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Transferability of Natural Bond Orbitals

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Abstract: We have examined the transferability of C–H bonds (σ_{CH}) and amine lone pairs (n_N) in the framework of the natural bond orbital (NBO) method applied to a series of small organic molecules at the ab initio RHF/6-31G* level. We determined root-mean-square deviations for σ_{CH}, n_N NBOs in all pairs of molecules and compared these with corresponding values for localized molecular orbitals (LMOs), which have been employed in many previous discussions of bond transferability. Although the degree of bond transferability is found to be similar for NBOs and LMOs when chemical substitution occurs directly at an atom of the transferred unit, the transferability of NBOs is found to be significantly superior (by factors of 2–4 over corresponding LMOs) when the perturbation of the bond environment is more remote. Thus, an NBO *better* corresponds to the classical concept of a transferable localized bond than does an LMO. The interactions between a localized bond and its chemical environment which limit the concept of bond transferability are discussed in terms of an approximate decomposition into orthogonality (steric), rehybridization (Bent's rule), and chemical delocalization (hyperconjugative) effects.

I. Introduction

The concept of the transferable chemical bond is one of the central empirical tenets of chemistry.[1] As is well-known, the bond concept allows one to rationalize many molecular properties (bond enthalpies,[2a] interatomic distances,[2b] IR stretching frequencies,[2c] dipole moments,[2d] and others[2e,f]) in terms of intrinsic bond contributions, approximately transferable from one molecular environment to another.

Despite the empirical evidence supporting the concept of transferable chemical bonds, it has proven surprisingly difficult to provide a rigorous formal and numerical basis for this concept. In the formative years of quantum theory, the theoretical basis of the bond concept was extended by Pauling,[3a] Slater,[3b] and others,[3c] but this work was based on semiempirical wave functions that were directly constructed to incorporate the concept of transferable valence bonds, and could therefore provide only qualitative (and somewhat circular) support for the bond concept. As emphasis shifted toward ab initio SCF–MO and other more general forms of wave functions, it became less clear what constituted a chemical bond, or how the degree of bond transferability could be quantatively assessed.

Questions of bond transferability are intimately bound up with the definition of the bond itself. It is generally recognized that one cannot give a unique, mathematically precise quantum mechanical definition of a bond in terms of a definite Hermitian operator. The bond-like units are generally of lower symmetry than the Born–Oppenheimer molecular electronic Hamiltonian operator and cannot form a basis for an irreducible representation of the molecular point group of the Hamiltonian. These units therefore do not provide "good" quantum numbers for the description of the exact wave function. In a perturbative framework, however, such bond units may have approximate validity in the sense of providing a sufficiently accurate zeroth-order description of the system, e.g., as a suitably antisymmetrized separable product of bond functions. The bond description can thereby be justified if an optimized zeroth-order wave function corresponding to this description is of sufficient quantitative accuracy.

Given the specific form of a bond function for two different molecules, the transferability of the function can be assessed in general quantum mechanical terms. For example, if $\sigma_{CH}^{(A)}$, $\sigma_{CH}^{(B)}$ denote C–H bond functions from two molecules A, B, we can measure C–H bond transferability in terms of the "overlap error" δ_{AB},

$$\delta_{AB} = (1 - \langle \sigma_{CH}^{(A)} | \sigma_{CH}^{(B)} \rangle^2)^{1/2} \qquad (1a)$$

which, to leading order, is equivalent to a root-mean-square deviation integral,

$$\delta_{AB} \simeq \left[\int |\sigma_{CH}^{(A)} - \sigma_{CH}^{(B)}|^2 \, d\tau \right]^{1/2} \qquad (1b)$$

and whose value vanishes if and only if the overlap integral between these functions is unity.[4]

Lennard-Jones[5] first pointed out that the notion of C–H bonds in methane could be partially justified by transforming the delocalized SCF–MOs to "equivalent orbital" form, localized on individual C–H bond units. This observation was subsequently generalized to molecules of lower symmetry by Edmiston and Ruedenberg,[6a] Boys,[6b] and others,[6c] giving rise to the method of

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(1) See: Sidgwick, N. V. *Some Physical Properties of the Covalent Link in Chemistry*; Cornell University Press: Ithaca, NY, 1933 for an early discussion of bond additivity to various molecular properties.

