

Speed and Accuracy in Molecular Orbital Calculations. A Comparison of CNDO/2, INDO, PRDDO, STO-3G, and Other Methods, Including AAMOM, VRDDO, and ESE MO

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Abstract: The CNDO/2, INDO, PRDDO, and STO-3G methods are compared with respect to computational speed and to accuracy in reproducing ab initio SCF calculations using minimum basis sets of Slater orbitals for 11 organic molecules and for 16 boron hydrides, carboranes, and boron hydride ions. The PRDDO, STO-3G, and reference SCF (ref SCF) calculations are found to be consistently in close agreement for relative total energies, orbital eigenvalues, atomic charges, and dipole moments. The CNDO/2 and INDO calculations, in contrast, were frequently in serious disagreement with both the reference calculations and experiment. PRDDO is found to be ~16 times faster than STO-3G and ~100 times faster than the ref SCF calculations for a molecule having 40 atomic orbitals, while CNDO/2 and INDO, in turn, are ~6 times faster than PRDDO. Detailed comparisons show that PRDDO eliminates over 90% of the CNDO/2 or INDO error while requiring an additional computing time which is only about 6% of that required by STO-3G. The VRDDO method is essentially equal in accuracy to STO-3G, but is only slightly faster than STO-3G. The VRDDO/MODPOT combination is approximately twice as accurate as PRDDO, but is ~5 times slower. Finally, the ESE MO (SBD/2C) and AAMOM methods are somewhat faster but less accurate than PRDDO, and the SBD/3C version of ESE MO is both slower and less accurate.

I. Introduction²

Every chemist now has access through the Quantum Chemistry Program Exchange³ to a dazzling, if not bewildering, array of molecular orbital methods and programs. In this paper, we shall compare several such methods with respect to their computational speed and their accuracy in reproducing ab initio self-consistent field (SCF) calculations using minimum basis sets (MBS) of Slater atomic orbitals. Whenever ab initio MBS calculations are themselves appropriate, the two factors of speed and accuracy largely determine the suitability of a given approximate method for a particular computational task.

Detailed comparisons will be presented for the CNDO/2,⁴ INDO,^{4,5} STO-3G,⁶ and PRDDO^{7,8} methods. The first three methods are available through QCPE and are widely used. The PRDDO method, developed by us,^{7,8} will soon be available through QCPE. It is employed in 40 current and 17 forthcoming papers⁹ in the fields of organic,^{10a-t} inorganic,^{10u-uu} and biochemistry.^{10vv-eee}

Three additional SCF methods, AAMOM,¹¹ ESE MO,¹² and VRDDO,¹³ which like PRDDO seek to increase computational speed without unduly sacrificing accuracy, will also be discussed.

All of these methods share, and presumably enlarge upon, the limitations of MBS single-determinant theory, which by now are well known. Nevertheless, recent studies by Pople and co-workers¹⁴ and by others^{15,16} have shown that MBS calculations yield reasonably accurate molecular properties, including molecular geometries, in many cases. Since the MBS geometries can then be treated by single calculations using more elaborate methods, the ability of an approximate method to predict geometries accurately and economically is potentially of considerable significance.

The systems to be examined—11 organic compounds and 16 boron hydrides, carboranes, and boron hydride ions which range in size from C₂H₂ (12 AOs) to B₁₀H₁₄²⁻ (64 AOs)—are expected to provide a difficult computational test for the CNDO/2, INDO, PRDDO, and STO-3G methods. The latter systems are moderately large and have the unusual geometries associated with electron-deficient compounds. For many of

these systems, PRDDO calculations have recently been employed in place of, or together with, the ab initio ref SCF calculations.^{10aa,cc-ee} The present comparisons, especially the more detailed comparisons presented in Appendix I, will present the justification for this procedure. Previous comparisons of PRDDO and ref SCF results were limited to smaller systems.^{7,8}

The boron-containing molecules are particularly appropriate for this study because they form the only major group of large molecules for which published calculations using a minimal Slater basis are available. The organic molecules studied are not presented as a complete survey but rather serve to illustrate that the results previously established for small organic molecules⁸ and now established for large boron hydrides hold for moderately sized organic molecules as well.

For AAMOM, VRDDO, and ESE MO, the comparison will be more limited and will be based on published data.¹¹⁻¹³

II. Methods

The CNDO/2⁴ and INDO^{4,5} methods (QCPE No. 141) are well known and require little comment. These methods make some use of experimental data, but ultimately are parametrized to reproduce ab initio MBS calculations.⁴ STO-3G⁶ (QCPE No. 236) is itself an ab initio method but approximates the reference (ref) SCF procedure by employing short linear combinations of Gaussian-type orbitals to mimic the Slater AOs.

The PRDDO (partial retention of diatomic differential overlap) method^{7,8} is an approximate ab initio method which essentially is defined by its retention of all molecular integrals having at most one zero-overlap (usually diatomic) charge distribution. Specifically, PRDDO retains one-, two-, and three-center integrals of the form $(\chi_{i_a}\chi_{j_b} | \chi_{k_c}^2)$, where χ_{i_a} is a symmetrically orthogonalized AO¹⁷ mainly centered on the atom *a*. Also retained are one- and two-center exchange integrals of the forms $(\chi_{i_a}\chi_{j_a} | \chi_{i_a}\chi_{j_a})$ and $(\chi_{i_a}\chi_{j_b} | \chi_{i_a}\chi_{j_b})$. The set of ~*N*³ PRDDO integrals, where *N* is the number of AOs, represents only a small fraction of the full complement of ~*N*⁴/8 two-electron integrals,¹⁸ but nevertheless is sufficiently large and complete for all elements of the Fock matrix to be

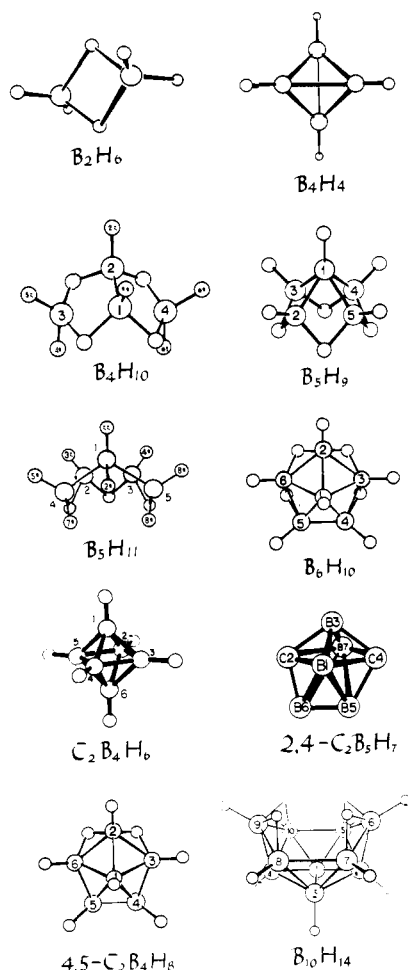


Figure 1. Molecular geometries and atomic numbering.

constructed entirely from constituent integrals. Some current capabilities of the PRDDO program are summarized in Appendix II.

The AAMOM (an approximate molecular orbital method) introduced by Zerner¹¹ bears similarities to both CNDO/2 or INDO and to PRDDO. In particular, all one-, two-, and three-center nuclear attraction integrals are computed fairly accurately over orthogonalized AOs, as in PRDDO, but certain electron-repulsion contributions to two-center elements of the Fock matrix are approximated, much as in CNDO/2 and INDO, by proportioning them to quantities derived from the corresponding overlap integrals over Slater AOs. Inner shells are handled via a pseudopotential approach.

The VRDDO (variable retention of diatomic differential overlap) method of Popkie and Kaufman¹³ is an approximate *ab initio* method based on the charge-conserving integral approximations introduced by Wilhite and Euwema.¹⁹ One such approximation, for example, systematically neglects all one- and two-electron integrals including overlap integrals which involve diatomic basis-function products, $\phi_a\phi_b$, whose *pseudo*-overlap integral is smaller than a preassigned tolerance, τ_1 . The approximations are capable of reducing the cost of the ref SCF calculation by ca. 30% with negligible loss in accuracy.¹⁹ Popkie and Kaufman also report VRDDO/MODPOT calculations in which the VRDDO approximations are coupled with the use of a Bonifacic-Huzinaga model potential for inner shell electrons.^{13d}

The ESE MO (essential structure elements MO) method introduced by Burton and Brown¹² is a nonempirical method which, like PRDDO, seeks a balanced assessment of attractive

one-electron and repulsive two-electron contributions to the Fock matrix. For example, all one- and two- and three-center integrals over Slater AOs of the forms

$$\int \phi_{iA}(1) \phi_{jB}(1) r_{1C}^{-1} d\tau_1 \quad (1)$$

$$\int \int \phi_{iA}(1) \phi_{jB}(1) r_{12}^{-1} \phi_{kC}(2) \phi_{lC}(2) d\tau_1 d\tau_2 \quad (2)$$

are retained in the SBD/3C version. A second version, SBD/2C, retains only the one- and two-center integrals in eq 1 and 2. All four-center integrals are discarded in both versions.

III. Comparisons for Boron Hydrides and Carboranes

In this section, we shall compare relative energies for several formal reaction processes, eigenvalues for occupied and lowest unoccupied molecular orbitals, atomic charges, and dipole moments given by the CNDO/2, INDO, and PRDDO methods to ref SCF¹⁶ results for B₂H₆, B₄H₄, B₄H₁₀, B₅H₉, B₅H₁₁, B₆H₁₀, 1,2-C₂B₄H₆, 1,6-C₂B₄H₆, 2,4-C₂B₅H₇, 4,5-C₂B₄H₆, B₁₀H₁₄, B₆H₆²⁻, B₈H₁₂, B₉H₁₅, B₁₀H₁₀²⁻, and B₁₀H₁₄²⁻.^{10v,20-28} A more detailed comparison of the PRDDO and ref SCF results is given in Appendix I. The labeling for the atoms and structures for the first 11 molecules may be found in Figure 1. The comparisons for the last five molecules extend published remarks^{10v} and are included here to allow a wider discussion. In addition, STO-3G²⁹ and ref SCF results will be compared for six small boron hydrides (the first six molecules in the above list). All calculations employ the same (usually X-ray) molecular geometries, and the PRDDO and STO-3G calculations also employ the ref SCF orbital exponents. The standard exponents^{4a} supplied by the program³⁰ have been used in the CNDO/2 and INDO calculations.

Relative Energies. In order to test the ability of the several methods to reproduce the ref SCF values for relative energies, we compare in Table I some results for 12 prototype reactions. These 12 processes constitute a complete set in the sense that any balanced chemical reaction involving only the 16 molecules and ions included here can be written as a linear combination of processes in the set.³¹

The data show that the PRDDO, STO-3G, and ref SCF calculations agree in all cases for which comparison is possible as to the sign and approximate magnitude of the heat of reaction. Taking the ref SCF results as standard values, the root mean square (rms) errors are 6.8 kcal/mol for PRDDO (5.2 kcal/mol for processes 1-4) and 1.2 kcal/mol for STO-3G (processes 1-4). Clearly, both methods perform well.

