J. Am. Chem. Soc. 1989, 111, 6154-6156

confidence in the predicted structural features for the hitherto unobserved 4-amino radical. Theory has also accurately specified the structures and energetics of the manifold of excited states of the cation **1a**, the former of considerable interest and often not available, and the latter for comparison with experiment, viz., photoexcitation (UV/vis) of **1a** or photoionization (UPS) of **1b**. To achieve accuracies beyond the simple Koopmans' theorem arguments and verify the assignment of the low-energy region of the photoelectron spectrum, electron correlation to partial fourth order was required.

Acknowledgment. The technical assistance of W.-T. Chan in performing the ROHF open-shell singlet calculations using GAMESS is acknowledged. Funding, in the form of operating grants, was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) (to J.D.G., R.T.O., and N.P.C.W.), the ESPCOR program of the National Science Foundation (to A.W.C.), and the State of Arkansas. Calculations on the Ontario Centre for Large Scale Computation CRAY-XMP/22 were made possible through a time allocation grant to J.D.G. under the NSERC Supercomputer Access Program.

Supplementary Material Available: Tables of crystallographic data (S1), atomic coordinates (S2), bond and angle data (S3 and S4), and anisotropic thermal parameters (S5) for $[(Me_2N)CN_2S_2]_2$ (S1) and $[(Me_2N)CN_2S_2]^+[SbF_6]^-$ (11 pages); tables of calculated and observed structure factors (31 pages). Ordering information is given on any current masthead page.

Effect of Electron Correlation on Atomic Electron Populations

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Abstract: Atomic electron populations for a variety of molecules have been calculated at the HF/6-31G* and MP2/6-31G* levels using the natural population analysis method of Weinhold and co-workers. Correlation effects on electron populations act consistently to reduce charge separation and may be interpreted in terms of redistribution of electron density from high-lying filled molecular orbitals into low-lying unfilled orbitals.

Electron correlation is known to have significant influence on the properties of molecular systems. Extensive systematic studies of electron correlation effects as estimated from Møller–Plesset (MP) and configuration interaction (CI) models on equilibrium geometries[1,2] and normal-mode vibrational frequencies[2,3] have been reported. Bonds between electronegative elements were found to lengthen significantly, with a corresponding decrease in harmonic stretching frequencies. The role of electron correlation in altering relative thermochemical stabilities has also been examined.[2] Correlated descriptions generally appear to favor unsaturated and hypervalent bonding arrangements as opposed to the Hartree–Fock model, which tends to favor more conventional bonding patterns. Systematic investigations of correlation effects on atomic charge distributions have not previously been carried out and are the subject of the present report.

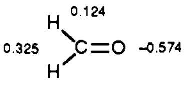
Quantum Mechanical Methods

All calculations have been carried out using the second-order Møller–Plesset (MP2) model for treatment of electron correlation[4,5] and the 6-31G* basis set.[6] Unless otherwise noted, all geometries correspond to HF/6-31G* optimized values. The SPARTAN system of electronic structure programs[7] has been employed.

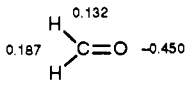
The assessment of correlation effects on atomic electron populations is based on the natural population analysis of Weinhold and co-workers,[8] although reference has also been made to the more commonly-employed Mulliken scheme.[9]

Results and Discussion

Calculated atomic charges for formaldehyde obtained from Hartree–Fock and MP2 densities

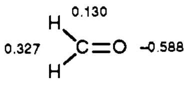


RHF/6-31G*

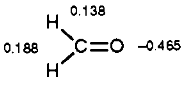


MP2/6-31G*

exhibit differences that are typical of many systems examined to date. Differences in HF and MP2 atomic charges appear to be relatively insensitive to basis set. For example, HF and MP2 charges, as well as differences between the two sets of charges for formaldehyde obtained at the 6-31+G* level



RHF/6-31+G*



MP2/6-31+G*

are nearly identical with those obtained at the 6-31G* level (above). Correlation corrections of similar magnitude are also

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[1] (a) DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085–4089. (b) DeFrees, D. J.; Krishnan, R.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5576–5580.

[2] For a general discussion, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[3] Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234–250.

[4] (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622. (b) Pople, J. A.; Seeger, R. *J. Chem. Phys.* **1975**, *62*, 4566.

[5] The frozen-core (valence-only) approximation has been employed. Calculations using this approximation yield atomic charges that are within +0.002 e of those obtained from all-electron calculations.

[6] (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665.

