position (on the order of several parts per million, reversible on cooling) as the probe temperature was increased gradually to about 75°. We prepared a sample of 2-heptanone (~0.1 *M*) in carbon tetrachloride, added the maximum amount of $Eu(dpm)_3$, and recorded the nmr spectrum of the sample at temperatures throughout the liquid range of CCl_4. Proportional enhancement of all signals in the substrate is observed (Table III) as the sample temperature is lowered, and suggests possible utility of reduced temperature determinations in cases where the limited solubility of the lanthanide complex is inadequate, or of variable temperature studies in lieu of measurements at a number of different relative concentrations.

Table III. Temperature-Dependent Chemical Shifts[a] of Protons of 2-Heptanone in CCl_4 Containing $Eu(dpm)_3$

T, °C	C-7	C-6	C-5	C-4	C-1	C-3
−30[b]	1.06	1.48	2.12	2.93	3.71	3.99
−12	1.04	1.44	2.04	2.81	3.52	3.82
0	1.02	1.38	1.93	2.55	3.25	3.55
35	1.01	1.37	1.91	2.49	3.18	3.48
66	0.99	1.32	1.75	2.28	2.93	3.23
Ref[c]	0.90	1.19	~1.39	~1.55	2.01	2.31

[a] Parts per million. [b] Freezing occurs after a few minutes. [c] 2-Heptanone in CCl_4.

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Balanced Zero-Differential-Overlap Approximations in Nonempirical Molecular Orbital Calculations[1]

Sir:

We have made a critical study of the effects of various diatomic zero-differential-overlap (ZDO) approximations in nonempirical molecular orbital theory.[2] More particularly, we sought to identify the most effective ways to approach Hartree–Fock wave functions and energies by methods involving zero differential overlap. We found that the errors associated with ZDO approximations depend not only upon the integrals thereby neglected but also upon the way in which the molecular energies are determined. As a result, we searched for methods which minimize the error associated with a given level of ZDO approximation. In this communication we report such methods and some data indicating their effectiveness.

Our actual calculations were carried out for a series of homopolar and heteropolar diatomic molecules: LiH, BH, NH, HF, BF, LiF, CO, C_2, N_2, and F_2. For each molecule we used the minimal Slater-type atomic orbital basis set of Ransil[3] and made ground-state Hartree–Fock calculations for a range of internuclear separations by several methods involving ZDO approximations. The ZDO approximations were applied in the original STO basis to both the one- and two-electron integrals involving the two-center charge distributions under consideration. We also made corresponding calculations without integral approximations. The results were evaluated by comparing the interatomic potential curves and the bond-order matrices produced from the various calculations. In general, we found the comparisons to be insensitive to basis-set choice, to exhibit strong qualitative regularities, and to vary only slightly with the polarity of the molecules. These facts gave us confidence that our conclusions could be extrapolated to more accurate calculations and to larger molecules.

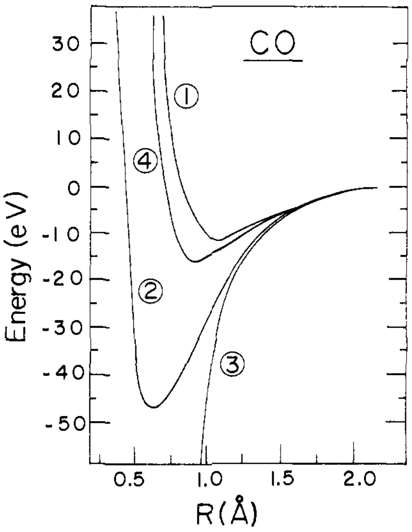

Figure 1. Calculated minimal-basis Hartree–Fock interatomic potential curves for CO: curve 1, without neglect of integrals; curve 2, core–valence ZDO; curve 3, core–valence ZDO for electron-repulsion integrals only; curve 4, core–valence ZDO balanced-error calculation (described in text).