In contrast, the CNDO/2 and INDO values differ from the ref SCF, PRDDO, and STO-3G values by as much as 600 kcal/mol and by ~200 kcal/mol on the average (Table I). Even the isomerization of 1,2- to 1,6-C₂B₄H₆^{10z} (process 10) is described poorly.³² The experimental observation³³ that 1,2-C₂B₄H₆ isomerizes to 1,6-C₂B₄H₆ overnight at 250°C strongly supports the PRDDO and ref SCF assessments that the 1,6 isomer is the more stable. The wholly unreasonable CNDO/2 and INDO values for various other processes lends support to the growing evidence³⁴ that these methods contain serious deficiencies which frequently render them unsuitable for use in energy evaluations.

We conclude from these comparisons that CNDO/2 and INDO are ~30 times less accurate than PRDDO in reproducing ref SCF results for relative energies, whereas STO-3G is four to five times more accurate than PRDDO. Moreover, CNDO/2 and INDO appear to be too inaccurate to be of much value for energy comparisons in systems of the types considered here.

Molecular Orbital Eigenvalues. The comparisons given in Tables II and III show that the PRDDO method reproduces the ref SCF eigenvalues consistently well. The overall rms deviation is just 0.016 au, not much larger than found previ-

Table III. Summary of PRDDO and Reference SCF Results for Energies, Atomic Charges, and Eigenvalues^a

molecule	$E_{\text{ref SCF}}$	ΔE_{tot}^b	ΔT	ΔV	ΔG	ΔQ_{rms}^c	$\Delta \epsilon_{\text{rms}}^d$	$\Delta \epsilon_{\text{mean}}^e$
B ₂ H ₆	-52.718	-0.030	-0.073	0.144	-0.105	0.007	0.010	-0.007
B ₄ H ₄	-100.760	-0.106	-0.019	-0.012	-0.074	0.016	0.012	-0.010
B ₄ H ₁₀	-104.256	-0.075	-0.107	0.208	-0.170	0.011	0.010	-0.009
B ₅ H ₉	-128.306	-0.118	-0.105	0.198	-0.210	0.011	0.014	-0.012
B ₅ H ₁₁	-129.428	-0.101	-0.135	0.263	-0.230	0.010	0.015	-0.011
B ₆ H ₁₀	-153.517	-0.153	-0.118	0.239	-0.275	0.007	0.014	-0.013
1,2-C ₂ B ₄ H ₆	-177.601	-0.162	-0.048	0.108	-0.222	0.013	0.019	-0.014
1,6-C ₂ B ₄ H ₆	-177.620	-0.165	-0.064	0.067	-0.169	0.019	0.018	-0.014
4,5-C ₂ B ₄ H ₈	-178.744	-0.171	-0.100	0.269	-0.333	0.009	0.015	-0.014
2,4-C ₂ B ₅ H ₇	-202.897	-0.204	-0.055	0.150	-0.314	0.010	0.018	-0.016
B ₁₀ H ₁₄	-254.479	-0.318	-0.212	0.536	-0.672	0.008	0.021	-0.018
B ₆ H ₆ ²⁻	-151.078	-0.213	-0.077	0.060	-0.196	0.030	0.018	-0.014
B ₈ H ₁₂	-203.985	-0.227	-0.145	0.345	-0.426	0.010	0.018	-0.016
B ₉ H ₁₅	-230.319	-0.242	-0.183	0.477	-0.464	0.011	0.016	-0.015
B ₁₀ H ₁₀ ²⁻	-252.173	-0.385	-0.102	0.364	-0.646	0.009	0.025	-0.021
B ₁₀ H ₁₄ ²⁻	-254.378	-0.358	-0.172	0.526	-0.712	0.009	0.021	-0.020

^a The entries for the last six molecules are based on results cited in ref 10v. ^b PRDDO-reference SCF energy, in atomic units. T , V , and G represent the kinetic, nuclear-attraction, and electron-repulsion energy components. ^c Root mean square error in PRDDO Mulliken atomic charges. The rms error taken over all molecules is 0.014 electrons. ^d Root mean square error in PRDDO eigenvalues for valence-shell occupied and lowest unoccupied molecular orbitals, in atomic units. Rms error taken over all molecules is 0.018 au. Rms error for inner-shell eigenvalues is 0.007 au. ^e Mean error, $(\sum_i (\epsilon_i(\text{PRDDO}) - \epsilon_i(\text{ref SCF}))) / n$ in atomic units, for valence-shell eigenvalues, ϵ_i .

Table IV. Some Comparisons of Orbital Energies for CNDO/2 and Reference SCF Calculations^a

molecule	LOMO ^b		HOMO ^c		LUMO ^d		rms dev ^e
	CNDO/2	ref SCF	CNDO/2	ref SCF	CNDO/2	ref SCF	
B ₂ H ₆	-1.404 (a _g)	-0.877 (a _g)	-0.587 (b _{2g})	-0.467 (b _{2g})	0.174 (b _{3g})	0.206 (b _{3g})	0.292
B ₄ H ₄	-1.794 (a ₁)	-0.937 (a ₁)	-0.576 (t ₂)	-0.398 (t ₂)	-0.016 (e)	0.055 (e)	0.391
B ₄ H ₁₀	-1.807 (a ₁)	-0.946 (a ₁)	-0.540 (a ₁)	-0.431 (a ₁)	0.095 (b ₁)	0.244 (b ₁)	0.359
B ₅ H ₉	-2.154 (a ₁)	-1.022 (a ₁)	-0.498 (e)	-0.379 (e)	0.137 (b ₂)	0.190 (b ₁)	0.427
B ₅ H ₁₁	-2.026 (a')	-1.002 (a')	-0.513 (a'')	-0.401 (a'')	0.080 (a')	0.177 (a'')	0.392
B ₆ H ₁₀	-2.192 (a')	-1.016 (a')	-0.496 (a')	-0.342 (a')	0.083 (a'')	0.158 (a')	0.428
1,2-C ₂ B ₄ H ₆	-2.439 (a ₁)	-1.206 (a ₁)	-0.554 (b ₂)	-0.364 (b ₂)	0.191 (b ₁)	0.266 (a ₁)	0.443
1,6-C ₂ B ₄ H ₆	-2.528 (a _{1g})	-1.184 (a _{1g})	-0.559 (a _{2u}) ^f	-0.340 (a _{2g})	0.209 (e _u)	0.279 (e _u)	0.477
4,5-C ₂ B ₄ H ₈	-2.212 (a')	-1.116 (a')	-0.527 (a'')	-0.347 (a'')	0.121 (a'')	0.237 (a'')	0.404
2,4-C ₂ B ₅ H ₇	-2.537 (a ₁)	-1.172 (a ₁)	-0.534 (a ₁) ^g	-0.372 (b ₁)	0.201 (b ₁)	0.281 (b ₁)	0.461
B ₁₀ H ₁₄	-2.578 (a ₁)	-1.060 (a ₁)	-0.536 (b ₂)	-0.389 (b ₂)	0.059 (a ₁)	0.069 (a ₁)	0.475
B ₆ H ₆ ²⁻	-1.869 (a _{1g})	-0.498 (a _{1g})	-0.078 (t _{1u})	-0.144 (t _{1u})	0.708 (a _{1g})	0.808 (t _{2g})	0.476
B ₈ H ₁₂	-2.369 (a')	-1.033 (a')	-0.464 (a')	-0.338 (a')	0.073 (a'')	0.096 (a'')	0.449
B ₉ H ₁₅	-2.344 (a')	-1.031 (a')	-0.472 (a')	-0.353 (a')	0.086 (a')	0.101 (a'')	0.435
B ₁₀ H ₁₀ ²⁻	-2.316 (a ₁)	-0.619 (a ₁)	-0.099 (e ₁)	0.056 (e ₁)	0.578 (e ₁)	0.604 (e ₁)	0.506
B ₁₀ H ₁₄ ²⁻	-2.128 (a ₁)	-0.624 (a ₁)	-0.046 (a ₂)	0.090 (a ₂)	0.526 (b ₂)	0.567 (b ₁)	0.459

^a All energies are given in atomic units. ^b Lowest occupied (valence) MO. ^c Highest occupied MO. ^d Lowest unoccupied MO. ^e Rms difference between CNDO/2 and ref SCF eigenvalues for occupied valence MOs. ^f The a_{2g} eigenvalue is -0.596 au. ^g The b₁ eigenvalue is -0.579 au.

charges. STO-3G, in turn, is ~four times more accurate than PRDDO, but neither STO-3G nor PRDDO makes significant errors with respect to the ref SCF results.

Dipole Moments. The PRDDO dipole moments for the neutral molecules range from 1 to 8% larger than the ref SCF values, while the STO-3G values usually agree with the latter to within 1% (Table VII).³⁸ The rms deviations are 0.20 and 0.02 D (5.8 and 0.8%, respectively), in each case much smaller than the difference of 50–100% between the ref SCF and experimental values. The CNDO/2 and INDO dipole moments, in contrast, are from 5 to 89% larger than the ref SCF values (rms deviation 2.2 D) and typically are two to three times larger than experiment, suggesting that these more approximate methods give a much less reliable account of the molecular charge distributions.

Thus, we find that PRDDO is ~ten times more accurate than CNDO/2 or INDO, but ~seven times less accurate than STO-3G in reproducing the ref SCF dipole moments. In comparison to experiment, however, the PRDDO, STO-3G, and ref SCF methods are all essentially equivalent.

In summary, both PRDDO and STO-3G reproduce the

reference MBS calculations consistently closely, often to well within the inherent error in the MBS approximation. In contrast, the CNDO/2 and INDO calculations frequently are in serious disagreement with both the ref SCF results and with experiment.