[7] Carpenter, J. E.; Hehre, W. J.; Kahn, S. D.; Weinhold, F. SPARTAN, a system of molecular electronic structure programs for large-memory, vector-architecture computers, to be submitted for publication.

[8] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746.

[9] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–1840, 1841–1846, 2338–2342, 2343–2356.

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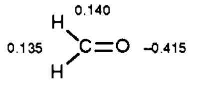
Table I. RHF and MP2 Natural Atomic Charges for Saturated Molecules[a]

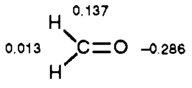
molecule	atom	natural atomic charge, electrons RHF	MP2(FC)	Δ[b]
H_2O	H	+0.4777	+0.4682	+0.0095
	O	−0.9554	−0.9364	−0.0190
CH_3CH_3	H	+0.2118	+0.2259	−0.0141
	C	−0.6354	−0.6777	+0.0423
CH_3Li	H	+0.1901	+0.2037	−0.0136
	C	−1.3909	−1.4020	+0.0111
	Li	+0.8206	+0.7907	+0.0299
CH_3F	H	+0.1709	+0.1841	−0.0132
	C	−0.0839	−0.1750	+0.0911
	F	−0.4289	−0.3774	−0.0515
LiF	F	−0.9237	−0.8660	−0.0577
	Li	+0.9237	+0.8660	+0.0577
MgF_2[c]	F	−0.9075	−0.8518	−0.0557
	Mg	+1.8150	+1.7036	+0.1114
B_2H_6	H	−0.0149	+0.0092	−0.0241
	B	−0.0514	−0.1359	+0.0845
	H_b	+0.0812	+0.1176	−0.0364
NH_2OH	H_N	+0.3599	+0.3616	−0.0017
	N	−0.5641	−0.5897	+0.0256
	O	−0.6422	−0.6087	−0.0335
	H_O	+0.4864	+0.4753	+0.0111
HOF	H	+0.4865	+0.4749	+0.0116
	O	−0.3163	−0.3417	+0.0254
	F	−0.1702	−0.1331	−0.0371
SiH_3F[c]	H	−0.2733	−0.2527	−0.0206
	Si	+1.4986	+1.3768	+0.1218
	F	−0.6785	−0.6187	−0.0598

[a] Unless otherwise noted, all calculations were carried out at the 6-31G* basis set level using the RHF/6-31G*-optimized geometries. [b] $\Delta = q_{RHF} - q_{MP2}$. [c] 3-21G(*) geometry employed.

found on charges obtained at the 6-31G* level using the Mulliken population analysis[9]



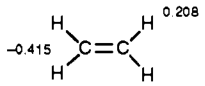
RHF/6-31G*



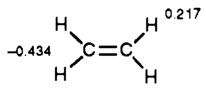
MP2/6-31G*

even though the charges themselves are markedly different. These conclusions regarding changes in basis set level and method of charge analysis, appear to hold up in a variety of systems examined to date in our laboratory.

The direction of the observed changes in the formaldehyde atomic charges may be easily rationalized by recognizing that the correlation correction transfers electron density from the occupied molecular orbitals of the Hartree–Fock wave function to the virtual molecular orbitals. In the simplest picture, electron density is transferred from the highest occupied molecular orbital (HOMO), in the case of formaldehyde, a nonbonded electron pair localized mainly on oxygen, into the lowest unoccupied molecular orbital (LUMO), in this case, π_{CO}^*, which is largely polarized toward carbon. In effect, electron density is transferred from oxygen to carbon; the two hydrogens, which are not involved to a great extent in either the HOMO or LUMO, remain largely unaffected. Such a picture is consistent with the very small correlation effects noted for ethylene



RHF/6-31G*



MP2/6-31G*

where both the HOMO (π_{CC}) and LUMO (π_{CC}^*) are equally localized on both carbons.

Calculated atomic charges for other unsaturated molecules (Table I) show similar and predictable correlation effects. Note, for example, the large shift in electron density from the exterior to the interior carbons in allyl cation and the redistribution of electrons from carbon to silicon in silaethylene. Note also that charge redistribution occurs to a greater extent in CO (Δ = +0.195 electron) than in the isoelectronic CN^- molecule (Δ = +0.106 electron). While the HOMO/LUMO gaps in the two diatomics are of comparable magnitude, the π^* orbitals in carbon monoxide are more polarized toward carbon than the corresponding orbitals in the cyanide anion.

