# Natural Bond Orbitals and the Nature of the Hydrogen Bond

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## Abstract

The charge-transfer component of the energy of interaction between molecules has been a controversial issue for many years. In particular, the values reported from the use of the Natural Bond Orbital analysis of Weinhold and his co-workers are several times larger than those obtained by other methods. I argue that these values are heavily contaminated with basis-set superposition error, and are not useful in the context of intermolecular interactions.

# Introduction

The concept of charge-transfer interaction was first proposed by Mulliken[1] in 1952 to explain the very intense spectroscopic absorptions that were observed for some molecular complexes but that had no analogue in the spectra of either component separately. These complexes comprise an electron donor $D$ with a low ionization energy and an electron acceptor $A$ with a high electron affinity, so that the complex has an excited state $\Psi_1 = D^+\cdots A^-$ with a relatively low excitation energy $\mathrm{IP}(D) - \mathrm{EA}(A) + E_{es}$, where $E_{es}$ is the electrostatic attraction energy between the $D^+$ and $A^-$ ions. There is mixing between this state and the neutral ground state $\Psi_0 = D\cdots A$, leading to states described approximately as $\Psi_0 + \lambda\Psi_1$ and $\Psi_1 - \lambda\Psi_0$. The transition dipole between these states, assumed normalized and orthogonal to $O(\lambda)$, is

$$\begin{aligned}&\langle\Psi_0 + \lambda\Psi_1|\hat{\mu}|\Psi_1 - \lambda\Psi_0\rangle\\&\quad= \langle D\cdots A + \lambda D^+\cdots A^-|\hat{\mu}|D^+\cdots A^- - \lambda D\cdots A\rangle\,,\end{aligned}$$

and the crucial part of this is the term $\lambda\,\langle D^+\cdots A^-|\hat{\mu}|D^+\cdots A^-\rangle$ involving the very large dipole moment of the ionic state $D^+\cdots A^-$. This leads to a very strong electronic transition that plainly cannot occur for isolated $D$ or $A$ molecules, and that because of the low excitation energy often occurs in the visible part of the spectrum, leading to striking colour changes when the components are mixed.

Mulliken observed that the mixing must lead to a lowering of the energy of the complex relative to the energy of the state $\Psi_0$ — a charge-transfer contribution to the interaction energy. It was quickly assumed that this was the dominant attractive energy term in such complexes, although there was no theoretical evidence at the time to support this assumption, and Dewar and Thompson[2] pointed out that the experimental evidence suggested that many such complexes were electrostatically bound.

The importance or otherwise of charge transfer in the binding of molecular complexes has remained a controversial issue ever since, and has affected thinking on the older question of whether hydrogen bonding is covalent in nature or primarily electrostatic. The matter is complicated by the difficulty of defining the charge-transfer energy theoretically. Of the various available methods, the Natural Bond Orbital (NBO) method has always yielded much larger values than the others, and its proponents have argued that the charge-transfer energy dominates the binding in many cases, especially hydrogen bonding.[3] It is argued in the present paper that the use of the NBO method in intermolecular interactions is seriously in error.

# Theory: The Induction Energy

The main contributions to the energy of interaction between non-covalently-bonded molecules are the electrostatic, exchange–repulsion, induction and dispersion terms. The induction energy is a negative term that arises when the electron distribution in each molecule of a complex distorts in response to the electric field of its partner. When the molecules are some distance apart, the electrons remain attached to the same molecule, and the induction energy can be viewed as a classical polarization energy. When they are closer together, it is possible for electron density to move from either molecule onto the other, leading to a possible charge-transfer effect. In addition the effect of electron exchange between the molecules at these shorter distances modifies the induction term, substantially reducing its magnitude, though the overall magnitude continues to increase as the molecules approach. There is no clear separation of the total induction energy into a part that can be designated polarization and a part that can be designated charge-transfer.

