Caussian contains version 3.1 of the NBO program by F. Weinhold and coworkers. NBO analysis is based on a method for optimally transforming a given wave function into localized form, corresponding to the one-center ("lone pairs") and two-center ("bonds") elements of the chemist's Lewis structure picture. In NBO analysis, the input atomic orbital basis set is transformed via natural atomic orbitals (NAOs) and natural hybrid orbitals (NHOs) into natural bond orbitals (NBOs). The NBOs obtained in this fashion correspond to the widely used Lewis picture, in which two-center bonds and lone pairs are localized. The Weinhold group offers updated versions of the NBO program. The corresponding web page offers a wealth of "natural" information and should be considered the most authoritative source of NBO-related information. The conceptual world of natural orbitals has been laid out recently in a very detailed manner in "Valency and Bonding - A Natural Bond Orbital Donor-Acceptor Perspective" by F. Weinhold, C. R. Landis, Cambridge University Press, 2005. An online-manual for the 3.0 version of the NBO program as combined with MOPAC 6.0 explaining some of the underlying concepts and some of the keywords can be found here.
A full NBO analysis is obtained in <i>Gaussian</i> when using the POP=NBO keyword, while POP=NPA requests just the Natural Population Analysis (NPA) phase of NBO, in which atomic partial charges are obtained through summation over NAOs. Details of the NBO analysis procedure can best be illustrated using a specific example and formaldehyde will in the following be used for this purpose. Results of the NBO analysis are given with respect to the standard orientation of the system as given at the beginning of the <i>Gaussian</i> output file. For formaldehyde in its RHF/STO-3G structure the following input file performs a standard NBO analysis at the RHF/STO-3G level: #P HF/STO-3G scf=tight pop=nbo HF/STO-3G sp formaldehyde
0 1 C1 02 1 r2 H3 1 r3 2 a3 H4 1 r3 2 a3 3 180.0 r2=1.21672286 r3=1.10137241 a3=122.73666566 The following output is obtaind for this example: ***********************************
NATURAL ATOMIC ORBITAL AND NATURAL BOND ORBITAL ANALYSIS ***********************************
the separate steps of the NBO process, compared to the total allocated memory. Increase the memory allocated to your current job with the "%mem" directive if the estimated NBO requests exceed the available storage. The next four NBO output segments summarize the results of natural population analysis (NPA). The first segment is the main NAO table, as shown below: NATURAL POPULATIONS: Natural atomic orbital occupancies NAO Atom No lang Type(AO) Occupancy Energy 1 C 1 s Cor(1s) 2.00000 -11.05947 2 C 1 s Val(2s) 1.08461 -0.26145 3 C 1 px Val(2p) 0.90165 -0.04494
4 C 1 py Val(2p) 0.99304 0.07032 5 C 1 pz Val(2p) 0.85379 0.14739 6 0 2 s Cor(1s) 1.99999 -20.15602 7 0 2 s Val(2s) 1.79982 -1.09031 8 0 2 px Val(2p) 1.09835 -0.11626 9 0 2 py Val(2p) 1.91857 -0.38126 10 0 2 pz Val(2p) 1.37055 -0.15404 11 H 3 s Val(1s) 0.98982 0.02250 For each of the 12 NAO functions, this table lists the atom to which the NAO is attached, the angular momentum type 'lang' (s, p _x , etc.), the orbital type (whether core, valence, or
Rydberg, and a conventional hydrogen-type label), the orbital occupancy (number of electrons, or 'natural population' of the orbital), and the orbital energy (in Hartree). Taking NAO 5 as an example we see that this NAO describes the energetically highest lying atomic orbital located at carbon and has the character of a $2p_z$ atomic orbital, occupied by 0.85379 electrons. The principal quantum numbers for the NAO labels (1s, 2s, 3s, etc.) are assigned on the basis of the energy order if a Fock matrix is available, or on the basis of occupancy otherwise. A message is printed warning of a 'population inversion' if the occupancy and energy ordering do not coincide. The next segment is an atomic summary showing the natural atomic charges (nuclear charge minus summed natural populations of NAOs on the atom) and total core, valence, and Rydberg populations on each atom:
Summary of Natural Population Analysis: Natural Natural Ocre Valence Rydberg Total
Core 3.99999 (99.9997% of 4) Valence 12.00001 (100.0001% of 12) Natural Minimal Basis 16.00000 (100.0000% of 16) Natural Rydberg Basis 0.00000 (0.0000% of 16) Atom No Natural Electron Configuration C 1 [core]2s(1.08)2p(2.75) 0 2 [core]2s(1.80)2p(4.39) H 3 1s(0.99) H 4 1s(0.99) This table succinctly describes the molecular charge distribution in terms of NPA charges. The