IV. Comparisons for Organic Compounds

We shall now undertake comparisons for organic compounds analogous to those presented in the previous section for boron hydrides and related compounds. The organic systems will consist of acetylene, ethylene, allene, cyclopropane, methyl cyanide, methyl isocyanide, diazomethane, diazine, *trans*-diaziridine, bicyclobutane, and *trans*-butadiene. While these compounds in general are considerably smaller than the boron hydrides treated in section III, they have the advantage of having previously been treated by ab initio methods using relatively large basis sets. We shall therefore also be able to examine the accuracy and limitations of the minimum basis set SCF calculations themselves. Comparisons for smaller organic compounds have previously been reported.⁸

The experimental geometries used by Snyder and Basch in

Table V. Ionization Potentials (au)^a

	CNDO/2	INDO	PRDDO	STO-3G	ref SCF	exptl ^b
B ₂ H ₆	0.587	0.581	0.472	0.463	0.467	0.441
B ₄ H ₁₀	0.540	0.537	0.442	0.428	0.431	0.382
B ₅ H ₉	0.498	0.485	0.400	0.377	0.379	0.386
B ₅ H ₁₁	0.513	0.507	0.414	0.398	0.401	0.379
B ₆ H ₁₀	0.496	0.481	0.369	0.340	0.342	0.343
rms SCF ^c	0.123	0.115	0.017	0.003		
rms exptl ^d	0.154	0.133	0.036	0.025	0.027	

^a Calculated from eigenvalues for highest occupied MOs via Koopmans' theorem. ^b Reference 36. ^c Rms deviation relative to ref SCF results. ^d Rms deviation relative to experiment.

their extended basis set calculations³⁹ will be employed throughout. We note that the Snyder-Basch calculations employ Gaussian basis sets of double- ζ quality, but do not include polarization functions. For computational convenience, the ref SCF calculations will here employ STO-6G, rather than STO, basis sets. Hehre, Stewart, and Pople have shown that 6G expansions reproduce the Slater AOs with negligible error.^{6a} Pople's standard molecular exponents^{6a} have been employed for the PRDDO, STO-3G, and STO-6G calculations,²⁹ and again the standard (Slater) exponents^{4a} supplied by the CNINDO program have been used in the CNDO/2 and INDO calculations.⁴⁰ For reference, total energies are listed in Table VIII.

Relative Energies. We compare in Table IX calculated heats of reaction for nine formal reaction processes. These processes constitute a complete set, in the sense that any balanced chemical reaction involving only H₂ plus the 11 organic compounds treated here can be written as a linear combination of members of the set.

With two exceptions, all of the approximate methods agree with the ref SCF method (STO-6G) as to the sign of the reaction energy, although CNDO/2 and INDO again incur very large errors (rms deviations are 131 and 122 kcal/mol, respectively). In contrast, as the table shows, the PRDDO errors are moderate in size, and the STO-3G errors are again quite small (Table IX).

When comparison is made to the Snyder-Basch double- ζ results and to the experimental heats of reaction, even the ref SCF minimum-basis calculations are found to incur sizable errors. Thus, while the moderately extended-basis 4-31G calculations^{29,41} reproduce the Snyder-Basch reaction energies quite well (rms deviation 2.8 kcal/mol), the ref SCF calculations (rms deviation 33.5 kcal/mol) do not. Indeed, as Table IX shows, the rms error is essentially the same for the ref SCF calculations as for both the STO-3G and PRDDO calculations, though the CNDO/2 and INDO errors again are much larger.

It is also evident that the Snyder-Basch results themselves compare poorly with experiment in some cases, although the rms deviation, 12.0 kcal/mol, is moderate in size. This observation might be taken to mean that even large basis set calculations cannot be relied upon when accurate energy comparisons are needed. Fortunately, however, computational experience, much of it accumulated by Pople and co-workers,¹⁴ provides considerable help in determining what level of theory is required to treat a given computational problem with suitable accuracy. Perhaps it will be helpful to summarize here some of the main conclusions derived from this work by showing their applicability to the data in Table IX.

Firstly, we note that isodesmic reactions (in which both the numbers and types of chemical bonds are unchanged)^{14h} usually are treated fairly accurately even by MBS ab initio (and thus also by PRDDO) single-determinant calculations. In contrast, various studies have shown that such MBS calculations strongly favor single-bonded (σ) over multiply

Table VI. Mulliken Atomic Charges, Q , for PRDDO and Reference SCF Calculations^a

Atom	Ref.	PRDDO	ΔQ	Atom	Ref.	PRDDO	ΔQ	Atom	Ref.	PRDDO	ΔQ
B ₂ H ₆				B ₂ H ₆				B ₂ H ₆			
B (2) ^b	0.125	0.136	0.011	3Rc (2)	-0.06	-0.071	-0.011	4,5-C ₂ B ₄ H ₆			
Hc (4)	-0.087	-0.079	-0.008	7Rc (2)	-0.07	-0.074	-0.004	1B (1)	0.020	-0.002	-0.022
Hb (2)	0.010	0.010	0.000	1Mb (1)	0.03	0.044	0.014	2B (1)	0.069	0.070	0.001
B ₄ H ₁₀				2Mb (2)	0.06	0.063	0.003	3B (2)	0.061	0.053	-0.008
B (4)	0.005	-0.011	-0.016	B ₅ H ₉				4C (2)	-0.016	0.000	0.016
H (4)	-0.005	0.021	0.016	B ₅ H ₁₀				1Mc (1)	-0.084	-0.074	0.010
B ₅ H ₉				B ₅ H ₁₀				2Mc (1)	-0.051	-0.053	-0.002
B (4)	0.005	-0.011	-0.016	1B (1)	-0.02	-0.041	-0.021	3Mc (2)	-0.080	-0.088	-0.008
H (4)	-0.005	0.021	0.016	2B (1)	0.07	0.069	-0.001	4Mc (2)	0.042	0.042	0.000
B ₅ H ₁₀				3B (2)	0.06	0.060	-0.001	7Mb (2)	0.018	0.021	0.003
1B (1)	-0.02	-0.038	-0.018	4B (2)	0.04	0.036	-0.004	2,4-C ₂ B ₂ H ₂			
2B (1)	0.08	0.097	0.017	1Mc (1)	-0.07	-0.062	0.008	1B (2)	3.118	-1.105	-0.013
1Mc (2)	-0.05	-0.048	0.001	2Mc (1)	-0.04	-0.036	0.002	2C (2)	-0.126	-0.125	0.001
2Mc (2)	-0.07	-0.077	-0.007	3Mc (2)	-0.04	-0.041	-0.001	3B (1)	0.123	0.124	-0.001
3Mc (2)	-0.07	-0.077	-0.007	4Mc (2)	-0.09	-0.081	0.009	5B (2)	0.064	0.052	-0.012
4Mc (2)	-0.07	-0.077	-0.007	7Mb (2)	0.00	0.033	0.033	1Mc (1)	-0.069	-0.061	0.008
7Mb (2)	0.06	0.071	0.011	8Mb (2)	0.02	0.027	0.007	2Mc (2)	0.071	0.072	0.001
B ₆ H ₁₀				1,2-C ₂ B ₄ H ₆				3Mc (2)	-0.080	-0.056	0.024
B (4)	0.005	-0.011	-0.016	1,2-C ₂ B ₄ H ₆				5Mc (2)	-0.080	-0.074	0.006
H (4)	-0.005	0.021	0.016	1,2-C ₂ B ₄ H ₆				1B (2)	0.029	0.016	-0.013
B ₆ H ₁₀				1,2-C ₂ B ₄ H ₆				2B (2)	-0.040	-0.027	-0.013
1B (1)	-0.02	-0.027	-0.027	1,2-C ₂ B ₄ H ₆				5B (1)	0.044	0.046	0.002
2B (4)	0.06	0.050	-0.010	1,2-C ₂ B ₄ H ₆				6B (2)	0.092	0.100	0.008
1Mc (1)	-0.09	-0.069	0.021	1,2-C ₂ B ₄ H ₆				1Mc (2)	-0.052	-0.047	0.005
2Mc (1)	-0.04	-0.036	0.004	1,2-C ₂ B ₄ H ₆				2Mc (2)	-0.061	-0.057	0.004
3Mc (1)	0.01	0.010	0.000	1,2-C ₂ B ₄ H ₆				5Mc (1)	-0.048	-0.050	-0.002
B ₆ H ₁₀				1,2-C ₂ B ₄ H ₆				5Mc (2)	-0.024	-0.037	-0.013
1B (1)	-0.02	-0.108	-0.028	1,2-C ₂ B ₄ H ₆				Hb (4)	0.021 ^d	0.030	0.009
2B (2)	0.05	0.045	-0.005	1,2-C ₂ B ₄ H ₆							
4B (2)	0.09	0.089	0.009	1,2-C ₂ B ₄ H ₆							
1Mc (1)	-0.07	-0.065	0.005	1,2-C ₂ B ₄ H ₆							
2Mc (1)	0.06	0.072	0.012	1,2-C ₂ B ₄ H ₆							
3Mc (2)	-0.02	-0.033	-0.003	1,2-C ₂ B ₄ H ₆							

Root-mean-square deviation, all molecules: 0.032

^a See refs 20-28 for literature references for the reference SCF calculations. ^b Number of equivalent atoms. ^c Root-mean square error in PRDDO atomic charges, taking all equivalent atoms into account. ^d Listed incorrectly in original reference.

bonded (π) systems. Process 1 in Table IX is a case in point; as anticipated, the calculated ΔH is much too negative in each of the MBS calculations. A related factor is the MBS bias in favor of small strained rings (e.g., over acyclic isomers having larger numbers of π bonds), as is reflected in the calculated STO-3G, STO-6G, and PRDDO ΔH 's for processes 2, 3, 6, and 8.

Moderately extended-basis (e.g. 4-31G, double- ζ) calculations make smaller errors in both of these regards, though small strained rings now are computed consistently to be too unstable. Thus, the 4-31G and Snyder-Basch error in ΔH differs in sign from the MBS error for processes 2, 6, and 8. It is of the same sign for process 1, in which ring strain is not involved. Pople and co-workers have found that polarization functions (on carbon) must be included in the basis set if strained rings are neither to be unrealistically favored nor disfavored.^{14h,42} Such functions appear to be less important when ring strain is not a factor.^{14h}






Apart from certain (mainly isodesmic) unimolecular reactions, differences in electron correlation energy usually must also be taken into account, as may be done by employing multideterminantal (e.g., CI) wave functions. Several important considerations arise here. One of these is that interpair contributions⁴³ to the correlation energy will tend to favor the composite system, C (in which they are more numerous), in processes of the type $A + B \rightarrow C$. Thus, configuration interaction stabilizes B₂H₆ relative to 2BH₃ by ~ 15 kcal/mol.⁴⁴

Table VII. Dipole Moments^a

molecule	$\mu_{\text{CNDO/2}}$	μ_{INDO}	μ_{PRDDO}	$\mu_{\text{STO-3G}}$	$\mu_{\text{ref-SCF}}$	μ_{exptl}
B ₄ H ₁₀	1.43	1.35	1.07	0.99	1.00	0.56 ^b
B ₅ H ₉	6.34	6.32	3.85	3.68	3.66	2.13 ^c
B ₅ H ₁₁	4.87	4.81	3.34	3.19	3.17	
B ₆ H ₁₀	7.04	6.90	3.85	3.72	3.69	
1,2-C ₂ B ₄ H ₆	4.33	4.32	2.97		2.95	1.50 ^d
4,5-C ₂ B ₄ H ₈	2.21	2.29	2.25		2.11	
2,4-C ₂ B ₅ H ₇	2.45	2.44	1.82		1.77	1.32 ^e
B ₈ H ₁₂	7.10	6.87	4.04		3.75	
B ₉ H ₁₅	6.18	6.02	3.95		3.70	
B ₁₀ H ₁₄	7.92	7.67	4.92		4.56	~3.4 ^f
rms dev	2.29	2.18	0.20	0.02		

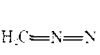

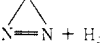

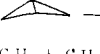


^a In debyes. ^b J. R. Weaver, C. W. Heitsch, and R. W. Parry, *J. Chem. Phys.*, **30**, 1075 (1959). ^c H. J. Hrostowski, R. J. Myers, and G. C. Pimentel, *ibid.*, **20**, 518 (1952). ^d R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **53**, 1899 (1970). ^e R. R. Olsen and R. N. Grimes, *J. Am. Chem. Soc.*, **92**, 5072 (1970). ^f Average of the values of 3.17, 3.39, and 3.62 D quoted in ref 28.

