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Ab initio Molecular Orbital Calculations

2. A Comparison of Polarisation Function Addition to Minimal Bases, and Molecular Scaling. Computations on Furan, Pyrrole and 1,2,5-Oxadiazole

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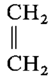
A series of non-empirical calculations on furan, pyrrole and 1,2,5-oxadiazole are reported in which the effect of polarisation functions added to the minimal $7s\,3p$ basis on each atom is studied. The effect on these planar molecules is largely through the σ rather than the π-system. A comparison with the results of work with scaled functions is reported. Both series are shown to lead to much improved agreement with the electron spectroscopy energy levels. The effect on the dipole moments of these changes in basis is more variable but, with the exception of furan, the agreement with experiment is improved in the present method.

Für die Moleküle Furan, Pyrrol und 1,2,5-Oxadiazol wurde eine Reihe von nichtempirischen Rechnungen durchgeführt, in denen der Einfluß von zusätzlichen Polarisationsfunktionen zur minimalen $7s\,3p$-Basis an jedem Atom untersucht wird. Die Ergebnisse werden mehr durch die Art der Beschreibung des Systems der σ-Elektronen als durch diejenige der π-Elektronen beeinflußt. