate linear combinations of the latter,[10] which means that one obtains the same many-electron wave functions also by filling with two electrons each

of the original atomic basis orbitals. This wave function does not exhibit any delocalization, so there are no interatomic exchange (electron-electron self-repulsion) effects either. In accord with that the bond order between two helium atoms is practically zero and no covalent chemical bond appears. (As the atomic orbitals of the two helium atoms slightly overlap, there is some repulsion of closed shells. That is the only effect at the single determinant level of theory. Dispersion, which is a *par excellence* electron correlation effect, causes a very-very shallow minimum to appear on the He...He potential curve, but that is out of our present scope.)

Of course, if more basis orbitals are involved on the individual atoms, then there can be one or more bonding electron pairs the effect of which is not compensated by an occupied antibonding counterpart. However, the fact that the core orbitals as well as the lone pairs do not contribute to the bond orders of homonuclear diatomics can be understood exactly in the same manner as the absence of the bonding in helium dimer. Thus one arrives[8] to the the definition of the well known "chemist's bond order"

$$B = \frac{N_{bond} - N_{antibond}}{2} \tag{3}$$

where N_{bond} and $N_{antibond}$ are the number of electrons occupying bonding and antibonding orbitals, respectively. This equality is fulfilled[8] for all first row homonuclear diatomics at the minimal basis level, except C_2.[12] Instead of each pair of occupied bonding and antibonding orbitals one can always turn to the respective localized core or lone pair orbitals. Thus one may argue that the localized orbital picture is more adequate for discussing the ground state chemical structure of molecules — while the delocalized picture is better to describe global ionization or excitation processes. The two representations are complementary in that sense.

Double and triple bonds are formed if bonding combinations of atomic basis orbitals of different symmetry — *e.g.,* of σ and π-type — are occupied, and the respective antibonding combinations are not. Then the bond-order will also equal (or, in more general case, close) to two or three. (Sometimes there are claims concerning of even higher bond orders, but we wish not consider that point here.) Behind every such bond order there is an attractive energy contribution of the electron-electron self repulsion, representing an inseparable part of exchange. This contribution is of utmost importance for forming the covalent chemical bonds; this connection explains why the bond order index is a successful measure of the bond strengths and a useful quantum chemical counterpart of the number of the valence lines used in a chemical formula.

It is to be noted that the bond order equals some ideal integer or half-

integer value only in some very special cases. Thus, independently of the basis set used, the bond order is exactly equal $1/2$ for H_2^+ and 1 for an RHF calculation of H_2; for other homonuclear diatomics (except C_2) this is true only if minimal basis set is used[8]. If one uses larger basis sets or considers heteropolar bonds, then deviations from the ideal integer values are obtained, and the bond orders obtained in the calculations are usually close, but slightly lower than the ideal values.[14] The use of integrer bond multiplicities in these cases may be considered as a sort of generalization (or simplification) which distinguishes the chemist's way of thinking from the the physicist's way of description of molecular systems.

The above discussion also indicates that among the large (conceptually infinite) number of different localization procedures the classical Edmiston–Ruedenberg one[16] may be considered the most adequate. Essentially it produces orbitals for which the intra-orbital self-repulsion exchange effect is maximal, therefore they reflect best to the intimate connection between exchange and chemical bonding.

To summarize the message of this short note, we may stress that the two-center exchange energy components lead to a significant lowering of the total molecular energy because of exclusion of self-repulsion, and this is inevitable for covalent bond formation. The success of the two-center bond order index relies on the fact that it gives a qualitative estimate of this important phenomenon.

References

1. Bacskay G. B.; Nordholm S. Covalent Bonding: The Fundamental Role of the Kinetic Energy. *J. Phys. Chem. A*, **2013**, *117*, 7946–7958.

2. Ruedenberg K. The Physical Nature of the Chemical Bond. *Rev. Mod. Phys.* **1962**, *34*, 326–376.

3. Ruedenberg, K.; Schmidt, M. W. Physical Understanding through Variational Reasoning: Electron Sharing and Covalent Bonding. *J. Phys. Chem. A* **2009**, *113*, 1954–1968.

4. Bitter, T.; Wang, S. G.; Ruedenberg, K.; Schwarz, W. H. E. Toward a Physical Understanding of Electron-Sharing Two-Center Bonds. II. Pseudo-Potential Based Analysis of Diatomic Molecules. *Theor. Chem. Acc.* **2010**, *127*, 237–257.

5. Mayer I. *Simple Theorems, Proofs, and Derivations in Quantum Chemistry*, Kluwer Academic/Plenum Publishers, New York 2003.

6. Mayer I. Towards a "Chemical" Hamiltonian. *Int. J. Quantum Chem.* **1983**, *23*, 341–363.

7. Mayer I. Charge, Bond Order and Valence in the Ab Initio SCF Theory. *Chem. Phys. Lett.* **1983**, *97*, 270–274.

8. Mayer I. Bond Order and Valence Indices: A Personal Account. *J. Comput. Chem.* **2007**, *28*, 204–221.

9. In Ref. 7 the coefficient 1/2 was misprinted as 2.

10. If there were no interatomic overlap, then the original atomic orbitals could be recovered simply as the normalized sum and difference of the bonding and antibonding MO-s. Owing to the overlap, this procedure does not lead to the atomic orbitals but to their Löwdin-orthogonalized counterparts[5]. The latter will be the appropriate orthonormalized *equivalent orbitals* for such a system.