There was no possibility of carrying out meaningful calculations of molecular interaction energies in the 1950s and 1960s, but recent methods such as Symmetry-Adapted Perturbation Theory (SAPT),[4–6] and its variants based on density functional theory (DFT), namely SAPT(DFT)[7–9] and DFT-SAPT,[10–12] can provide reliable interaction energies, with the total induction energy (including the contribution arising from electron exchange) as a distinct component. The calculations usually give good results at second order, but it is often necessary to add an estimate of the higher-order induction contributions called the $\delta^{\mathrm{HF}}$ term.[13,14] Although the induction energy can be separated in principle into a 'polarization' term, describing the response of each molecule to the electric field of the other, and a 'charge transfer term', arising from admixture of virtual orbitals on each molecule into the occupied orbitals of the other, there is still no definitive way to carry out this separation. Several methods have been proposed for estimating it.[15–18] They give broadly similar values for any particular system, and are negative values $E_{\mathrm{ct}}$ satisfying $E_{\mathrm{ind}} < E_{\mathrm{ct}} < 0$, as would be expected, where $E_{\mathrm{ind}}$ is the total induction term. The charge-transfer energies reported for the NBO method are much larger, and do not satisfy this relationship. For example, in the case of HF dimer at its equilibrium geometry, as obtained using Gaussian09 with the aug-cc-pVTZ basis set, the total second-order induction energy from the SAPT(DFT) calculation is $-11.03\,\mathrm{kJ\,mol^{-1}}$. (The energy components for this calculation are listed in Table 1.) Of this, $-1.47\,\mathrm{kJ\,mol^{-1}}$ is estimated to be charge transfer, using the method of Misquitta[18]. The NBO procedure claims a charge-transfer contribution of $-6.64$ kcal/mol or $-27.78\,\mathrm{kJ\,mol^{-1}}$,[19] more than twice the entire induction energy from SAPT(DFT). Such values have been used to support the view that the charge-transfer energy is the dominant contribution to hydrogen bonding.[3] The discrepancy has been noted by several authors,[20–22] but not yet explained.

**Table 1: SAPT(DFT) energies** ($\mathrm{kJ\,mol^{-1}}$) **for the HF dimer in its equilibrium geometry. elst = electrostatic, exch = exchange, ind = induction, including exchange–induction and $\delta^{\mathrm{HF}}$, disp = dispersion, including exchange–dispersion. Calculated by CamCASP,[23] aug-cc-pVTZ basis, PBE0 functional, with asymptotic correction.**

| elst | exch | ind | disp | total |
|---|---|---|---|---|
| −27.92 | 27.24 | −11.03 | −7.54 | −19.25 |

In order to understand what is happening here we need to review the basics of the NBO approach. It is based on the idea of natural atomic orbitals, which are the natural orbitals of isolated atoms, defined as eigenfunctions of the first-order density matrix.[24] However the natural bond orbitals of the NBO procedure are derived from an ab initio calculation on the system at some level of theory, usually Hartree–Fock SCF or Kohn–Sham DFT with some suitable basis set. They are classified in the NBO procedure as core, lone-pair and bond orbitals, the first two kinds extending over a single atom and the last over two atoms. They are orthogonalized to each other to form the NBO occupied orbital set, the 'Lewis' orbitals, so called in reference to the old Lewis bonding picture.[25] There are also unoccupied or 'non-Lewis' orbitals, comprising antibond and 'Rydberg' orbitals, orthogonalized to the occupied orbitals and to each other. For full details of the construction procedure the reader is referred to Glendening et al.[19] or Weinhold and Landis[26].

It will be apparent that the orbitals so obtained are artificial constructs, despite the 'natural orbital' label. They are mutually orthogonal by construction; this is a fundamental requirement of the NBO method, imposed in order that the NBOs can be regarded as eigenfunctions of some Hermitian operator.

The wavefunction in which the core, bond and lone-pair orbitals are occupied is the 'Lewis' wavefunction in the NBO terminology, and its energy, evaluated with only these orbitals in the basis set, is the 'Lewis energy'. This energy is not variationally optimized, so it is higher than that of the original variationally optimized wavefunction. For the HF molecule with an aug-cc-pVTZ basis, the Lewis energy is 99.99% of the (negative) variational energy, which is fairly typical, and such figures are adduced in the NBO literature as evidence that the Lewis wavefunction is very close to the variational wavefunction. However both energies are relative to separated nuclei and electrons, and the remaining 0.01% for HF, like the 99.99%, is a percentage of the Kohn–Sham or Hartree–Fock energy of about $-100$ hartree, and is about 25 kJ mol$^{-1}$. The study of the difference between the Lewis energy and the variational energy is the basis of NBO theory; it is useful for understanding the nature of bonding effects such as conjugation,[26] and this paper does not seek to cast doubt on such applications. However its interpretation in the context of intermolecular interactions, where the energies involved are of the order of tens of kJ mol$^{-1}$ or less, is highly questionable.