Table VIII. Total Energies (au)

	CNDO/2	INDO	PRDDO	STO-3G	STO-6G	4-31G	Snyder-Basch	exptl ΔH_f kcal/mol
H ₂	-1.4746	-1.4746	-1.1269	-1.1167	-1.1253	-1.1267	-1.134	0.0
HC≡CH	-15.3414	-14.8367	-76.6507	-75.8529	-76.6026	-76.7109	-76.7919	54.3 ^a
H ₂ C=CH ₂	-17.0659	-16.5596	-77.8918	-77.0721	-77.8266	-77.9209	-78.0054	12.5 ^a
H ₂ C=C=CH ₂	-24.0435	-23.2809	-115.6581	-114.4197	-115.5452	-115.6976	-115.8203	45.6 ^a
	-25.9418	-25.1637	-116.9089	-115.6655	-116.7955	-116.8823	-117.0099	12.7 ^a
CH ₃ CN	-27.8911	-26.8824	-131.6369	-130.2703	-131.5443	-131.7266	-131.8674	20.9 ^b
CH ₃ N≡C	-27.7764	-26.7728	-131.5970	-130.2323	-131.5063	-131.6930	-131.8400	35.6 ^b
H ₂ C=N=N	-31.6247	-30.3790	-147.4256	-145.9078	-147.3335	-147.6052	-147.7702	71 ^c
	-31.8265	-30.5403	-147.4710	-145.9438	-147.3700	-147.5527	-147.7287	79 ^c
	-33.3811	-32.0994	-148.5306	-146.9998	-148.4328	-148.6608	-148.8430	
	-33.0326	-31.9863	-154.6567	-152.9980	-154.4984	-154.6223	-154.7889	51.9 ^a
	-32.7300	-31.7153	-154.6778	-153.0173	-154.5187	-154.6976	-154.8648	26.0 ^a

^a J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. ^b D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Baily, and R. H. Schumm, *Natl. Bur. Stand. (U.S.), Tech. Note, No. 270-3* (1968). ^c S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

Table IX. Comparison of Calculated Reaction Energies (kcal/mol)

reaction	CNDO/2	INDO	PRDDO	STO-3G	STO-6G	4-31G	Snyder-Basch	exptl ΔH
1. H ₂ + C ₂ H ₂ → C ₂ H ₄	-156.8	-155.8	-71.7	-64.4	-62.0	-52.3	-49.9	-41.8 ^a
2. ³ / ₂ C ₂ H ₄ → C ₃ H ₆	-215.3	-203.5	-44.7	-36.0	-34.8	-0.6	-1.1	-6.0 ^a
3. H ₂ + C ₃ H ₄ → C ₃ H ₆	-265.9	-256.2	-77.7	-81.0	-80.1	-36.4	-34.9	-33.1 ^a
4. CH ₃ C≡N → CH ₃ N≡C	72.0	68.7	25.0	23.9	23.9	21.1	17.2	14.7 ^b
5. 2CH ₃ C≡N → H ₂ C=N=N + C ₃ H ₄	71.5	65.8	119.2	133.7	131.8	94.3	90.6	75 ^{a-c}
6.  → 	-126.7	-101.2	-28.5	-22.6	-22.9	31.4	26.0	8 ^c
7.  + H ₂ → 	-50.1	-53.0	-42.2	-38.1	-39.2	-13.8	-12.4	
8.  → 	189.9	170.1	-13.2	-12.1	-12.8	-47.3	-47.6	-25.9 ^a
9. C ₂ H ₂ + C ₂ H ₄ → 	-202.6	-200.2	-84.9	-57.9	-56.2	-41.3	-42.4	-41 ^a
rms dev vs. STO-6G	131	122	11.7	1.4				
vs. Snyder-Basch	163	140	33.2	33.3	33.5	2.8		
vs. experiment	160	150	35.1	34.5	34.8	14.0	12.0	

^a J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. ^b D. D. Wagman, W. H. Evans, V. B. Parker, I. Halo, S. M. Baily, and R. H. Schumm, *Natl. Bur. Stand. (U.S.), Tech. Note, No. 270-3* (1968). ^c S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

Nevertheless, it is evident (since polarization functions would be expected to have little net effect) that the CI correction for process 1 favors $H_2 + C_2H_2$ over C_2H_4 . Here, the dominant factor appears to be the fact that typical intrapair correlation energies are much larger for π bonds (~ 20 – 30 kcal/mol)⁴⁵ than for σ bonds (~ 5 – 10 kcal/mol),⁴⁵ where the participating AOs overlap more strongly. Thirdly, the CI stabilization is expected to be particularly large for conjugated π systems (e.g., for butadiene in processes 8 and 9), since energy differences between occupied and unoccupied MOs are unusually small in such systems.

Many processes, of course, will be influenced by two or more of these factors, which either may act in concert to produce large errors or in such a way as to largely cancel against one another in the computed ΔH . Processes 3 and 9, for which the 4-31G and Snyder–Basch calculations are in close agreement with experimental heats of reaction, illustrate the latter alternative. For process 3, for example, the (omitted) larger intrapair CI stabilization for π -bonded C_3H_4 evidently largely balances against the relative stabilization of cyclopropane which would result from the addition of polarization functions to the basis set. In process 9, considerable CI stabilization is expected both for reactants $C_2H_2 + C_2H_4$ (3π bonds) and for butadiene (composite system; conjugated π system), with the result that the 4-31G and Snyder–Basch ΔH 's again are in close agreement with the experimental value.

Fortunately, the frequent need for including polarization functions and/or configuration interaction in order to properly assess relative energies is not so inhibiting a factor as might at first seem to be the case. Thus, relatively simple methods increasingly are used to determine molecular geometries via energy minimization (computationally the most time-consuming step). These geometries, which even single-determinant MBS calculations usually obtain rather accurately,^{14–16} then are employed in single calculations carried out at the required higher theoretical level. The comparisons in Table IX, as well as comparisons of optimized geometries,^{8,10f} suggest that PRDDO, STO-3G, and the ref SCF MBS method can all be expected to serve essentially equally well in this regard, but that satisfactory results cannot consistently be expected from the far less accurate CNDO/2 and INDO methods.

To summarize the comparison of the MBS methods to the reference MBS SCF method, we note that STO-3G is ~ 8 times more accurate than PRDDO, and that CNDO/2 and INDO are ~ 11 times less accurate than PRDDO in reproducing the ref SCF reaction energies.

Molecular Orbital Eigenvalues. As Table X records, PRDDO and STO-3G rms errors in eigenvalues for occupied MOs in the test molecules are very similar in magnitude to the rms errors for boron compounds reported in section III. Specifically, rms deviations from the ref SCF values are 0.0107 and 0.0034 au, respectively. (We note that the STO-3G comparison excludes inner-shell eigenvalues on carbon and nitrogen, which are systematically too positive by 0.152 ± 0.004 and 0.220 ± 0.002 au.) For CNDO/2 and INDO, much larger rms errors (0.275 and 0.273) are again found, and individual eigenvalues are too negative by from 0.3–0.7 au for lowest occupied valence-shell eigenvalues to 0.2–0.3 au for the highest occupied MOs. Moreover, CNDO/2 and INDO errors for unoccupied MOs are larger still, whereas PRDDO and STO-3G obtain eigenvalues for unoccupied MOs nearly as accurately as for occupied MOs.

As to ordering, just three inversions in sequence are found for PRDDO, and one for STO-3G, among the ref SCF eigenvalues for occupied MOs. In addition, each break in sequence is small and would be rectified by a change of 0.002 au or less in one of the misordered eigenvalues. Only one (PRDDO) and three (STO-3G) inversions are found for unoccupied MOs.

Table X. Comparisons for Molecular Orbital Eigenvalues, ϵ_i

method	inversions ^a		rms dev. ^b		rms dev. ^c	
	occ	unocc	ref SCF		first IP	
	ϵ_i	ϵ_i	occ ϵ_i	HOMO	au	eV
CNDO/2	7	19	0.275	0.199	0.172	4.69
INDO	5	23	0.273	0.177	0.157	4.28
PRDDO	3	1	0.0107	0.0119	0.044	1.20
STO-3G	1	3	0.0034	0.0042	0.052	1.43
STO-6G					0.049	1.33
4-31G					0.014	0.37

^a Number of inversions in ordering of eigenvalues using STO-6G as reference calculations. ^b Rms deviations vs. STO-6G (au). ^c Rms deviations in Koopmans' theorem first ionization potentials vs. experiment.

For CNDO/2 and INDO, seven and five inversions are found, respectively, for occupied valence-shell eigenvalues, of which one involves a highest occupied MO (Table XI). In addition, many inversions are found for unoccupied MOs, indicating that even the moderate success attained for occupied-orbital eigenvalues depends substantially on cancellations of underlying errors in the CNDO/2 and INDO approximations to the Fock matrix.

Table XI lists Koopmans' theorem first ionization potentials. Here, rms errors vs. the ref SCF calculations are 0.0034, 0.0119, 0.199, and 0.177 au, respectively, for STO-3G, PRDDO, CNDO/2, and INDO (Table X). For comparison, rms errors vs. experiment are 0.049, 0.052, 0.044, 0.157, and 0.172 au, respectively, for the ref SCF and the four more approximate calculations (Table X). Thus, PRDDO and STO-3G again perform about as well as can be expected of a minimum basis set method, but the more severe CNDO/2 and INDO approximations cause these methods to suffer sharply in performance. Finally, we note that the extended-basis 4-31G calculations fare considerably better in reproducing the experimental first ionization potentials (rms deviation 0.014 au) than do the MBS methods. Appropriately, the 4-31G eigenvalues are consistently more negative by 0.03–0.07 au than their PRDDO or STO-3G counterparts.






In summary STO-3G is two to three times more accurate than PRDDO in reproducing the ref SCF values for all occupied MOs, as well as for the highest occupied MO, while PRDDO is ~ 30 times more accurate than CNDO/2 or INDO for occupied valence MOs and is ~ 17 times more accurate for highest occupied MOs.

Atomic Charges. As reported in Table XII, rms errors in Mulliken atomic charges vs. the ref MBS SCF calculations for PRDDO and STO-3G are just 0.0089 and 0.0034 e, respectively. For PRDDO, the largest individual error is 0.031 e and occurs in diazomethane (Table XIII).

For CNDO/2 and INDO, as emphasized in section III, comparisons for atomic charges should properly be made over orthogonalized AOs and should be based on calculations carried out using identical orbital exponents. We therefore performed a duplicate set of PRDDO calculations using CNDO/2–INDO exponents and compared atomic charges computed over OAOs. The rms errors vs. PRDDO were found to be 0.11 e for CNDO/2 and 0.13 e for INDO. Essentially the same result would have been obtained in comparisons to ref SCF atomic charges over OAOs if such comparisons were made.

Thus, both PRDDO and STO-3G maintain the consistently good performance reported in section III, and CNDO/2 and INDO again perform quite unevenly. For the present organic systems, PRDDO is about three times less accurate than STO-3G at reproducing the ref SCF atomic charges (though in both cases absolute errors are too small to be of much con-

Table XI. First Ionization Potentials (eV)

molecule	HOMO symmetry	CNDO/2	INDO	PRDDO	STO-3G	STO-6G	4-31G	exptl
H ₂	σ_g	20.86	20.86	15.88	15.72	15.84	16.20	15.98 ^a
HC≡CH	π_u	17.49	16.84	9.62	9.49	9.60	10.95	11.40 ^a
H ₂ C=CH ₂	b_{1u}	15.82 ^c	15.51	9.05	8.79	8.88	10.07	10.51 ^a
H ₂ C=C=CH ₂	e	13.90	13.41	8.95	8.60	8.73		10.07 ^b
	e'	15.40	14.81	10.88	10.36	10.42	11.33	11.0 ^a
CH ₃ C≡N	e	15.89	15.61	11.21	10.99	11.09	12.52	12.21 ^a
CH ₃ N≡C	a_1	15.52	13.55	10.30	10.39	10.49	12.48	11.27 ^a
H ₂ C=N=N	b_2	11.05	10.04	7.04	6.67	6.84		
	b_1	14.15	12.85	10.64	9.77	9.88		10.75 ^d
	a	12.22	10.50	6.98	6.55	6.69		
	a_1	12.17	11.54	8.72	8.20	8.28		
	b_g	13.21	12.63	7.50	7.21	7.32	8.64	9.08 ^a

^a D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970. ^b F. Broglie, J. K. Crandall, E. Heilbronner, E. KlosterJensen, and S. A. Sojka, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 455 (1973). ^c b_{1g} . ^d C. R. Brundle, N. A. Kuebler, G. B. Ellison, and K. B. Wiberg, *J. Chem. Phys.*, **57**, 1758 (1972).

Table XII. Comparisons for Atomic Charges (e)

method	rms dev vs. STO-6G	rms dev vs. PRDDO
CNDO/2		0.11
INDO		0.13
PRDDO	0.0089	
STO-3G	0.0034	

cern), while CNDO/2 and INDO are an additional 12-15 times less accurate than PRDDO.



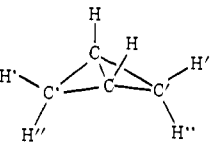
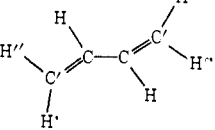
Dipole Moments. Calculated and experimental dipole moments are listed and compared in Table XIV. In comparison to the ref SCF (STO-6G) values, the expected progression in accuracy (CNDO/2 ~ INDO < PRDDO < STO-3G) is again found. Interestingly, however, none of the MBS methods fares appreciably better than any other in reproducing the Snyder-Basch double- ζ results: only 4-31G does well in this respect (Table XIV). Moreover, even the 4-31G and Snyder-Basch calculations attain only limited accuracy (rms deviations 0.41, 0.37 D) in reproducing the experimental values, though these calculations do reasonably well for all molecules except diazirine. (Interestingly, all seven methods predict a much higher dipole moment for diazirine than for the isomeric diazomethane, though the experimental values cited in Table XIV differ by only 0.09 D.)

Thus, the differences among the MBS methods in calculated dipole moments are less extreme for these systems than for the boron hydrides. Moreover, the limitations in the MBS framework are even more evident in the present comparisons. Except for the fact that CNDO/2 and INDO predict the wrong ordering for CH₃CN and CH₃NC, there is little to choose among the MBS methods. However, in comparison to the ref SCF calculations, it is again clear that PRDDO, and especially STO-3G, perform much more accurately than CNDO/2 and INDO. Specifically, STO-3G is ~three times more accurate than PRDDO in this respect, and PRDDO is ~three times more accurate than CNDO/2 or INDO. Thus, the conclusions reached for boron hydrides in section III largely carry over to the present systems.

V. Computing Times

Central processor unit (CPU) computing times for the IBM 360/91 listed in Table XV, and additional CNDO/2, INDO, and PRDDO timings for larger molecules (up to $N = 112$), are

Table XIII. PRDDO and Reference SCF Mulliken Atomic Charges (e)

molecule	atom	PRDDO	STO-6G
HC≡CH	H	0.116	0.108
	C	-0.116	-0.108
H ₂ C=CH ₂	H	0.063	0.063
	C	-0.125	-0.126
H ₂ C=C=CH ₂	H	0.077	0.078
	C	-0.168	-0.173
	C'	0.031	0.035
	H	0.069	0.066
	C	-0.138	-0.132
CH ₃ C≡N	H	0.102	0.101
	C	-0.170	-0.183
	C'	0.081	0.085
	N	-0.218	-0.205
CH ₃ N≡C'	H	0.096	0.99
	C	-0.031	-0.059
	C'	0.112	0.108
	N	-0.369	-0.345
H ₂ C=N=N'	H	0.082	0.083
	C	-0.088	-0.119
	N	-0.036	-0.025
	N'	-0.041	-0.022
	H	0.107	0.091
	C	-0.043	-0.045
	N	-0.085	-0.068
	H	0.063	0.059
	H'	0.243	0.231
	C	0.038	0.027
	N	-0.325	-0.304
	H	0.087	0.076
	H'	0.069	0.070
	H''	0.067	0.061
	C	-0.116	-0.106
	C'	-0.107	-0.101
	H	0.063	0.062
	H'	0.062	0.063
	H''	0.059	0.064
	C	-0.051	-0.056
	C'	-0.133	-0.133

described to within ~10% by the expressions

$$\text{CNDO/2, INDO (s)} = 1.5 \times 10^{-3} M^2 + 4.2 \times 10^{-5} M^3 \quad (3)$$

Table XIV. Dipole Moments (D)

molecule	CNDO/2	INDO	PRDDO	STO-3G	STO-6G	4-31G	Snyder-Basch	exptl
CH ₃ C≡N	3.06	2.95	3.17	3.06	3.11	4.11	4.18	3.92 ^a
CH ₃ N≡C	3.88	3.81	2.90	2.91	2.91	3.41	3.65	3.85 ^a
CH ₂ =N=N	0.73	0.93	1.30	0.96	1.00	1.52	1.42	1.50 ^a
	1.30	1.30	1.85	1.55	1.60	2.34	2.34	1.59 ^a
	0.75	0.51	0.68	0.55	0.59	1.37	1.41	
	1.27	1.19	0.64	0.66	0.65	0.89	0.80	0.68 ^b

^a R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 10* (1967). ^b M. D. Harmony and K. W. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966).

$$\text{PRDDO (s)} = 5.0 \times 10^{-3} N^2 + 1.6 \times 10^{-4} N^3 + 7.0 \times 10^{-7} N^4 \quad (4)$$

$$\text{STO-3G (s)} = 8.0 \times 10^{-4} N^3 + 2.4 \times 10^{-4} N^4 \quad (5)$$

where N is the number of MBS atomic orbitals and M is the number of valence AOs in the smaller CNDO/2 or INDO basis set. Equation 4⁴⁶ represents an improvement in the efficiency of PRDDO of ~20% over earlier performance.⁸ In particular, the N^4 term, as a result of improved programming, now accounts for only ~10% of the total CPU time for $N = 45$ (e.g., norbornylene) and, by extrapolation, for less than half of the total time until $N = 240$ (e.g., hexaphenylethane). Thus, PRDDO, like CNDO/2 and INDO, is essentially an N^3 method, whereas STO-3G, as a consequence of the calculation and subsequent manipulation of the $\sim N^4/8$ two-electron integrals, is essentially an N^4 method.

The CPU times show that CNDO/2 and INDO⁴⁷ are five to six times faster than PRDDO over a wide range in molecular size and that PRDDO in turn is ~20–30 times faster than STO-3G.⁴⁸ Moreover, the ratio of STO-3G and PRDDO CPU times increases rapidly with molecular size. This ratio is given fairly accurately by

$$\text{STO-3G/PRDDO} = 0.8N \quad (6)$$

For these molecules, however, we have employed unequal 2s and 2p exponents in order to model the ref SCF calculations. Usually, equal 2s and 2p exponents are employed in STO-3G calculations in the interest of efficiency.⁴⁹ When this restriction is imposed, as was done for the calculations on organic systems reported in section IV, the ratio of CPU times (on the City University IBM 370/168) becomes

$$\text{STO-3G/PRDDO} = 0.4N \quad (7)$$

We shall take eq 7 as our estimate of the intrinsic relative speed of the two methods under the conditions most commonly encountered.

As expected, the ref SCF calculations using the efficient Stevens POLYCAL program¹⁶ are even slower, e.g., by a factor of ~150 relative to PRDDO for B₁₀H₁₄ and B₁₀H₁₄²⁻ ($N = 64$) as judged from published timings.⁵⁰ This comparison suggests that

$$\text{ref SCF/PRDDO} = 2.3N \quad (8)$$

We note, however, that eq 8 will be subject to large fluctuations since symmetry, when present, is exploited in POLYCAL.

Thus, the relative CPU computing times for $N = 40$ AOs for the IBM 360/91 computer are approximately 1:6:100:600 for the CNDO/2 (INDO), PRDDO, STO-3G, and ref SCF methods. While the relative timings will differ slightly for other computers and with variations in molecular size, the CNDO/2, INDO, and PRDDO methods clearly are sufficiently faster

Table XV. Central Processor Unit (CPU) Computing Times (IBM 360/91)

system	N	CPU time, s			rel CPU time	
		CNDO/2, INDO	PRDDO	STO-3G ^a	PRDDO/CNDO-/2	STO-3G ^a /PRDDO
B ₂ H ₆	16	0.5	1.8	19	3.6	11
B ₄ H ₄	24	0.7	5.0	106	7.1	21
B ₄ H ₁₀	30	1.8	8.8	191	4.9	22
B ₅ H ₉	34	2.1	12.0	305	5.7	25
B ₅ H ₁₁	36	2.9	14.3	438	4.9	31
1,6-C ₂ B ₄ H ₆	36	2.1	14.5	(440)	6.9	(30)
B ₆ H ₁₀	40	3.3	19.3	665	5.8	34
B ₈ H ₁₂	52	6.6	38.0	(1867)	5.8	(49)
B ₉ H ₁₅	60	9.6	61.1	(3283)	6.4	(54)
B ₁₀ H ₁₄	64	11.6	74.8	(4236)	6.4	(57)
B ₁₀ H ₁₄ ²⁻	64	10.5	68.0	(4236)	6.5	(62)

^a Values in parentheses are projected values based on eq 5.

than the ref SCF procedure to bring calculations on much larger molecules into economic reach. The STO-3G method, in contrast, enjoys a considerably narrower advantage over the ref SCF procedure.