Table II. RHF and MP2 Natural Atomic Charges for Unsaturated Molecules[a]

molecule	atom	natural atomic charge, electrons RHF	MP2(FC)	Δ[b]
CO	C	+0.6098	+0.4151	+0.1947
	O	−0.6098	−0.4151	−0.1947
HCN	H	+0.2301	+0.2333	−0.0032
	C	+0.1249	+0.0624	+0.0625
	N	−0.3550	−0.2957	−0.0593
HCO^+	H	+0.3226	+0.3335	−0.0109
	C	+0.9442	+0.7235	+0.2187
	O	−0.2648	−0.0570	+0.2078
CN^-	C	−0.1887	−0.2953	+0.1066
	N	−0.8113	−0.7047	−0.1066
$HCONH_2$	H	+0.1275	+0.1380	−0.0105
	C	+0.6707	+0.4811	+0.1896
	O	−0.7008	−0.5719	−0.1289
	N	−0.9323	−0.8860	−0.0463
	H_{syn}	+0.4209	+0.4182	+0.0027
	H_{anti}	+0.4140	+0.4108	+0.0032
SiH_2CH_2[c]	H_{Si}	−0.2110	−0.1874	−0.0236
	Si	+1.0818	+0.9775	+0.1043
	C	−1.1596	−1.1203	−0.0393
	H_C	+0.2499	+0.2588	−0.0089
C_4H_6 (1,3-butadiene)[c]	H_{syn}	+0.2042	+0.2135	−0.0093
	H_{anti}	+0.2137	+0.2232	−0.0095
	C_{ex}	−0.4026	−0.4158	+0.0132
	C_{int}	−0.2339	−0.2501	+0.0162
	H_{int}	+0.2186	+0.2292	−0.0105
$C_3H_5^+$ (allyl cation)	H_{syn}	+0.2606	+0.2713	−0.0107
	H_{anti}	+0.2417	+0.2518	−0.0101
	C_{ext}	+0.0821	+0.0081	+0.0740
	C_{int}	−0.4602	−0.3600	−0.1002
	H_{int}	+0.2916	+0.2976	−0.0060

[a] Unless otherwise noted, all calculations were carried out at the 6-31G* basis set level using the RHF/6-31G*-optimized geometries. [b] $\Delta = q_{RHF} - q_{MP2}$. [c] 3-21G(*) geometry employed.

Table III. RHF and MP2 Natural Atomic Charges for Hypervalent Molecules[a]

molecule	atom	natural atomic charge, electrons RHF	MP2(FC)	Δ[b]
$FClO_2$	F	−0.4958	−0.4483	−0.0475
	Cl	+2.1757	+1.9008	+0.2749
	O	−0.8399	−0.7263	−0.1136
$FClO_3$	F	−0.4607	−0.4187	−0.0420
	Cl	+2.9042	+2.5641	+0.3401
	O	−0.8145	−0.7151	−0.0994
ClF_3	Cl	+1.4779	+1.3112	+0.1667
	F_{ax}	−0.5608	−0.4926	−0.0682
	F_{eq}	−0.3563	−0.3260	−0.0303
SO_2	S	+1.8543	+1.5610	+0.2933
	O	−0.9272	−0.7805	−0.1467
F_3PO	F	−0.5984	−0.5415	−0.0569
	P	+2.9343	+2.6415	+0.2928
	O	−1.1390	−1.0170	−0.1220
SF_4	S	+2.2688	+2.0158	+0.2530
	F_{ax}	−0.5077	−0.4516	−0.0561
	F_{eq}	−0.6268	−0.5563	−0.0705
SO_3	S	+2.7715	+2.4158	+0.3557
	O	−0.9238	−0.8053	−0.1185

[a] All calculations were carried out at the 6-31G* basis set level using the RHF/6-31G*-optimized geometries. [b] $\Delta = q_{RHF} - q_{MP2}$.

Sizable correlation effects on atomic charges are also seen in formally saturated molecules, the largest being for systems with highly polar σ bonds (Table II). Again the direction of the changes may be rationalized in terms of the structure of the frontier molecular orbitals. For example, the shift in density away from fluorine and toward silicon in silyl fluoride, as a result of consideration of electron correlation, may be explained in terms of transfer of electrons from a nonbonded lone pair on the halogen into the degenerate pair of $\pi^*_{\mathrm{SiH}_3}$ functions.

Very large correlation effects on atomic charges are found for hypervalent compounds (Table III). As with the normal-valent compounds discussed previously, electron correlation generally reduces charge separation, although the highly polar character of these molecules apparent in their RHF descriptions is retained at the MP2 level.