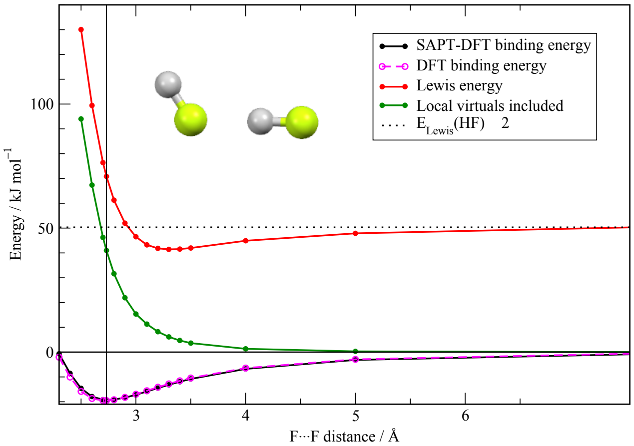

Figure 1: Energy of HF···HF relative to separated HF molecules

# Results and Discussion

One example is enough to explain the fundamental flaw in the NBO approach. We take the case of hydrogen fluoride dimer. Figure 1 shows the energies of the dimer at a range of separations. The energy zero is taken as the energy of two isolated HF molecules. The structures were optimized at fixed F···F distances using the B3LYP DFT functional in Gaussian09[27] with the Dunning aug-cc-pVTZ basis,[28] and the magenta dashed line and circles show the optimized B3LYP interaction energies. The vertical line is at the F···F separation for the minimum. The black line and dots show the interaction energies obtained with SAPT(DFT) as implemented in the CamCASP program,[23] using the aug-cc-pVTZ dimer-centred basis and the PBE0 functional[29,30] with asymptotic correction,[31] and including the $\delta^{\mathrm{HF}}$ estimate of the higher-order induction energy terms. The agreement is evidently good, though the DFT energies would vary somewhat with different functionals.

The red line and dots show the energies of the Lewis wavefunction at each separation, evaluated by Gaussian09. At long range it is 50 kJ mol$^{-1}$ above the Kohn–Sham energy of the isolated HF molecules, as shown by the dotted horizontal line, because of the 25 kJ mol$^{-1}$ error in the Lewis energies of each one. At shorter distances there is a small drop in the energy, but at the equilibrium geometry of the dimer it is 70 kJ mol$^{-1}$ above the energy of the isolated molecules and 90 kJ mol$^{-1}$ above the optimized energy of the dimer. It is this high-energy wavefunction that is used as the reference for evaluating the charge-transfer energy in the NBO approach.

Recall that this wavefunction has double occupancy of the artificial 'Lewis' core, bond and lone-pair orbitals. It is possible to study the effect of adding one or more of the virtual antibond and 'Rydberg' orbitals into the molecular-orbital basis. If mixing with all the virtual orbitals is permitted, the variational energy is recovered. If local mixing is permitted, i.e. mixing with only the antibond and Rydberg orbitals on the same molecule, the variational energy is recovered at long range, as shown by the green line and dots. At shorter range, however, this energy increases substantially.

An alternative viewpoint is to construct the Fock or Kohn–Sham matrix from the complete set of Lewis orbitals, and to delete all off-diagonal elements between occupied and virtual orbitals. This yields the Lewis energy. If now one or more of these off-diagonal elements is restored, the resulting change in energy can be attributed to that particular term, though such changes are not additive. In the case of HF dimer, it turns out that the off-diagonal element between one of the H-acceptor lone pairs and the HF antibond of the H-donor leads to a substantial drop in energy, and it is this that is described as the charge-transfer energy in the NBO scheme.