VI. Comparison of Speed and Accuracy for the CNDO/2, INDO, PRDDO, and STO-3G Methods

In one sense, the comparisons made in sections III–V, and now summarized for convenience in Tables XVI and XVII, simply show that CNDO/2 and INDO achieve relatively high speed but low accuracy, that STO-3G is highly accurate but relatively slow, and that PRDDO falls somewhere in between. However, these comparisons also lend themselves to the following statement: *The PRDDO approximation eliminates 90–95% of the additional CNDO/2 or INDO error (~93% overall) but requires just 6% of the additional cost in computing time needed for STO-3G.*

As is illustrated in Figure 2 through comparisons of relative error and CPU-time cost measured in "PRDDO units", this statement shows that PRDDO achieves nearly the accuracy of STO-3G and nearly the economy of CNDO/2 and INDO.

With respect to the relative uses and merits of the methods, we note that CNDO/2 or INDO will be the best choice if, for example, only a rough assessment of the wave function and charge distribution is needed. When greater accuracy is essential, the choice between PRDDO and STO-3G will depend largely on how much accuracy is required. Here, however, we must remember that the inherent error vs. experiment in the MBS approximation (cf. section IV) can easily outweigh the difference in accuracy between PRDDO and STO-3G, making

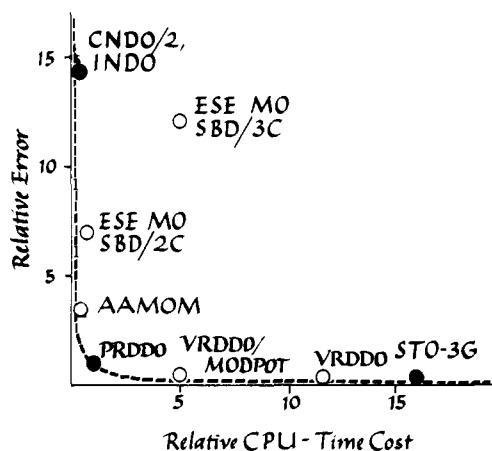


Figure 2. Relative error vs. relative CPU-time cost for the SCF methods discussed. The dashed line represents rel error \times rel cost = 1, or unit cost efficiency. Solid circles based on direct comparison. Open circles based on indirect comparison (see text).

PRDDO the better choice on the basis of its large advantage in computational speed.

By and large, the PRDDO program (cf. Appendix II) has served our computational needs well. Nevertheless, we ourselves do find frequent use for STO-3G calculations. In particular, we routinely determine molecular geometries, computationally the difficult step, using PRDDO, and then sometimes reassess energy relationships via individual STO-3G and, if feasible, 4-31G or other more elaborate ab initio calculations. Pople and co-workers have long employed STO-3G vs. 4-31G or 6-31G* calculations in the same fashion. While we present no comparisons of optimized geometries in this paper, good results have been reported for small molecules^{8,10u} and have been obtained for $C_3H_5^+$ ions and for C_4H_6 isomers.^{10f}

VII. Comparison of the PRDDO, AAMOM, VRDDO, and ESE MO Methods

AAMOM. While AAMOM is ~ 2.5 times faster than PRDDO¹¹ it apparently also is ~ 3.5 times less accurate, judging from reported rms errors for small molecules of 0.03 au for Fock matrix elements, 0.03 au for molecular orbital eigenvalues, 0.02 e for density matrix elements over orthogonalized AOs, and 0.05 e for Mulliken atomic charges.¹¹ The corresponding PRDDO errors are 0.006 au, 0.013 au, 0.008 e, and 0.010 e, respectively (Table XVI and ref 8). Moreover, large errors occasionally crop up in AAMOM. For example, the C-C bond length in ethane is predicted to be too long by 0.09 Å, and H-X-H angles are typically too large by $\sim 10^\circ$. Nevertheless, further comparisons clearly are warranted.

VRDDO. As noted in section I, the first of Wilhite and Euwema's charge-conserving integral approximations¹⁹ is utilized in the VRDDO method. Initially, Popkie and Kaufman implemented this approximation at a rather severe level ($\tau_1 = 10^{-2}$).^{13a} In subsequent work,^{13b-e} however, they have computed the needed pseudo-overlap integral S_{ij}^* solely from the most diffuse component of each of the Gaussian-orbital expansions for basis functions ϕ_i and ϕ_j ; this modification increases S_{ij}^* for widely separated centers, and thus serves much as would a reduced τ_1 value if used in conjunction with the original procedure for calculating S_{ij}^* . Popkie and Kaufman also implement a second approximation, controlled by a threshold $\tau_2 = 10^{-n}$, which in one instance^{13c} is related to Wilhite and Euwema's third charge-conserving integral approximation¹⁹ (though it is not clear that charge is conserved in the VRDDO implementation). In other work, τ_2 , usually set at $\tau_2 = 10^{-4}$, controls the accuracy to which the two-electron

Table XVI. Summary of Root Mean Square and Relative Errors for CNDO/2, INDO, PRDDO, and STO-3G Calculations^a

	CNDO/2	INDO	PRDDO	STO-3G
Rms Error				
ΔE^b	170	162	9.2	1.3
ϵ^c	0.18	0.16	0.013	0.003
Q^d	0.14	0.16	0.010	0.003
D^e	1.4	1.4	0.18	0.04
Relative Error				
ΔE	18	18	1	0.14
ϵ	14	12	1	0.23
Q	14	16	1	0.30
D	8	8	1	0.22
av ^f	14	14	1	0.22

^a Rms errors relative to ref SCF results. ^b Error in reaction energies of Tables I and IX (kcal/mol). ^c Error in highest occupied MOs (au). ^d Error in atomic charges. (e); see text. ^e Rms error in dipole moments of Tables VII and XIV. ^f Average relative error used in Figure 2.

Table XVII. Relative Computing Times^a

CNDO/2	INDO	PRDDO	STO-3G	ref SCF
0.18	0.18	1	16 ^b	100 ^b

^a Based on comparisons in Table XV for the IBM 360/91 computer. ^b For $N = 40$ AOs; see eq 7 and 8.

tron integrals (those not zeroed under the τ_1 criterion) are calculated; as described in a footnote in ref 13d, only those integral contributions over primitive Gaussians that are larger than 10^{-n} in magnitude are computed,⁵¹ and only integrals larger than 10^{-n} are retained in the subsequent SCF calculation. With $\tau_1 = 10^{-2}$ and $\tau_2 = 10^{-4}$, negligible errors (less than 0.001 au for eigenvalues and less than 0.001 e for atomic charges) are made relative to the STO-6,3G calculations (6G expansions for inner-shell AOs, 3G expansions for valence-shell AOs) which are used, for reasons that are not entirely clear to us, instead of STO-3G calculations as reference calculations in their recent work. Consequently, since STO-6,3G and STO-3G are expected to be of comparable accuracy for valence eigenvalues, atomic charges, and relative energies, VRDDO errors relative to the ref STO calculations should be essentially the same as the STO-3G rms errors (0.003 au and 0.003 e) summarized in Table XVI. Based on reported timings,^{13d} a maximum reduction of roughly 25% of the STO-3G (or 40% of the STO-6,3G) computing time is expected for a molecule of the size of benzonitrile (45 Slater AOs); as Popkie and Kaufman point out, considerably smaller savings are realized for spatially compact systems, such as boron hydrides. Accordingly, we conclude that while VRDDO, like STO-3G, is about four times more accurate than PRDDO, it remains about 12 times slower⁵² (for a molecule having 40 AO basis functions), as shown in Figure 2.

Popkie and Kaufman also report composite VRDDO/MODPOT calculations in which a Bonifacic-Huzinaga model potential is used for inner shell electrons. As implemented at the STO-3G level,^{13d} a reduction in computing time of approximately a factor of 3^{13d} (relative to STO-3G calculations) is thereby achieved in exchange for relatively modest rms errors of ~ 0.007 au for molecular orbital eigenvalues and ~ 0.006 e for atomic charges.⁵³ VRDDO/MODPOT therefore appears to be approximately twice as accurate as PRDDO in reproducing the ref STO calculations, but to be about five times more costly in computer time for a 40-AO system (Figure 2).

Of their two approaches, VRDDO/MODPOT seems to us to achieve the more attractive balance between accuracy and

Table XVIII. Summary of Errors for ESE MO Calculations^a

system	total energy ^b		eigenvalues ^c		atomic charges ^d		dipole moments ^e	
	SBD/2C	SBD/3C	SBD/2C	SBD/3C	SBD/2C	SBD/3C	SBD/2C	SBD/3C
HF	-1.313		0.21		0.07		0.43	
H ₂ O	-2.675	-3.003	0.42	0.48	0.07	0.20	0.11	0.98
NH ₃	-2.938	-4.529	0.43	0.72	0.17	0.35	0.23	1.00
FCN	-6.224	-10.059	0.69	0.84	0.16	0.19	0.78	0.37
O ₃	-2.970	-4.449	0.30	0.33	0.09	0.08	0.36	0.35
OF ₂	-2.760	-3.746	0.27	0.28	0.08	0.08	0.44	0.45
rms ^f	3.481	5.737	0.40	0.52	0.12	0.22	0.44	0.70
							32%	50%

^a Based on results vs. STO-3G calculations from Tables 1–6 of ref 12b. ^b Atomic units. ^c Rms error for valence-shell eigenvalues (au). ^d Rms error (e). ^e Debye. ^f Overall rms error; percent error for dipole moments based on rms value for STO-3G dipole moments of 1.39 D.

computational speed, though neither approach attains the savings in cost realized at the PRDDO level. Nevertheless, we think that the VRDDO/MODPOT combination may be well received, especially if the combined integral approximations prove capable of removing the fundamental N^4 dependence of computation time on basis-set size which is present in the parent STO-3G or STO-6,3G calculations. We note, however, that two boron or carbon atoms (for example) must be separated by ~ 4 Å or more if the pseudo-overlap threshold of $\tau_1 = 10^{-2}$ is to lead to neglect of those integrals to which the associated diatomic-overlap basis-function products contribute. Moreover, the small reported savings in computational time for VRDDO calculations on polyhedral boranes^{13e} imply that atomic centers must also be quite widely separated before significant savings are achieved under the τ_2 criterion. Consequently, an effective N dependence lower than N^4 might only be attained for very large molecules, and the VRDDO/MODPOT:PRDDO CPU-time ratio might not stabilize until a limiting ratio of 10:1 or 20:1, or even larger, is reached.