Conclusion

Electron correlation as introduced by way of the MP2 model has a sizable effect upon atomic charge distributions, particularly for hypervalent and unsaturated molecules. In all cases considered to date in our laboratory, the effect of the MP2 correlation correction is to *reduce* charge separation in the molecule. Such behavior is consistent with the notion of electron transfer from the occupied molecular orbitals, which tend to be polarized toward the more electronegative elements in the molecule, to the unoccupied orbitals, which are oppositely polarized. It should be noted that the consideration of only the HOMO and LUMO, as in our discussion of formaldehyde, is overly simplistic. Other filled and virtual orbitals also participate in the MP2 density correction.

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Ligand Effects on Metal–R Bonding, Where R Is Hydrogen or Alkyl. A Quantum Chemical Study

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Abstract: Ligand effects on the metal–hydrogen and metal–methyl binding energies are studied by using quantum chemical methods including near degeneracy and dynamical correlation effects. The metals studied are nickel and palladium, and the ligands used are olefins (C_2H_4 and C_2F_4), carbonyl, phosphine, dinitrogen, water, and chloride (Cl^-). These types of lone-pair ligands can have both destabilizing and stabilizing effects on the metal–R bonds. Using a valence-bond description of the bonding, we show that these ligands have a varying amount of covalent bonding to the metal and that there is a correlation between the amount of covalency in the metal–ligand bonding and the destabilizing effect of the ligand on the metal–R bond. Since the maximum number of covalent bonds is only two for nickel and palladium and these are already used in the ligand-free complexes, there will be a competition for the covalent bonding between the R groups and the ligands, which explains the observed trend. The stabilizing effects of the ligands, on the other hand, vary much less among the ligands.

I. Introduction

The search for suitable homogeneous catalysts that can activate the chemically inert saturated hydrocarbons is currently a very active research area. During the last decade several important experimental findings have been made in the study of C–H activation by transition-metal complexes.[1-3] Oxidative addition of an alkane C–H bond to transition-metal complexes was suggested in 1979 by Crabtree et al.[1] as the initial step in the dehydrogenation of a number of alkanes. Janowicz and Bergman were, however, the first ones to report the discovery of an organo-transition-metal system capable of intermolecular oxidative addition to single C–H bonds in saturated hydrocarbons, leading to hydridoalkylmetal complexes in high yield at room temperature in homogeneous solution.[2] They showed that photolysis of Cp^*IrLH_2 (Cp = cyclopentadienyl) in a wide range of alkanes gives the corresponding alkyl hydride adducts with extrusion of H_2. Jones and Feher[3] studied the related rhodium complex Cp^*RhLH_2 and found that photolysis gave insertion into both arene and alkane C–H bonds. Theoretically, the information about transition-metal activation of H–H, C–H, and C–C bonds is now rapidly increasing,[4-10] but there are still a large number of questions remaining before a detailed understanding of the reaction mechanisms will be obtained. The present study is a continuation of a systematic study of simple catalytic reactions. In previous papers[7-10] we have mainly focused on the mechanisms for a naked transition-metal atom in the breaking of H–H, C–H, and C–C bonds. In this paper we will ask the general question of how important the nonparticipating ligands are for these reactions. The answer we seek is both quantitative in terms of actual numbers for reaction energetics and qualitative in terms of a classification of the ligands with respect to their influence on the reaction mechanisms.

The oxidative addition of a H–H, C–H, or C–C bond to transition metals can be written as follows:

$$L_nM + R_1\text{–}R_2 \Rightarrow L_nM(R_1)(R_2) \qquad (1)$$

where we use the notation R to symbolize either H or alkyl groups.

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(1) (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (b) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

(2) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(3) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240.

(4) Kitaura, K.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1981**, *103*, 2891.

(5) Noell, J. O.; Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4578.

(6) (a) Low, J. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 8321. (b) Low, J. J.; Goddard III, W. A. *Organometallics* **1986**, *5*, 609. (c) Low, J. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6928. (d) Low, J. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

(7) Blomberg, M.; Brandemark, U.; Pettersson, L.; Siegbahn, P. *Int. J. Quantum. Chem.* **1983**, *23*, 855.

(8) (a) Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Chem. Phys.* **1983**, *78*, 986. (b) Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Chem. Phys.* **1983**, *78*, 5682.

(9) Blomberg, M. R. A.; Brandemark, U.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1983**, *105*, 5557.

(10) Brandemark, U. B.; Blomberg, M. R. A.; Pettersson, L. G. M.; Siegbahn, P. E. M. *J. Phys. Chem.* **1984**, *88*, 4617.

0002-7863/89/1511-6156$01.50/0