However the energy difference of interest for intermolecular interactions is the difference between the energies of the HF dimer and two isolated HF molecules. Taking the isolated molecules as the reference, these energies are at about $-19$ kJ mol$^{-1}$ and zero respectively. However the NBO 'charge-transfer energy' of about $-28$ kJ mol$^{-1}$ is relative to the energy of the Lewis structure, and is only part of the difference between the Lewis energy of about 70 kJ mol$^{-1}$ at equilibrium and the dimer energy at about $-19$ kJ mol$^{-1}$. The NBO procedure has nothing to say about the rest of the energy path, from the isolated HF molecules to the Lewis energy of the dimer, and the rest of the 90 kJ mol$^{-1}$ between the Lewis energy and the dimer energy, and makes no attempt to give a complete account of all the contributions to the total interaction energy. However even the limited information about the interaction that is provided by the NBO estimate of the charge-transfer energy is seriously flawed. Indeed I assert that no useful meaning can be attached to it, for the following reasons.

Plainly the construction of the Lewis wavefunction for the dimer from the separated molecules leads to a substantial increase in energy, which must be associated with a significant change in the electron density, and this change in density must be concentrated mainly in the region of overlap between the molecules, that is in the region of the hydrogen bond. Consequently the relaxation of the wavefunction back to the variational wavefunction of the dimer will inevitably involve the orbitals in the hydrogen bond region.

Furthermore we can observe that the Lewis wavefunction of each molecule is described in terms of orbitals that are not only confined to that molecule but are orthogonalized to the orbitals of the other molecule. Recall that basis-set superposition error (BSSE) arises when the basis set of each molecule is inadequate, so that mixing with orbitals of the other molecule improves the description of each monomer as well as describing the interaction, leading to an exaggerated binding energy.[20,32]

Now the calculation leading to the green curve in Fig. 1 is a calculation for each molecule of the dimer using the NBO basis orthogonalized to the other molecule. Most of the interaction with the other molecule is missing, because all elements of the Kohn–Sham matrix between the molecules have been suppressed. However, at the geometry of the dimer there will be electrostatic and polarization energies of each molecule in the classical electric field of the other, and these will be negative in the hydrogen-bonded geometry. (They are responsible for the slight dip in the red curve near 3.5 Å.) In a calculation for separated molecules using the individual NBO basis sets for the dimer structure, these terms would be absent. That is, the energy of the separated molecules, calculated using for each molecule the set of orthogonalized Lewis orbitals assigned to that molecule at a particular distance, would be even higher than the energy of the green curve at that distance. At long range, the orthogonalization has no effect because the orbitals of the two molecules have negligible overlap, but at shorter distances its effect is to increase the energy, by at least $40\,\mathrm{kJ\,mol^{-1}}$ at the equilibrium geometry.

That is, the NBO orthogonalization causes a deterioration in the quality of the basis set on each molecule. This means that any calculations of intermolecular energy terms are subject to a basis set superposition error which increases as the molecules approach. The BSSE for the system at any distance is at least the height of the green curve above the zero, i.e. at least 40 kJ mol$^{-1}$ for the equilibrium dimer geometry. The charge-transfer energy arises when the wavefunctions overlap, and is particularly susceptible to BSSE. The large value attributed by the NBO method to the charge-transfer energy can therefore be attributed to an extreme case of basis set superposition error. We should note in passing that SAPT is immune to BSSE because the same basis set is used for each molecule throughout a SAPT calculation, while the BSSE correction for a conventional supermolecule calculation of the HF dimer energy with the aug-cc-pVTZ basis set is about 0.35 kJ mol$^{-1}$ at the equilibrium geometry.

# Conclusion

The recognition that the NBO estimate of the charge-transfer energy is swamped by BSSE means that it is useless in any discussion of intermolecular interactions. Moreover correction for BSSE is normally done by using the complete dimer basis set at the dimer geometry to calculate the energy of each isolated molecule. However the *complete* NBO basis set, unlike the part of it assigned to each molecule, spans the same space as the original dimer basis, so construction of NBOs becomes irrelevant.

Recall that the SAPT methods provide a description of the complete interaction, broken down into individual components – electrostatic, exchange, induction and dispersion – that are well-founded in theory, give valuable physical insights, and can be used as a basis for constructing reliable analytical approximations to the complete intermolecular energy surface.[23] The NBO approach does not attempt any such description. In its application to intermolecular interactions it provides only a supposed value for the charge-transfer energy that is now seen to be worthless.