carbon atom of formaldyde, for example, is assigned a net NPA charge of +0.16692 e at this level. Note also the slightly less positive charge on H3 and H4. Next follows a summary of the populations in the Natural Minimal Basis (NMB) and the Natural Rydberg Basis (NRB) for the composite system, summed over atoms. The natural populations are summarized as an effective valence electron configuration ("Natural Electron Configuration") for each atom. Although the occupancies of the atomic orbitals are non-integer in the molecular environment, the effective atomic configurations can be related to idealized atomic states in 'promoted' configurations. For example, the carbon atom in the above table is most nearly described by an $1s^22s^12p^{2.75}$ (or idealized sp ²) electron configuration. The next segments of the output summarize the results of the NBO analysis. The first segment
NATURAL BOND ORBITAL ANALYSIS: Occupancies Lewis Structure Low High Occ. Cycle Thresh. Lewis Non-Lewis CR BD 3C LP (L) (NL) Dev 1(1) 1.90 15.90533 0.09467 2 4 0 2 0 0 0.04 Structure accepted: No low occupancy Lewis orbitals
Normally there is a single cycle in the NBO search. The table summarizes a variety of information for each cycle: the occupancy threshold for a 'good' pair in the NBO search; the total populations of Lewis and non-Lewis NBOs; the number of core (CR), 2-center bond (BD), 3-center bond (3C), and lone pair (LP) NBOs in the natural Lewis structure; the number of low-occupancy Lewis (L) and 'high-occupancy' (> 0.1e) non-Lewis (NL) orbitals; and the maximum deviation ('Dev') of any formal bond order from a nominal estimate (NAO Wiberg bond index) for the structure. If the latter exceeds 0.1, additional NBO searches are initiated (indicated by the parenthesized number under 'Cycle') for alternative Lewis structures. The Lewis structure is accepted if all orbitals of the formal Lewis structure exceed the occupancy threshold (default: 1.90 electrons). Next follows a more detailed breakdown of the Lewis and non-Lewis occupancies into core, valence, and Rydberg shell contributions: Core 3.99999 (100.000% of 4) Valence Lewis 11.90534 (99.211% of 12) Total Lewis 15.90533 (99.408% of 16) Valence non-Lewis 0.09467 (0.592% of 16)
Rydberg non-Lewis 0.00000 (0.000% of 16) Total non-Lewis 0.09467 (0.592% of 16) This shows the general quality of the natural Lewis structure description in terms of the percentage of the total electron density (in the above case about 99.4 %). The table also exhibits the relatively important role of the valence non-Lewis orbitals relative to the extra-valence orbitals (e.g. Rydberg NBOs which occur when using a non-minimal basis set) in the slight departures from a localized Lewis structure model. Next follows the main listing of NBOs, displaying the form and occupancy of the complete set of NBOs that span the input AO space: (Occupancy) Bond orbital/ Coefficients/ Hybrids 1. (1.99777) BD (1) C 1 - 0 2 (41.41%) 0.6435* C 1 s (34.36%) p 1.91 (65.64%) 0.0000 0.5862 0.0000 0.0000 0.8102 1s 2s 2px 2py 2pz (58.59%) 0.7654* 0 2 s (24.04%) p 3.16 (75.96%)
0.0000 0.4903 0.0000 0.0000 -0.8716 This first NBO corresponds to a sigma(C-O) bond with approximate composition of 0.6435 C (sp ^{1.91}) + 0.7654 O(sp ^{3.16}). The weights are obtained from the squares of the coefficients as (0.6435) ² = 0.4141, corresponding to 41.41 % localization on carbon C1. In a similar way the 58.59 % localization on oxygen 02 is obtained. Overall, this describes a polar sigma(C-O) bond. 2. (2.00000) BD (2) C 1 - 0 2 (45.08%) 0.6714* C 1 s(0.00%)p 1.00(100.00%) 0.0000 0.0000 1.0000 0
4. (1. 99322) BD (1) C 1 = H 4
0.0000 0.0000 0.0000 1.0000 0.0000 NBO 7 and NBO 8 correspond to lone pairs on oxygen 02 with sp _z ^{0.32} and with pure p _y character, respectively. 9. (0.00338) BD*(1) C 1 - 0 2 (58.59%) 0.7654* C 1 s(34.36%)p 1.91(65.64%) 0.0000 0.5862 0.0000 0.0000 0.8102 (41.41%) -0.6435* 0 2 s(24.04%)p 3.16(75.96%) 0.0000 0.4903 0.0000 0.0000 -0.8716 10. (0.00000) BD*(2) C 1 - 0 2 (54.92%) 0.7411* C 1 s(0.00%)p 1.00(100.00%) (45.08%) -0.6714* 0 2 s(0.00%)p 1.00(100.00%) 11. (0.04564) BD*(1) C 1 - H 3 (48.43%) 0.6959* C 1 s(32.82%)p 2.05(67.18%) 0.0000 -0.5729 0.0000 -0.7071 0.4145
(51.57%) -0.7181* H 3 s(100.00%) -1.0000 12. (0.04564) BD*(1) C 1 - H 4
non-Lewis NBOs, respectively), a serial number (1, 2, if there is a single, double, bond between the pair of atoms), and the atom(s) to which the NBO is affixed. The next lines summarize the natural atomic hybrids h_A of which the NBO is composed, giving the percentage $(100xc_A^{\ 2})$ of the NBO on each hybrid (in parentheses), the polarization coefficient c_A , the atom label, and a hybrid label showing the sp composition (percentage s-character, p-character, etc.) of each h_A . The next segment summarizes the second-order perturbative estimates of 'donor-acceptor' (bond-antibond) interactions in the NBO basis: Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis Threshold for printing: 0.50 kcal/mol $E(2) E(j) -E(i) F(i,j)$ Donor NBO (i) Acceptor NBO (j) kcal/mol a.u. a.u.