Not unexpectedly, we found that two-center core–core and core–(π valence) differential overlaps could be set to zero with essentially negligible effect. For example, in CO, the assumption of two-center 1s–1s and/or 1s–2pπ ZDO produced errors of the order of 0.05% in the bond-order matrices and raised total energies by 0.0001–0.001 eV. On the scale used for the CO potential curves shown in Figure 1, these ZDO approximations yield curves indistinguishable from those obtained not using integral approximations (curve 1).

We next considered the neglect of the larger differential overlaps of the two-center core–(σ valence) type. This level of approximation has a significant effect, as illustrated by CO calculations assuming 1s–2s and 1s–2pσ ZDO. At the equilibrium internuclear separation, the bond-order matrix elements exhibited errors averaging 7%. However, the potential curve was more substantially affected (curve 2), yielding an equilibrium separation, dissociation energy, and force constant very different from those given by the more accurate calculations. The errors in the potential curves and bond-order matrices became even larger as the ZDO approximations for any or all of the one-electron integrals were removed. This situation is illustrated for CO (curve 3).

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(2) We gratefully acknowledge the assistance of Dr. H. J. Monkhorst, who has conducted similar investigations (H. J. Monkhorst, Ph.D. Thesis, University of Groningen, The Netherlands, 1968).

(3) B. J. Ransil, *Rev. Mod. Phys.*, 32, 239 (1960).

Further analyzing the core–(σ valence) ZDO approximation, we note that the relatively modest error in the bond-order matrix results from the fact (also verified directly) that the approximate Fock matrix is rather accurate. The accuracy is achieved because the neglected nuclear-attraction integrals essentially cancel against the main energy contributions arising from the neglected (hybrid) electron-repulsion integrals. The elimination of the corresponding exchange integrals produces minor effects. This cancellation depends on the fact that the electron-repulsion energy is multiplied by 2 in the Fock matrix, thereby causing the electron-repulsion energy to be approximately equal in magnitude to the electron–nuclear attraction energy. In contrast, the electron-repulsion contribution to the total molecular energy has approximately one-half the magnitude of the electron–nuclear attraction energy, causing ZDO calculations of the total energy to be more seriously in error.

One way to remedy the error imbalance in the energy computation is to build a total energy expression from quantities not subject to large errors. Writing the total energy in the form[4]

$$E_{\text{total}} = \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + E_{\text{nucl rep}}$$

where $H_{\mu\nu}$, $F_{\mu\nu}$, and $P_{\mu\nu}$ are the one-electron energy, Fock, and bond-order matrix elements, we meet our objective by taking $P_{\mu\nu}$ and $F_{\mu\nu}$ from the ZDO calculation while using values of $H_{\mu\nu}$ in which no integrals are neglected (balanced ZDO). For CO, this procedure leads to greatly improved and qualitatively satisfactory results (curve 4). Corresponding results are obtained for the other first-row diatomic molecules and for the 1s–1s two-center ZDO approximation in diatomic hydrides. If all the one-electron integrals, and two-electron hybrid integrals involving core–(σ valence) two-center charge distributions are retained, most of the remaining error is removed. This result further supports our argumentation.

Even the last procedure described in the preceding paragraph failed to enable us to obtain reliable results from valence–valence ZDO approximations near the equilibrium internuclear separations. However, we note that at typical second-neighbor separations in polyatomic molecules, valence–valence overlaps are comparable to the core–valence overlaps treated above. We therefore expect that the balanced ZDO procedure should be applicable to all but nearest-neighbor valence–valence overlaps. This method has the important advantage of automatically satisfying the requirement of invariance under axes rotation.[5]

(4) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, pp 41–46.

(5) Reference 4, pp 60–62.

(6) National Institutes of Health Fellow, 1968–1970.