We may note that the SAPT(DFT) estimate of the charge-transfer energy in this case, about

$-1.5\,\mathrm{kJ\,mol^{-1}}$ at equilibrium, is a very modest contribution to the total interaction energy of $-19\,\mathrm{kJ\,mol^{-1}}$, while the electrostatic contribution is $-28\,\mathrm{kJ\,mol^{-1}}$. The claim that the hydrogen-bonding energy is dominated by the charge-transfer energy cannot be sustained.

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## References

(1) Mulliken, R. S. *J. Amer. Chem. Soc.* **1952**, *74*, 811–824.

(2) Dewar, M. J. S.; Thompson, C. C. *Tetrahedron* **1966**, *22 (S7)*, 97–114.

(3) Reed, A. E.; Weinhold, F.; Curtiss, L. A.; Pochatko, D. J. *J. Chem. Phys.* **1986**, *84*, 5687–5705.

(4) Jeziorski, B.; Moszynski, R.; Ratkiewicz, A.; Rybak, S.; Szalewicz, K.; Williams, H. L. SAPT: a program for many-body symmetry-adapted perturbation theory calculations of intermolecular interaction energies. In *Methods and Techniques in Computational Chemistry: METECC94*; Clementi, E., Ed.; STEF: Cagliari, 1993; Vol. B, p 79.

(5) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887–1930.

(6) Szalewicz, K. *WIREs Comp. Molec. Sci.* **2012**, *2*, 254–272.

(7) Misquitta, A. J.; Szalewicz, K. *Chem. Phys. Lett.* **2002**, *357*, 301–306.

(8) Misquitta, A. J.; Jeziorski, B.; Szalewicz, K. *Phys. Rev. Lett.* **2003**, *91*, 033201.

(9) Misquitta, A. J.; Podeszwa, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **2005**, *123*, 214103.

(10) Hesselmann, A.; Jansen, G. *Chem. Phys. Lett.* **2002**, *357*, 464–470.

(11) Hesselmann, A.; Jansen, G. *Chem. Phys. Lett.* **2002**, *362*, 319–325.

(12) Hesselmann, A.; Jansen, G. *Chem. Phys. Lett.* **2003**, *367*, 778–784.

(13) Jeziorska, M.; Jeziorski, B.; Čižek, J. *Int. J. Quantum Chem.* **1987**, *32*, 149–164.

(14) Moszynski, R.; Heijmen, T. G. A.; Jeziorski, B. *Molecular Phys.* **1996**, *88*, 741–758.

(15) Stone, A. J. *Chem. Phys. Lett.* **1993**, *211*, 101–109.

(16) Khaliullin, R. Z.; Cobar, E. A.; Lochan, R. C.; Bell, A. T.; Head-Gordon, M. *J. Phys. Chem.* **2007**, *111*, 8753–8765.

(17) Stone, A. J.; Misquitta, A. J. *Chem. Phys. Lett.* **2009**, *473*, 201–205.

(18) Misquitta, A. J. *J. Chem. Theory Comput.* **2013**, *9*, 5313–5326.

(19) Glendening, E. D.; Landis, C. R.; Weinhold, F. *WIREs Comp. Molec. Sci.* **2012**, *2*, 1–42.

(20) Stone, A. J. *The Theory of Intermolecular Forces*, 2nd ed.; Oxford University Press: Oxford, 2013.

(21) Khaliullin, R. Z.; Bell, A. T.; Head-Gordon, M. *Chem. Eur. J* **2009**, *15*, 851–855.

(22) Ronca, E.; Belpassi, L.; Tarantelli, F. *Comp. Phys. Comm.* **2014**, *15*, 2682–2687.

(23) Misquitta, A. J.; Stone, A. J. *J. Chem. Theory Comput.* **2016**, *12*, 4184–4208.

(24) Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1474–1488.

(25) Lewis, G. N. *J. Amer. Chem. Soc.* **1916**, *38*, 762–785.

(26) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, 2005.

(27) Frisch, M. J. et al. *Gaussian 09 Revision E.01*, Gaussian Inc. Wallingford CT 2009.

(28) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(29) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.

(30) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158–6170.

(31) Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 10180–10189.

(32) Boys, S. F.; Bernardi, F. *Molec. Phys.* **1970**, *19*, 553–566.

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