(2) (a) Cottrell, T. L. *The Strengths of Chemical Bonds*; Butterworths Scientific Publications: London, 1958; Chapter 6 and Section 11.5, p 268. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7. (c) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill Book Company, Inc.; New York, 1955; pp 174–182. (d) Exner, O. *Dipole Moments in Organic Chemistry*; George Thieme: Stuttgart, 1975; pp 27–54. (e) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill Book Company, Inc.; New York, 1959; Chapters 7 and 11 (NMR chemical shifts). (f) Kauzman, W. J.; Walter, J. E.; Eyring, H. *Chem. Rev.* **1940**, *26*, 339–407. Kirkwood, J. G. *J. Chem. Phys.* **1937**, *5*, 479–491 (bond polarizabilities).

(3) (a) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367–1400. (b) Slater, J. C. *Phys. Rev.* **1931**, *37*, 481–489. (c) For example: Coulson, C. A. *Valence*, 2nd ed.; Oxford University Press: London, 1952.

(4) Qualitative error-bound considerations (see: Weinhold, F. *Adv. Quantum Chem.* **1972**, *6*, 299–331) suggest that δ_{AB} is of the order of fractional differences in properties calculated with the two functions $\sigma_{CH}^{(A)}$, $\sigma_{CH}^{(B)}$, so that, for example, the value $\delta_{AB} = 0.05$ would correspond to ~5% nontransferability in bond properties.

(5) Lennard-Jones, J. *Proc. R. Soc. (London)* **1949**, *A198*, 14–26.

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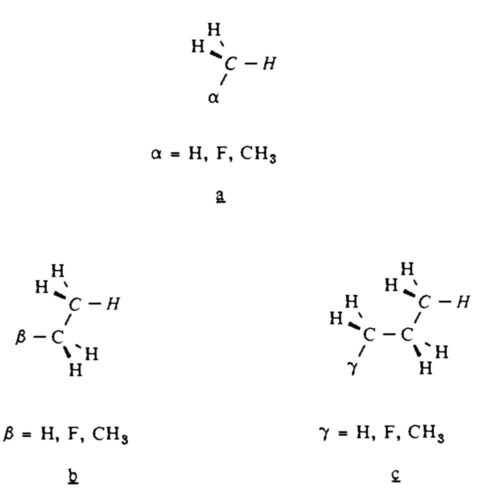

Figure 1. The set of substituted alkanes used to measure the degree of transferability of the σ_{CH} bond (marked in italics) from one molecule to another.

localized molecular orbitals (LMOs). The LMO method generally leads to functions that correspond closely to the basic bond units of chemical structure, and theoretical aspects of bond transferability are usually discussed in this framework. Shull and coworkers[7] noted the important role of orbital orthogonality in limiting transferability of an OH bond function from H_2O to HOOH in the separated pair approximation. A particularly thorough investigation of transferability in the LMO framework was carried out by Ruedenberg and coworkers,[8] who concluded that significant contributions to the nontransferability of LMOs correspond to chemical delocalization effects as well as to the constraint of orbital orthogonality.

In the present work, we consider bond functions obtained by the natural bond orbital (NBO) procedure,[9] which provides an alternative means of identifying intrinsic bond functions. While LMOs specifically are associated with the uncorrelated SCF-MO approximation, NBOs can be obtained for very general forms of wave functions, correlated or uncorrelated. NBO analysis has been applied to a variety of molecular wave functions,[10] leading to a highly accurate "nature Lewis structure" representation which serves as an optimal zeroth-order description based on intrinsic bond-like units. In this paper we examine a series of small organic molecules in order to test and compare NBO and LMO transferability of two types of chemical units: (i) the C–H bond of alkanes, and (ii) the nitrogen lone pair of amines. We shall show by direct comparisons that the NBO functions are *more* transferable than LMOs, and thus that the former functions provide a closer mathematical realization of the empirical bond concept.

Table I. Percentage of the Electron Density in the Formal Lewis Structure (Minimal Set of Valence NBOs) Computed for the Set of Substituted Alkanes Shown in Figure 1 at the RHF/6-31G* Level

figure ref	molecule	ρ_{Lewis}, %
1a	CH_4	99.97
1a	FCH_3	99.69
1a,b	CH_3CH_3	99.74
1b	CH_2FCH_3	99.59
1b,c	$CH_3CH_2CH_3$	99.65
1c	$CH_2FCH_2CH_3$	99.56
1c	$CH_3(CH_2)_2CH_3$	99.60