11. Mayer I. Improved Chemical Energy Component Analysis. *Phys. Chem. Chem. Phys.* **2012**, *14*, 337–344.

12. For C_2 there are occupied bonding and antibonding orbitals that are not counterparts of each other, because they are built of different atomic hybrids[13].

13. Jug K., personal communication, 1985.

14. If one accounts properly for electron correlation, then the making/breaking of the chemical bonds can also be followed[15]: at the equilibrium distance one obtains a value close to the ideal integer one, which then smoothly decreases and goes to zero as the interatomic distance increases.

15. Mayer I. Improved Definition of Bond Orders for Correlated Wave Functions. *Chem. Phys. Lett.* **2012**, *544*, 83–86.

16. Edmiston, C.; Ruedenberg K. Localized Atomic and Molecular Orbitals. Rev. Mod. Phys. **1963**, *35*, 457–465.

FIGURE CAPTION

Figure 1
Potential curve of the H_2^+ ion (cc-pVTZ basis).

Table 1

Selected energetic parameters (in a.u.) of the H_2^+ system, calculated by using cc-pTVZ basis set at different internuclear distances.

R (a.u.)	2	5	10
Electrostatic energy[a]	0.0529	0.0465	0.0249
- " - point charge approx.	0.1250	0.0500	0.0250
Exchange energy	-0.1482	-0.0533	-0.0251
- " - point charge approx.	-0.1250	-0.0500	-0.0250
Total energy	-0.6022	-0.5221	-0.5002

[a] Including internuclear repulsion.

Table 2

Selected Hartree-Fock energetic parameters (in a.u.) of the H_2 system, calculated by using cc-pTVZ basis set at different internuclear distances.

R (a.u.)	1.4	2	3
Electrostatic energy[a]	-0.1418	-0.0912	-0.0263
- " - point charge approx.	0	0	0
Exchange energy	-0.3139	-0.2546	-0.1801
- " - point charge approx.	-0.3571	-0.2500	-0.1667
One-center el.-el. repulsion	0.3420	0.3015	0.2639
Total energy	-1.1330	-1.0911	-0.9886

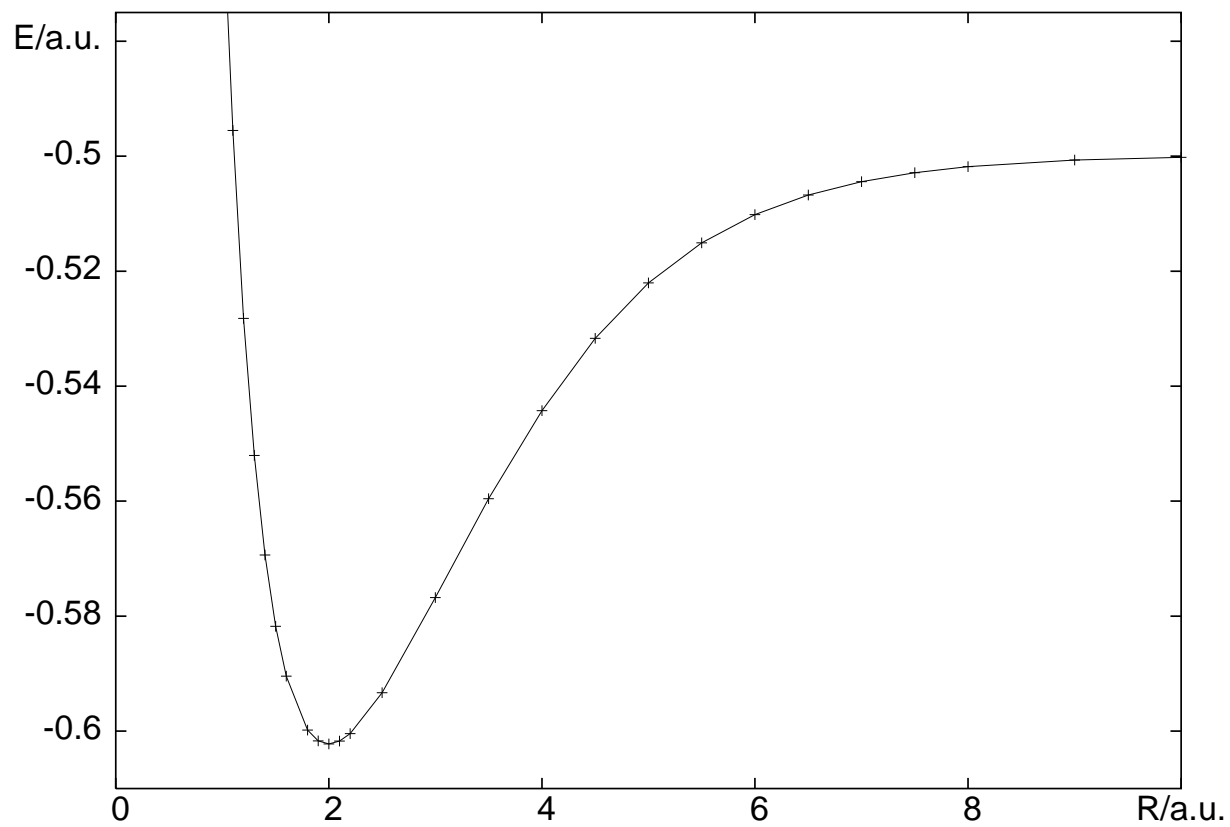[a] Including internuclear repulsion.

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Potential curve of the H_2^+ ion (cc-pVTZ basis).

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