ESE MO. Judging from the larger number of three-center electron-repulsion integrals retained in the ESE MO approach as a consequence of eq 2, we estimate that the SBD/3C version of ESE MO¹² will be about five times slower than PRDDO. Moreover, the neglect of other important integrals significantly limits the accuracy of the method. Especially questionable, in our view, is the neglect of two-center exchange integrals, $\langle \phi_{i_a} \phi_{j_b} | \phi_{i_a} \phi_{j_b} \rangle$, which in PRDDO are essential even over orthogonalized AOs, where they take on smaller values.⁸ Over nonorthogonal AOs, even four-center integrals can be as large as 0.1 au and individually can make contributions to the Fock matrix elements of ~ 0.05 au.

The result is that SBD/3C rms errors (relative to STO-3G values) for the six small molecules shown in Table XVIII range from 0.08 to 0.35 e for atomic charges (overall rms, 0.22 e) and from 0.28 to 0.84 au for molecular-orbital eigenvalues (overall rms, 0.52 au).⁵⁴ Furthermore, computed dipole moments are usually too large by $\sim 50\%$.⁵⁴ The corresponding PRDDO errors for similar small molecules reported here and in ref 8 (atomic charges, 0.010 e, occupied eigenvalues, 0.013 au) and dipole moments reported in sections III and IV (rms deviation $\sim 10\%$) indicate that the SBD/3C version is less accurate than PRDDO by factors of ~ 20 , 40, and 5, respectively. Averaging of the two lower figures⁵⁵ leads to the approximate placement for SBD/3C ESE MO shown in Figure 2.

The SBD/2C version, which retains diatomic charge distributions only in two-center integrals, figures to be ~ 1.2 – 1.5 times faster than PRDDO.⁵⁶ Since the neglected three-center integrals in eq 1 and 2 make important contributions in polar and ionic systems, the SBD/2C version ought to be less accurate than the SBD/3C version. Surprisingly, however, slightly smaller errors are in fact found.¹² The rms deviations for atomic charges and for dipole moments (Table XVIII)⁵⁴ suggest that this version is about seven times less accurate than PRDDO, though only slightly faster (Figure 2).

Table XIX. Comparisons of Speed and Accuracy^a

method	rel error ^b	rel CPU-time cost ^c	cost efficiency ^d
CNDO/2	14	0.18	0.4
INDO	14	0.18	0.4
PRDDO	1	1	1
STO-3G	0.2	16	0.3
AAMOM	(~ 3.5)	(~ 0.4)	(~ 0.7)
VRDDO	(0.2)	(12)	(0.4)
VRDDO/MODPOT	(0.5)	(5)	(0.4)
ESE MO			
SBD/2C	(~ 7)	(~ 0.7)	(~ 0.2)
SBD/3C	(~ 12)	(~ 5)	(~ 0.02)

^a Values employed in Figure 2; parentheses denote indirect comparisons. ^b Based on Table XVI and as described in the text. ^c Based on relative computing times in Table XVII. $N = 40$ AOs and as described in text. ^d Cost efficiency $\equiv (\text{rel error} \times \text{rel cost})^{-1}$.

VIII. Discussion and Conclusions

An approximate molecular orbital method can be judged in large part by the balance it achieves between speed and accuracy in reproducing reference ab initio calculations or, ultimately, experiment. The greater the computational effort expended, the greater should be the accuracy achieved. Figure 2 indicates that, with one notable exception, all of the methods considered here conform fairly closely to the inverse relationship between accuracy and speed which might be expected on this basis. Within a factor of 3, most have the same *cost efficiency*, or $(\text{cost} \times \text{error})^{-1}$, in approximating the ref SCF STO calculations (Table XIX) and may be said to be *well balanced*.

Nevertheless, it is clear that the attainment of an attractive balance between accuracy and speed is a delicate matter. To channel future program development along the most productive lines, we suggest that explicit numerical comparisons of speed and accuracy be made to one or more of the better characterized methods specified in Table XIX. Unfortunately, not all authors seem inclined to provide such comparisons, especially with respect to computational speed. This reticence makes the evaluation of new methods more difficult.

With respect to the specific comparisons, we note that PRDDO and STO-3G reproduced the ref ab initio calculations consistently closely in every respect, often to well within the intrinsic error vs. experiment in the ref MBS procedure itself. In contrast, CNDO/2 and INDO yielded results in much poorer, and sometimes in unsatisfactory, agreement with both ref SCF calculations and experiment. On balance, PRDDO eliminates $\sim 93\%$ of the additional CNDO/2 or INDO error while incurring just 6% of the additional STO-3G cost.

Indirect comparisons to PRDDO for three other recently introduced methods indicate that AAMOM is two to three times faster but three to four times less accurate in reproducing

Table XX. Correlations between PRDDO and Reference SCF Total Energies^a

atomic correction energy, au		residual rms error, au
α_B, α_C	$\alpha_{H_b}, \alpha_{H_t}$	
+0.0434	-0.0095	0.0270
+0.0384	-0.0118, -0.0042	0.0264
+0.0497, +0.0257	-0.0129	0.0186
+0.0422, +0.0285	-0.0090	0.0145 ^b

^a Based on least-squares fits of adjusted PRDDO total energies to reference SCF total energies using eq A1. ^b In addition to the listed atomic correction energies, a least-squares-optimized correction energy of 0.0215 au per unit excess negative charge is added to the PRDDO total energy. The residual errors, $E(\text{PRDDO}_{\text{adj}}) - E(\text{ref SCF})$, are 0.000, +0.027, +0.004, +0.012, +0.011, +0.010, +0.010, +0.007, -0.017, +0.001, -0.022, +0.029, +0.002, +0.003, -0.010, and -0.019 for B_2H_6 - $B_{10}H_{14}^{2-}$ in Table III.

ab initio MBS results, that VRDDO is approximately equal in accuracy to STO-3G but is ~ 12 times slower than PRDDO for $N = 40$ AOs, that VRDDO/MODPOT is about twice as accurate as PRDDO, but ~ 5 times slower, that the SBD/2C version of ESE MO is 1.2–1.5 times faster but ~ 7 times less accurate than PRDDO and that SBD/3C ESE MO is ~ 12 times less accurate than PRDDO and ~ 5 times slower (Figure 2).

Acknowledgments. We thank Dr. Irene M. Pepperberg for her assistance with some of the calculations. We also thank the Office of Naval Research and the National Science Foundation for support of this research.

Appendix I. More Detailed Comparisons of PRDDO and Ref SCF Results

Table III reveals that the errors made by PRDDO in the total energy (as well as in the kinetic, nuclear attraction, and electron repulsion energies) are largely systematic. The systematic nature of these errors and the modest errors made in the reaction energies (Table I) suggest that the errors in the PRDDO total energies must largely be determined by the numbers and types of constituent atoms, and not by the details of the molecular geometry. This suggestion is abundantly confirmed by the results of least-squares fits of adjusted PRDDO total energies

$$E_{\text{adj}}(\text{PRDDO}) = E(\text{PRDDO}) + \sum_k n_k \alpha_k \quad (\text{A1})$$

to the ref SCF values (Table XX). Here, n_k denotes the number of atoms of type (or environment) k , and α_k is an atomic correction energy. Thus, the rms deviation in the adjusted PRDDO total energies is about eight times smaller for even the simplest model tested (0.027 au) than for the unadjusted PRDDO total energies (0.212 au). Interestingly, independent treatment of bridge and terminal hydrogens leads to quite different atomic correction energies for these atoms. However, the rms deviation is essentially unchanged. Thus, we can isolate no energy-related difference in the PRDDO treatment of bridge and terminal hydrogens. Finally, separate treatment of boron and carbon atoms and the inclusion of ionic charge as an additional term in eq A1 produce modest further improvements in the fit (Table XX). Appropriately, the residual rms error of 0.0145 au, or 9 kcal/mol, is comparable to the rms error in the PRDDO reaction energies of Table I.⁵⁷

The rms errors in the PRDDO eigenvalues are not only small ($\Delta\epsilon_{\text{rms}} = 0.016$ au) for these 16 molecules, but also are highly systematic. In nine of every ten cases, the eigenvalues for occupied valence and lowest unoccupied molecular orbitals are too low, typically by ca. 0.02 au. The good results for lowest (indeed, all) unoccupied orbitals are especially encouraging,

in that methods dependent on internal cancellations of error generally yield poor results in this respect.

In section III we reported that the PRDDO atomic charges had an rms error, ΔQ_{rms} , of 0.012 e. Interestingly, all "apical" borons⁵⁸ listed in Table VI are too negative by 0.01–0.03 e, and the attached hydrogens are all too positive by similar amounts. By and large, therefore, PRDDO simply partitions the same number of electrons slightly differently between boron and hydrogen, and the main PRDDO errors are again seen to be highly systematic.

In view of observed correlations of atomic charge and chemical reactivity^{10v,cc,28} which we have recently exploited using PRDDO wave functions,^{10w,cc-ee} a comparison of the ordering of PRDDO and ref SCF atomic charges is of particular interest. Here, we find no differences in ordering for boron atoms: the few inversions found for hydrogen atoms would be corrected by a change of 0.01 e or less in one of the inverted charges. Since predictions of chemical reactivity would need to be based on considerably larger differences,^{10cc,28} even these qualitative errors present little difficulty. Finally, in order to provide a more exacting comparison of charge distributions, we computed the classical ionic (Mulliken point charge), atomic, and bond contributions to the dipole moment⁵⁹ for the molecules in Table VII. Relative to the ref SCF values, PRDDO almost always slightly overestimates the classical ionic moment (mean error, 0.14 D; rms error, 0.17 D), but underestimates the bond moment (mean error, -0.09 D; rms error, 0.16 D), and underestimates the atomic moment (mean error, -0.04 D; rms error, 0.07 D). Since individual bond moments between neighboring atoms, for example, are typically ~ 1 D in magnitude,²² we again find that the good overall agreement is not the result of internal cancellations of large errors.

This consistently good performance implies that PRDDO must closely approximate the ref SCF Fock matrix itself. Explicit comparisons for smaller molecules have found these errors usually to be smaller than 0.01 au (rms deviation 0.006 au).⁸ Evidently, the relatively long-range interactions present in the larger systems examined here are also accommodated well. Indeed, all the main errors discussed above can be accounted for by assuming that the diagonal elements of the PRDDO Fock matrix are consistently too negative on boron and carbon, perhaps by 0.01–0.02 au, and are too positive on hydrogen by similar amounts.