Table II. Occupancy and Hybridization of the σ_{CH} NBO for the Set of Substituted Alkanes Shown in Figure 1 at the RHF/6-31G* Level[a]

figure ref	molecule	σ_{CH} occupancy	c_C	hybridization of h_C			
				sp^{λ}	% s	% p	% d
1a	CH_4	1.9994	0.7801	$sp^{2.99}$	25.00	74.84	0.16
1a	FCH_3	1.9979	0.7678	$sp^{2.75}$	26.64	73.15	0.21
1a,b	CH_3CH_3	1.9928	0.7788	$sp^{3.09}$	24.39	75.44	0.17
1b	CH_2FCH_3	1.9886	0.7796	$sp^{3.10}$	24.37	75.46	0.01
1b,c	$CH_3CH_2CH_3$	1.9922	0.7795	$sp^{3.12}$	24.24	75.59	0.17
1c	$CH_2FCH_2CH_3$	1.9916	0.7829	$sp^{3.05}$	24.67	75.17	0.16
1c	$CH_3(CH_2)_2CH_3$	1.9923	0.7793	$sp^{3.13}$	24.20	75.64	0.17

[a] The C–H bond, σ_{CH}, is given by $\sigma_{CH} = c_C h_C + c_H h_H$ where h_C and h_H are the atomic hybrids on carbon and hydrogen, respectively, and c_C and c_H are the corresponding polarization coefficients. The hydrogen hybrid, h_H, is a pure s-type hybrid, and the hydrogen polarization coefficient, c_H, is related to the carbon coefficient, c_C, by the normalization condition on σ_{CH}.

Comparison of NBOs and LMOs also serves to clarify the relative roles of orthogonalization and chemical delocalization, indicating the nature of the interactions between a localized bond and the molecular environment that ultimately limit the concept of bond transferability.

II. Transferability of C–H Bonds

In order to assess the transferability of C–H bonds (σ_{CH}) in hydrocarbons, we have carried out ab initio RHF/6-31G* calculations[11] on a series of seven substituted alkanes, as shown in Figure 1. We compared the form of the C–H bond of a terminal methyl group for all pairs of molecules in the series by the root-mean-square deviation criterion of eq 1. The geometries of all molecules were fixed at idealized Pople–Gordon values,[12] so that effects of geometry variation on bond transferability are reduced as far as possible.

Since the degree of bond transferability should depend on similarity of bond environment, we selected the molecules to vary the C–H bond environment in a systematic way. The chosen molecules correspond to substituted methyl (R–CH_3), ethyl (R–CH_2CH_3), or propyl (R–$CH_2CH_2CH_3$) groups, where R = H, F, or CH_3. The degree of *similarity* of the C–H environment in any two molecules can be compared in terms of the number of bonds that *separate* the chosen C–H bond from the first point of dissimilarity in the carbon skeletons. Thus, molecules marked as α-substituted (Fig. 1a) differ by *geminal* substitution on the carbon that forms the C–H bond, those marked as β-substituted (Figure 1b) differ by *vicinal* substitution at the adjacent carbon atom, and those marked as γ-substituted (Figure 1c) differ at the second-nearest carbon atom. C–H bonds are expected to be more strongly perturbed by α-substitution, whereas bond transferability should be successively enhanced for more remote (β, γ, δ, ...) substitution sites.

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(6) (a) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457–465. (b) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300–302. Boys, S. F. In *Quantum Theory of Atoms, Molecules, and Solid State*; Löwdin, P.-O., Ed.; Academic Press: New York, 1966; pp 253–262. (c) See: Weinstein, H.; Pauncz, R.; Cohen, M. *Adv. At. Mol. Phys.* **1971**, *7*, 97–140 and references mentioned there.

(7) Levy, M.; Stevens, W. J.; Shull, H.; Hagstrom, S. *J. Chem. Phys.* **1974**, *61*, 1844–1856. See also: Allen, T. L.; Shull, H. *J. Chem. Phys.* **1961**, *35*, 1644–1651.

(8) England, W.; Gordon, M. S.; Ruedenberg, K. *Theor. Chim. Acta (Berlin)* **1975**, *37*, 177–216.

(9) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218. Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066–4073. Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746. For open-shell systems, the corresponding "different hybrids for different spins" NBO analysis permits a similar treatment: Carpenter, J. E.; Weinhold, F. *University of Wisconsin Theoretical Chemistry Institute Report* **1985**, *WIS-TCI-689*. Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (Theochem)*, in press. Blair, J. T.; Weisshaar, J. C.; Carpenter, J. E.; Weinhold, F. *J. Chem. Phys.* **1987**, *87* 392–410. A version of the Natural Bond Orbital program suitable for general usage is available from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana: Reed, A.; Weinhold, F. *QCPE Bull.* **1985**, *5*, 141.