within unit 1 1. BD (1) C 1 - 0 2 / 11. BD*(1) C 1 - H 3 0.92 1.76 0.036 1. BD (1) C 1 - 0 2 / 12. BD*(1) C 1 - H 4 0.92 1.76 0.036 3. BD (1) C 1 - H 3 / 9. BD*(1) C 1 - H 4 1.71 1.36 0.048 3. BD (1) C 1 - H 3 / 12. BD*(1) C 1 - H 4 1.71 1.36 0.043 4. BD (1) C 1 - H 4 / 9. BD*(1) C 1 - H 2 1.71 1.36 0.043 4. BD (1) C 1 - H 4 / 9. BD*(1) C 1 - H 3 1.71 1.36 0.043 8. LP (2) 0 2 / 11. BD*(1) C 1 - H 3 29.85 1.04 0.159 This analysis is carried out by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as 'delocalization' corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j), the stabilization energy E(2) associated with delocalization ("2e-stabilization") is estimated. As the heading indicates, entries are included in this table only when the interaction energy exceeds a default threshold of 0.5 kcal/mol. The strongest interaction is in this example identified for the interaction of lone pair orbital NBO 8 localized on 02 with the adjacent sigma*(C-H) bonds. Next appears a condensed summary of the principal NBOs, showing the occupancy, orbital energy, and the qualitative pattern of delocalization interactions associated with each: Natural Bond Orbitals (Summary):
Principal Delocalizations NBO (gominal vicinal romato)
NBO Occupancy Energy (geminal, vicinal, remote) Molecular unit 1 (CH2O) 1. BD (1) C 1 - 0 2 1.99777 -1.09402 11(g), 12(g) 2. BD (2) C 1 - 0 2 2.00000 -0.44319 3. BD (1) C 1 - H 3 1.99522 -0.69465 9(g), 12(g) 4. BD (1) C 1 - H 4 1.99522 -0.69465 9(g), 11(g) 5. CR (1) C 1 2.00000 -11.05946 6. CR (1) 0 2 1.99999 -20.15611 7. LP (1) 0 2 1.99857 -0.98034 8. LP (2) 0 2 1.91857 -0.38126 11(v), 12(v) 9. BD*(1) C 1 - D 2 0.00338 0.89756 10. BD*(2) C 1 - 0 2 0.00000 0.28199 11. BD*(1) C 1 - H 3 0.04564 0.66156 12. BD*(1) C 1 - H 4 0.04564 0.66156
NBO Occupancy Energy (geminal, vicinal, remote)
NBO
Molecular unit 1 (0.950) 1, BO (1) C 1 - 0 2 1, 99777 - 1,09402 11(a),12(a) 2, BO (1) C 1 - 0 2 2,00000 - 0.43319 1(a),12(a) 4, BO (1) C 1 - 10 3 1, 198522 - 0.84165 1(a),12(a) 4, BO (1) C 1 - 10 1, 198522 - 0.84165 1(a),12(a) 4, BO (1) C 1 - 10 1, 198522 - 0.84165 1(a),12(a) 4, BO (1) C 1 - 10 1, 198522 - 0.84165 1(a),12(a) 4, BO (1) C 1 - 10 1, 198522 - 0.84165 1(a),12(a) 4, BO (1) C 1 - 10 1, 19852 - 0.84165 1(a),12(a) 5, BO (1) C 1 - 10 2, 19857 - 0.98034 1(a),12(a) 7, BO (1) C 1 - 0 2, 0.0038 0, 80786 1(a),12(a) 1, 12(a) 9, BO (1) C 1 - 0 2, 0.0038 0, 80786 1(a),12(a) 1, 12(a) 1, BO (1) C 1 - 0 2, 0.0038 0, 80786 1(a),12(a) 1, 12(a) 1, BO (1) C 1 - 10 4, 0.4584 0, 66156 1(a),12(a) 1, 12(a) 1, BO (1) C 1 - 10 4, 0.4584 0, 66156 1(a),12(a) 1, 12(a) 1, BO (1) C 1 - 10 4, 0.4584 0, 66156 1(a),12(a) 1, 12(a) 1, BO (1) C 1 - 10 4, 0.4584 0, 66156 1(a),12(a) 1, 12(a) 1, BO (1) C 1 - 10 4, 0.4584 0, 66156 1(a),12(a),12(a) 1, BO (1) C 1 - 10 4, 0.4584 0, 66156 1(a),12
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