We draw three conclusions from these findings: (1) Since PRDDO accurately approximates the ref SCF Fock matrix, close simulation of ref SCF results is also expected for the many properties of computational interest which could not be examined here. (2) Equally good results can be anticipated for large molecules of types other than those examined here. (3) Since the principal PRDDO Fock matrix errors evidently are quite systematic, a reformulation or reparametrization of the method might well yield significantly improved results.

Appendix II. Program PRDDO

The PRDDO program performs minimum basis set SCF calculations for molecules and ions containing hydrogen and first-row atoms. Present limits are 80 atoms and 150 AOs.

The following types of SCF calculations are performed: (a) standard closed-shell single determinant calculations; (b) unrestricted Hartree-Fock calculations for open-shell systems;⁶⁰ (c) restricted Hartree-Fock calculations for open-shell systems;^{61,62} (d) generalized valence bond calculations for one split orbital pair (e.g., for diradicals);^{62,63} (e) two-configuration SCF calculations, an economical approximation to (d).⁶⁴

Auxiliary program tasks include: (a) configuration-interaction calculations for open- and closed-shell singlet states; (b) single-excitation CI calculations for singlet and triplet RHF states; (c) Mulliken population analysis;³⁷ (d) Armstrong-

Perkins-Stewart bond index and atomic valency calculations;^{10ff,65} (e) dipole moment calculations, using Ruedenberg's origin-invariant method of partitioning;⁵⁹ (f) molecular-orbital localization using Boys criterion;^{10aa} (g) geometry optimization;^{10f,bb} (h) synchronous-transit calculations for locating molecular transition states and determining optimal reaction pathway.^{10e,f,z,ff}

Program PRDDO (~15 000 cards) has been written in standard FORTRAN IV to promote compatibility with systems other than the IBM 360-370 computers for which it was developed. The IBM version employs a dynamic core allocation feature which minimizes core storage requirements, and includes a limited restart capability. Recent versions of the program have also been implemented for the CDC 6400 and PDP 10 computers. Submission of the IBM version to QCPE is planned for the spring of 1979.

The program is now being extended (by D. S. Marynick) to include d orbitals and elements beyond the first row.

References and Notes

- (1) (a) City University of New York; (b) Williams College; (c) Morehouse College; (d) Harvard University.
- (2) For the convenience of the reader, most of the abbreviations employed in this paper are collected here in order of their appearance: QCPE, Quantum Chemistry Program Exchange; SCF, self-consistent field; MBS, minimum basis set; CNDO (INDO), complete (intermediate) neglect of differential overlap; STO, Slater-type orbital; 3G, three Gaussian functions per STO; PRDDO, partial retention of diatomic differential overlap; AAMOM, an approximate molecular orbital method; VRDDO, variable retention of diatomic differential overlap; ESE MO, essential structure elements molecular orbital; AOs, atomic orbitals; OAOs, symmetrically orthogonalized AOs; CPU, central processor unit; 4-31G, extended AO basis having four Gaussian-type orbitals per inner-shell STO plus valence-shell AOs split into three-Gaussian inner and one-Gaussian outer parts; ref SCF, minimum basis set ab initio calculations over STOs which serves as a reference for these comparisons.
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- (9) The PRDDO method has been applied in the following areas: ref 10a, localized molecular orbitals (LMOs) for nitrogen lone pairs; 10b, LMO's for monocyclic aromatic rings; 10c,d, orbital steering in nucleophilic attack on C=O; 10e,f, synchronous transit (ST) pathways for electrocyclic ring openings of cyclobutene and the cyclopropyl cation; 10g, ST pathways for internal rearrangement in methylenecyclopropane; 10h, LMOs for fused aromatic rings; 10i, ground and lowest excited states for azoalkanes; 10j, LMOs and the electronic structure of TCNQ, TCNQ⁻, and TCNQ²⁻; 10k, localized molecular orbitals for cumulenes; 10l, LMOs for CO₂ and CO₃²⁻; 10m, hydration effects on amide torsional barriers; 10n, properties of vinylamines; 10o, hydroboration of ethylene; 10p, triazolines; 10q, pseudo-pericyclic rearrangements; 10r, CH₃O⁺ potential energy surface; 10s, proton and methyl cation affinities of enamines; 10t, PE spectra of nitrogen heterocycles; 10u, reaction pathways for dimerization of BH₃; 10v, SCF and PRDDO studies of boron hydrides and boron hydride ions; 10w, LMOs for B₁₀H₂₀; 10x, localized descriptions for boron fluorides; 10y, LMOs for B₄F₄; 10z, ST pathways for interconversion of 1,2- and 1,6-C₂B₄H₆; 10aa, comparison of the Boys and Edmiston-Ruedenberg localization criteria; 10bb, structures for and internal rearrangements in BH₃; 10cc-dd, ee, LMOs and reactivity predictions for open boron hydrides, large boron hydrides, and closo boron hydride ions and carboranes; 10ff, valence structures and localized orbitals for transient boron hydrides; 10gg, structures and fluxional behavior of Lewis base adducts of B₃H₇; 10hh, structure of dicyclopentadienylberyllium; 10ii, theoretical studies of boron hydrides and carboranes; 10jj, the boranes and their relatives; 10kk, 13-24 boron-atom closo hydrides; 10ll, structures of B₃H₆⁻ and B₅H₁₁⁻; 10mm, fluxional structure of B₁₁H₁₂²⁻; 10nn, classical structures for carboranes; 10oo, fluxional structure of B₆H₆²⁻; 10pp, isomeric structures for C₂B₃H₅; 10qq, LMO correlations in boron hydride rearrangements; 10rr, organoberyllium monomers and dimers; 10ss, model studies of solid-state beryllium borohydride; 10tt, localized-orbital interrelationships for boron hydrides; 10uu, LiH and LiR dimers and oligomers; 10vv, ww, xx, yy, reaction pathways for enzymatic activity of serine proteinases and of carboxypeptidase A; 10zz, conformations and energies of di-, tri-, tetra-, and pentapeptides of polyglycine; 10aaa, electronic structure and localized molecular orbitals of amino acids; 10bbb, effects of hydration on diglycine conformation; 10ccc, MO studies of isoalloxazines; 10ddd, MO studies of aflatoxins; 10eee, MO studies of carcinogens.
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Table VI: atomic charges should be -0.11 for H₁ in B₁₀H₁₀²⁻ (PRDDO), +0.08 for B₄ in B₈H₁₂ (PRDDO) and +0.01 for H₁₃ in B₁₀H₁₄²⁻ (SCF); the B₁ eigenvalue in B₁₀H₁₀²⁻ (SCF) should be -7.125. Table X: fifth highest eigenvalue listed for B₁₀H₁₀²⁻ should read 6a₁ -0.054, sixth highest eigenvalue listed for B₉H₁₅ should read 9a'' -0.463, highest eigenvalue listed for B₆H₆²⁻ should read 3t_{2g} +0.808. Table XVI: entries for B₆H₆²⁻ should read -676.455, 153.615, 153.227, 0.9874, and -151.291; first entry for B₉H₁₅ should be -1243.004; third entry for B₁₀H₁₀²⁻ should be -253.711. Table XVII: eigenvalue for 20a' in B₉H₁₅ should be -0.376; sixth highest eigenvalue listed for B₉H₁₅ should read: 9a'' -0.477; fifth, ninth, and twelfth highest eigenvalues listed for B₁₀H₁₀²⁻ should read 6a₁ -0.073, 5a₁ -0.236, 4a₁ -0.285, respectively; (w) D. A. Dixon, D. A. Kleier, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **96**, 2293 (1974); (x) J. H. Hall, Jr., T. A. Halgren, D. A. Kleier, and W. 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- (30) These calculations employ a CNINDO program originally brought to Harvard by Dr. N. S. Ostlund. We have taken the standard precaution of checking results for small molecules against published results.
- (31) Conservation of charge and of hydrogen, boron, and carbon atoms here provide four linearly independent conditions for chemical balancing. Twelve linearly independent reaction processes then suffice to determine all remaining mutual relations between the 16 molecules and ions considered here.
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- (47) The quoted CNDO/2 and INDO CPU times represent the basic SCF calculations plus the computational time required to print the MO coefficients and eigenvalues, and density matrices. The latter is $\leq 5\%$ of the whole.
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- (50) This figure was obtained by correcting the ref SCF CPU times of 15.5 h for $B_{10}H_{14}$ on the IBM 360/65 (ref 28) and of 1.5 h for $B_{10}H_{14}^{2-}$ on the IBM 360/195 (ref 10v) by factors of 0.2 and 2.0, respectively, for the conversion to the 360/91. The PRDDO CPU time is ~ 75 s in each case. The longer PRDDO times reported in ref 10v do not represent the basic SCF calculation and were obtained using an inefficient version of the present program.
- (51) It is not clear how Popkie and Kaufman determine whether or not an integral contribution computed over primitive Gaussians will exceed the 10^{-n} criterion.
- (52) We wish to correct the statement by Popkie and Kaufman (ref 13) that recent "PRDDO calculations on larger molecules took Halgren and Lipscomb about four times longer than would have been estimated from their original timing formulae" in ref 8. This statement is incorrect. In fact, modifications to the program have increased its speed, as noted in the text.
- (53) Based on tabulated results presented in ref 13d.
- (54) Based on detailed results presented in Tables 1-6 of ref 12b.
- (55) Burton suggests in ref 12b that the use of nonorthogonal Slater 1s and 2s AOs on first-row atoms produces much larger errors in total and orbital energies than would be characteristic of the SBD/3C method when optimally implemented. It is difficult to determine what effect this factor may have on atomic charges and dipole moments, if any.
- (56) PRDDO spends 35% of its time on the calculation and subsequent manipulation of three-center integrals. By subtracting this time from PRDDO and adding a small allowance for the additional transformation of the Fock matrix to orthogonal AOs before its diagonalization during the SCF cycling in SBD/2C, we arrive at the estimate for SBD/2C computing times and from thence relative speed given in the text.
- (57) STO-3G yields even larger errors in total energy, largely owing to inaccurate treatment of inner shells. For example, the deviations, $[E(\text{STO-3G}) - E(\text{ref SCF})]$, are 0.549, 1.067, 1.089, 1.344, 1.356, and 1.613 au for B_2H_6 , B_4H_4 , B_4H_{10} , B_5H_9 , B_5H_{11} , and B_6H_{10} , respectively. However, the rms difference between the ref SCF and adjusted STO-3G total energies falls to just 0.003 au, or 2 kcal/mol, if correction energies of -0.026 au per boron atom and -0.005 au per hydrogen atom are added to the STO-3G total energy. Consequently, we find on this basis also that STO-3G is four to five times more accurate than PRDDO for relative energies.
- (58) The term "apical" is used here to denote boron atoms attached to one terminal, but no bridge, hydrogens.
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