(10) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 1919–1921. Reed, A. E.; Weinhold, F.; Weiss, R.; Macheleid, J. *J. Phys. Chem.* **1985**, *89*, 2688–2694. Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1986**, *84*, 2428–2430. Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586–3593.

(11) Computations were performed with the program GAMESS [original version due to M. Dupuis, D. Spangler, J. J. Wendoloski, NRCC Software Catalog, Vol. 1 Program GG01 (1980), heavily modified by M. Schmidt at North Dakota State and S. T. Elbert at Iowa State]. We thank Dr. Mike Schmidt and Prof. Mark Gordon for providing us with this program. We further modified the program by adding NBO procedure routines to it. The 6-31G* basis parameters are defined in the following two papers: Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. All calculations reported here were carried out with the UW—Madison Chemistry Department VAX 8600.

(12) Pople, J. A.; Gordon, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 4253–4260.

Table III. Calculated Root-Mean-Square Deviation, δ_{AB}, of the σ_{CH} Bond from Molecule A to Molecule B within the Set of Substituted Alkanes Shown in Figure 1[a]

	substituent on B	
substituent on A	H	F
α substituents (Figure 1a)		
F	0.077 (0.088)	
CH_3	0.085 (0.082)	0.072 (0.087)
β substituents (Figure 1b)		
F	0.019 (0.058)	
CH_3	0.026 (0.041)	0.023 (0.046)
γ substituents (Figure 1c)		
F	0.009 (0.025)	
CH_3	0.008 (0.017)	0.012 (0.020)

[a] In each case, values are given for the NBO and LMO (in parentheses). δ_{AB} is defined by the equation $\delta_{AB}{}^2 = 1 - S_{AB}{}^2$, where S_{AB} is the overlap integral of the σ_{CH} orbital on molecule A with that on molecule B.

We computed σ_{CH} NBOs for each of the nine molecules and obtained corresponding δ_{AB} values for all pairs of molecules. For comparison, we also computed the corresponding localized molecular orbitals of each molecule by the method of ref 13. Evaluation of δ_{AB} for both NBOs and LMOs allows the transferability of the two types of bond-like units to be compared in a direct way.

Do the NBOs furnish a sufficiently accurate zeroth-order representation of the full SCF-MO wave function? Table I summarizes the accuracy of the NBO "natural Lewis structure" representation for all the molecules considered in this work in terms of the percentage (% ρ_{Lewis}) of the total electron density that is described by the NBOs of the formal Lewis structure. It can be seen that the NBO Lewis structure typically describes >99.5% of the total SCF electron density,[14] indicating that the localized NBOs indeed provide a satisfactory zeroth-order description of the wave function in each case. The accuracy of individual σ_{CH} NBOs can also be judged from their occupancies (cf. Table II below), which are usually very close to the maximum value 2.00*e* that could be attained if the localized bond functions were *exact* natural orbitals of the full SCF-MO wave function.

Table II presents details of the RHF/6-31G* σ_{CH} NBO for each of the nine molecules. The σ_{CH} NBO can be written in terms of the polarization coefficients (c_C, c_H) and natural hybrids (h_C, h_H) that compose the bond,

$$\sigma_{CH} = c_C h_C + c_H h_H \qquad (2)$$

At this basis set level, h_H is a pure s-type hybrid. It can be seen that for each molecule the nearly sp^3 carbon hybrid ($sp^{2.75}$–$sp^{3.13}$ in the cases examined) corresponds well to the traditional chemical description of a methyl carbon. The computed bond polarity also conforms well with the description of a more electronegative carbon than hydrogen. The NBOs are thus in accord with the large body of empirical data that is commonly rationalized in terms of bond hybridization and polarization parameters. However, it can be seen that the hybridization and polarization coefficients depend somewhat on the molecualr environment, indicating a degree of nontransferability of the optimal NBOs.

Table III gives the δ_{AB} value of the C–H bond for each pair of molecules. Values obtained for LMOs are listed in parentheses beside the corresponding NBO values. The tabulated values indicate that the orbitals are not exactly transferable. In the worst case, for example, δ_{AB} is as large as 0.085 for NBOs (0.088 for LMOs) when A = CH_4 and B = CH_3CH_3. The two molecules differ in this case at the α position, the most severe change in the local environment of the C–H bond. As would be expected on chemical grounds, the computed δ_{AB} values show that both NBOs and LMOs are more transferable as the environmental perturbations become more remote. Thus, for β-substitution, the δ_{AB} values are typically reduced to about 0.025 for NBOs (0.050 for LMOs), and for γ-substitution, they are further reduced to about 0.009 for NBOs (0.020 for LMOs).