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The Carbon-13 Intensity Problem. Elimination of the Overhauser Effect with an Added Paramagnetic Species

Sir:

The spectral simplification and increase in effective S/N produced by proton "decoupling" in ^{13}C nmr spectroscopy[1] is frequently accompanied by signal enhancement due to the operation of a ^{13}C–^{1}H Overhauser effect.[2] The magnitude of the Overhauser enhancement ordinarily differs for different ^{13}C nuclei, so the simple relationship between resonance intensity and the number of ^{13}C nuclei no longer holds. ^{13}C spectroscopy cannot therefore be generally employed for quantitative analysis, and spectral interpretation is made more difficult.

It was suggested by La Mar[3] that the ^{13}C–^{1}H Overhauser polarization might be eliminated by the presence of a paramagnetic species in solution. A theoretical analysis showing that the Overhauser effect should indeed be reduced by paramagnetic species is presented herein, and the criteria which govern the extent of the reduction are included. The existence of such reduction has been confirmed experimentally.[3]

The enhancement factor $(C_z - C_0)/C_0$ of ^{13}C nuclei (C) due to proton (H) irradiation in the presence of unpaired electrons (E) is given[4] by

$$\frac{C_z - C_0}{C_0} = \left[\frac{f_{\text{CH}}\rho_{\text{CH}} - f_{\text{CE}}\rho_{\text{CE}}f_{\text{EH}}\rho_{\text{EH}}}{1 - f_{\text{CE}}\rho_{\text{CE}}f_{\text{EC}}\rho_{\text{EC}}}\right]\frac{\gamma_{\text{H}}}{\gamma_{\text{C}}}S_{\text{H}} \qquad (1)$$

C_z and C_0 are magnetizations with and without proton irradiation, respectively. (Overhauser enhancements are often quoted as C_z/C_0.) S_{H} is the degree of saturation of the proton absorption such that

$$S_{\text{H}} = 1 - \frac{1}{1 + \gamma_{\text{H}}^2 H_2^2 (T_1T_2)_{\text{H}}} \qquad (2)$$

where γ_{H}, H_2, T_1, and T_2 are the gyromagnetic ratio, irradiation field strength, and spin–lattice and spin–spin relaxation times, respectively, of the protons. ρ_{CH} describes the nature and effectiveness of the dynamic coupling[5] between the C and H spins, and the other ρ terms are defined analogously. f_{CH} is that fraction of the total C relaxation due to coupling with the H spins and is given by[4]

$$f_{\text{CH}} = 1 - \frac{T_{1\text{C}}(\text{LEH})}{T_{1\text{C}}(\text{LE})} \qquad (3)$$

where $T_{1\text{C}}(\text{LEH})$ and $T_{1\text{C}}(\text{LE})$ are the spin–lattice relaxation times of the C spins in the presence and absence, respectively, of the H spins. L refers to the lattice. Definitions of the other f terms follow analogously.

Only a negligible fraction of the electron relaxation proceeds *via* C and H, so f_{EC} and f_{EH} are approximately zero. Equation 1 therefore simplifies to

$$\frac{C_z - C_0}{C_0} = f_{\text{CH}}\rho_{\text{CH}}\frac{\gamma_{\text{H}}}{\gamma_{\text{C}}}S_{\text{H}} \qquad (4)$$

The important ^{13}C spin–lattice relaxation processes are illustrated in Figure 1. Thus

$$\frac{1}{T_{1\text{C}}(\text{LE})} = \frac{1}{T_{1\text{CL}}} + \frac{1}{T_{1\text{CE}}} \qquad (5)$$

(1) R. E. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(2) K. F. Kuhlmann and D. M. Grant, *J. Amer. Chem. Soc.*, **91**, 7355 (1969).

(3) G. N. La Mar, private communications; *J. Amer. Chem. Soc.*, **93**, 1040 (1971).

(4) D. F. S. Natusch, R. E. Richards, and D. Taylor, *Mol. Phys.*, **11**, 421 (1966).

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