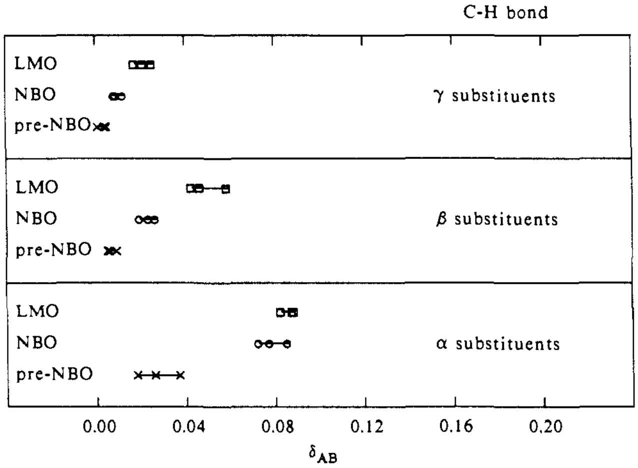

Figure 2. Plot summarizing the degree of transferability of the σ_{CH} bond from one molecule to another within the set of alkanes given in Figure 1. The degree of transferability is measured by the values of δ_{AB} given in Table III. The values given for the pre-NBOs are not present in the table and are included here as a basis for comparison with the other values (see text).

The important distinction appearing in Table III is that, while the nontransferability of NBOs and LMOs is generally of similar magnitude for α (geminal) substitutions, there is a dramatic difference in the relative transferability of NBOs and LMOs with respect to β (vicinal) or γ substitutions, the NBOs typically being 2–3 times *more* transferable. Thus, while the optimal forms of both NBOs and LMOs are dependent upon the local molecular environment of the bond, the degree of dependence is very different in the two cases, particularly with respect to non-geminal substituents. Figure 2 presents a composite picture of the δ_{AB} values for σ_{CH} NBOs and LMOs to illustrate these conclusions in graphical form. (The figure also includes corresponding values for "pre-NBOs", to be discussed below.)

III. Discussion of C–H Transferability

What is the physical and mathematical origin of the interactions that lead to non-transferability? We can identify three principal sources of breakdown of the concept of strict bond transferability:

(1) Rehybridization (Bent's Rule) Effects. Although each C–H bond hybrid is nominally of idealized sp^3 type, the actual carbon hybrids to distinct ligands are generally distinct, dependent on the relative ligand electronegativities. This is usually summarized in the statement[15] ("Bent's rule") that the central atom tends to direct hybrids of higher p-character to ligands of higher electronegativity. The NBO hybridizations of Table I are evidently in good agreement with Bent's rule. For example, substitution of F for H in methane to give CH_3F results in enrichment of p-character in the hybrid oriented toward F and corresponding depletion of p-character (to about $sp^{2.75}$) in the remaining hybrids. The rehybridization effects associated with Bent's rule are analogous to those that prevent the transfer of a C–H bond from an alkane (nominal sp^3 hybridization) to an alkene (sp^2) or alkyne (sp). Bent's rule rehybridization is expected to be most significant for α-substitutions and to affect NBO and LMO transferability in a similar degree.

(2) Orthogonalization ("Steric") Effects. The Pauli principle limits the number of electrons occupying a spatial region, and it may thus lead to distortions of the C–H bond distribution when a bulky group is substituted at a nearby position. Mathematically,

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(13) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736–1740.

(14) The accuracy is somewhat diminished at correlated levels of approximation by systematic omission of "left–right" intrabond correlation. For methane, for example, at the CISD/6-31G* (configuration interaction with single and double excitaitons) level, the value of ρ_{Lewis} is reduced from 99.97% to 98.87%. For a more detailed discussion of the stability of NBOs with respect to basis set extensions or inclusion of correlation effects, see, e.g.: Reed, A. E.; Weinhold, F.; Curtiss, L. A.; Pochatko, D. J. *J. Chem. Phys.* **1986**, *84*, 5687–5705.

(15) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275–311.

this leads to a distortion of the C–H bond function (and, generally, a raising of energy) to maintain orbital *orthogonality* with respect to the substituent group. Since both LMOs and NBOs are strictly orthonormal, this "steric" effect should manifest itself similarly in both sets of functions. The steric effects are severe for α-substitutions, but they are expected to diminish rapidly (exponentially) for more remote sites of substitution. The importance of maintaining strict orbital orthogonality in applying perturbative-style analysis to the physical interpretation of the wave function has been recently emphasized.[16]

(3) Delocalization ("Hyperconjugative") Effects. The proximity of a C–H bond to substituents having significant donor or acceptor character may induce chemical *delocalization* of the electronic distribution of a C–H bond onto adjacent positions. Such conjugative effects can have significant range and are expected to become the leading contribution to nontransferability for substitutions beyond the α carbon.

As remarked in the introduction, the relative importance of orthogonalization in limiting bond transferability has been discussed by several authors. An approximate measure of the effect of orthogonalization can be obtained by *relaxing* the orthogonality requirement between AOs, while holding the bond hybridization and polarization coefficients fixed. This leads to so-called "pre-NBOs", a set of non-orthogonal functions that differ from the final NBOs only in omission of the AO orthogonalization step.[17] Figure 2 includes δ_{AB} values of these pre-NBOs, to be compared with corresponding NBO and LMO values. From this comparison, it can be seen that NBO and pre-NBO values differ negligibly for γ-substitutions, corresponding to insignificant steric effects at this site. Somewhat larger differences are seen for β-substitutions, but these differences are still relatively unimportant for the substituents (F, H, CH_3) considered in this work. However, the pre-NBO and NBO values differ *sharply* for α-substitution, showing that steric effects are a dominant source of nontransferability in this case. (Since the rationale for Bent's rule is closely related to the requirement of hybrid orthogonality, one cannot draw sharp distinctions between orthogonality and Bent's rule effects in the case of α-substitution.) The large difference between NBO and pre-NBO α-transferability reflects the important role of the Pauli principle in limiting bond transferability (for both NBOs and LMOs) in the α-substituted case and suggests that a high degree of bond transferability can only be expected between molecules that differ at more remote (β, γ, ...) substitution sites.

For β- and γ-substituents, the "hyperconjugative" interactions that distinguish NBO and LMO transferability are the most significant environmental influence on a localized C–H bond. For these substitution sites, there is evidently a major difference between the degree of transferability of NBOs and LMOs, reflecting the much higher degree of environmental sensitivity to chemical delocalization effects in the latter case. The observed sensitivity of LMOs to chemical delocalization effects is in agreement with the conclusions of Ruedenberg and co-workers.[8]

In the LMO framework, the vicinal interactions of a σ_{CH} orbital with an acceptor (unfilled) σ^*_{CX} orbital at an adjacent position are directly incorporated into the form of the MO, since such delocalization leads directly to energy lowering. These effects remain when the canonical MOs are transformed to LMO form, resulting in small "delocalization tails" on the C–H bond LMO (of the form $\sigma_{CH} + \lambda\sigma^*_{CX}$, where λ is a small coefficient). In contrast, the NBOs preserve the two-center character of the function as far as possible so that the underlying σ_{CH}, σ^*_{CX} orbitals are retained as localized units. In the NBO framework, the hyperconjugative $\sigma_{CH} \rightarrow \sigma^*_{CX}$ interactions can be isolated and analyzed perturbatively in the basis of strictly localized σ_{CH} and σ^*_{CX} orbitals. It is thus not surprising that the NBOs better represent that aspect of the C–H bond unit which is *most* transferable from one molecule to another (i.e., "prior" to the hyperconjugative interactions with the environment), whereas LMOs necessarily incorporate hyperconjugative effects that partially break down the picture of a localized transferable bond, and thus correspond less closely to this picture. As Table III and Figure 2 indicate, the effect of choosing the strictly localized Lewis-type NBO description of the molecule is to considerably improve C–H bond transferability, while also laying the basis for systematic perturbative analysis of the important "noncovalent" interactions that must be considered to modify the elementary Lewis picture.

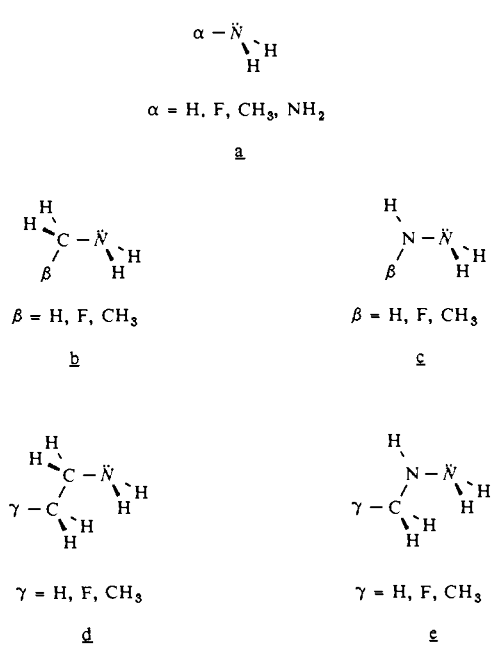

Figure 3. The set of amines used to measure the degree of transferability of the N lone pair (position indicated by $\dot{N}$) from one molecule to another.

Table IV. Percentage of the Electron Density in the Formula Lewis Structure (Minimal Set of Valence NBOs) Computed for the Set of Amines Shown in Figure 3 at the RHF/6-31G* Level

figure ref	molecule	ρ_{Lewis}, %
3a	NH_3	99.99
3a	FNH_2	99.81
3a,b	CH_3NH_2	99.69
3a,c	NH_2NH_2	99.72
3b	CH_2FNH_2	99.43
3b,d	$CH_3CH_2NH_2$	99.60
3c	$NHFNH_2$	99.51
3c,e	CH_3NHNH_2	99.57
3d	$CH_2FCH_2NH_2$	99.52
3d	$CH_3(CH_2)_2NH_2$	99.57
3e	CH_2FNHNH_2	99.47
3e	$CH_3CH_2NHNH_2$	99.54

IV. Transferability of Nitrogen Lone Pairs

Empirically, the C–H bond of hydrocarbons is a relatively "inert" unit of chemical structure, having intrinsically high transferability and weak interaction with its environment. We have therefore examined the transferability of amine lone pairs, which are generally considered to have much stronger interactions with their chemical environment and thus offer a more stringent test of transferability. The stereoelectronic interactions of nitrogen lone pairs with neighboring groups (particularly, those at vicinal antiperiplanar positions) have been extensively studied by many workers.[18]

To investigate nitrogen lone pair (n_N) transferability, we examined a series of substituted alkyl amines, as shown in Figure 3. We employed the same RHF/6-31G* (idealized Pople–Gordon

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[16] Weinhold, F.; Carpenter, J. E. *J. Mol. Struct. (Theochem)*, in press. *University of Wisconsin Theoretical Chemistry Institute Report* **1987**, *WIS-TCI-719*.

[17] For a previous application of pre-NBOs, see: Curtiss, L. A.; Pochatko, D. J.; Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *87*, 2679–2687.

[18] See, e.g.: Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*, Pergamon Press: Oxford, 1983, Chapter 4.

Table V. Occupancy and Hybridization of the Nitrogen Lone Pair NBO Computed for the Set of Amines Shown in Figure 3 at the RHF/6-31G* Level

		n_N	hybridization of n_N			
figure ref	molecule	occupancy	sp$^\lambda$	% s	% p	% d
3a	NH_3	1.9997	sp$^{4.30}$	18.87	81.07	0.07
3a	FNH_2	1.9985	sp$^{2.95}$	25.30	74.64	0.05
3a,b	CH_3NH_2	1.9776	sp$^{4.37}$	18.62	81.32	0.06
3a,c	NH_2NH_2	1.9853	sp$^{3.67}$	21.39	78.55	0.06
3b	CH_2FNH_2	1.9524	sp$^{4.54}$	18.05	81.89	0.06
3b,d	$CH_3CH_2NH_2$	1.9741	sp$^{4.75}$	17.37	82.57	0.06
3c	$NHFNH_2$	1.9561	sp$^{3.65}$	21.51	78.44	0.06
3c,e	CH_3NHNH_2	1.9835	sp$^{3.94}$	20.23	79.71	0.06
3d	$CH_2FCH_2NH_2$	1.9704	sp$^{4.51}$	18.13	81.80	0.07
3d	$CH_3(CH_2)_2NH_2$	1.9750	sp$^{4.78}$	17.28	82.66	0.06
3e	CH_2FNHNH_2	1.9802	sp$^{3.78}$	20.89	79.04	0.07
3e	$CH_3CH_2NHNH_2$	1.9844	sp$^{3.96}$	20.15	79.79	0.06

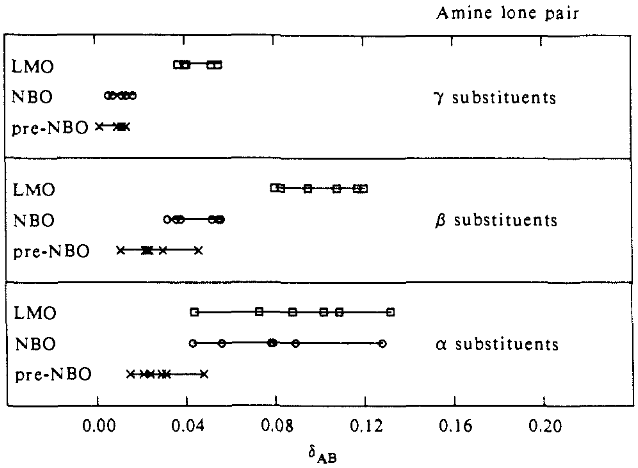

Figure 4. Plot summarizing the degree of transferability of the nitrogen lone pair from one molecule to another within the set of amines shown in Figure 3. The degree of transferability is measured by the values of δ_{AB} given in Table VI. The values given for the pre-NBOs are not present in the table and are included here as a basis for comparison with the other values (see text).

geometry) methodology as above and compared the transferability of n_N NBOs and LMOs in terms of the same heirarchical classification (α-, β-, or γ-substituted) of similarity in chemical environments. Table IV gives the percentage of the electron density found in the formal Lewis structure computed for each amine. The percentages in the table are all 99.4 or higher, indicating that a single Lewis structure again describes the electron density in these molecules very accurately. Table V summarizes details of the n_N NBO for the twelve chosen amines, and Table VI compares the δ_{AB} values of NBO and LMO n_N transferability for all pairs of molecules. Figure 4 summarizes the n_N numerical values of Table VI in graphical form.

Comparison of these amine results with the corresponding values (Tables I–III and Figure 2) for σ_{CH} bonds shows that similar conclusions would be drawn in the present case. Geminal (α-) substitution again has a strong effect on transferability, the effect being of similar magnitude for LMOs and NBOs. For weaker (β-, γ-) perturbations of the environment, the transferability of n_N NBOs is seen to be even more dramatically improved (by factors of ~3–4) relative to LMOs, particularly for fluorine substituents. It can be seen from comparison of Tables III and VI that the transferability of n_N NBOs is somewhat inferior to that for σ_{CH} NBOs, but the differences are small compared to the corresponding differences for LMOs, and to the differences that distinguish NBO and LMO transferability. The poorer transferability of n_N LMOs evidently reflects the higher degree of stereoelectronic chemical delocalization effects that are incorporated into the form of the "localized" LMO (as the NLMO[13] expansion makes explicit). Thus, as in the previous case of C–H bonds, the n_N NBO better represents that *invariant* aspect of the chemical unit which is approximately *transferable* from one molecule to another.

Table VI. Calculated Root-Mean-Square Deviation, δ_{AB}, of the Nitrogen Lone Pair from Molecule A to Molecule B within the Set of Amines Shown in Figure 3[a]

	substituent on B		
substituent on A	H	F	CH_3
α substituents (Figure 3a)			
F	0.078 (0.102)		
CH_3	0.128 (0.132)	0.089 (0.109)	
NH_2	0.079 (0.088)	0.056 (0.073)	0.043 (0.044)
β substituents (Figure 3b)			
F	0.032 (0.117)		
CH_3	0.052 (0.083)	0.038 (0.095)	
β substituents (Figure 3c)			
F	0.036 (0.120)		
CH_3	0.056 (0.080)	0.055 (0.108)	
γ substituents (Figure 3d)			
F	0.014 (0.055)		
CH_3	0.008 (0.041)	0.017 (0.041)	
γ substituents (Figure 3e)			
F	0.012 (0.052)		
CH_3	0.006 (0.037)	0.014 (0.040)	

[a] In each case, values are given for the NBO and LMO (in parentheses). δ_{AB} is defined by the equation $\delta_{AB}^2 = 1 - S_{AB}^2$, where S_{AB} is the overlap integral of the nitrogen lone pair on molecule A with that on molecule B.

V. Summary and Conclusion

We have tested the concept of a transferable chemical bond by measuring the transferability of C–H bond and nitrogen lone pair NBOs and LMOs in a variety of small organic molecules at the SCF–MO level, where the two methods can be directly compared. The optimal orbitals from different molecules are found to be generally similar in form, but to differ depending upon the local molecular environment. The "tails" that guarantee the orthogonality of each NBO to orbitals on surrounding atoms are the most important factor limiting the transferability of NBOs. Because the orthogonality tails fall away rapidly, the NBOs are particularly sensitive to changes in the α positions of the molecule, but less so to changes farther away. The transferability of LMOs is limited not only by orthogonality tails similar to those of the underlying NBO but also by the hyperconjugative *delocalization* tails that extend to acceptor orbitals at vicinal and more remote sites of substitution. These delocalization tails makes the LMO functions especially sensitive to substitutions at the β position. Thus, the NBO is defined for a broader class of wave functions and better realizes the classical concept of a transferable localized bond, but it too is limited in transferability by influences of the local chemical environment.

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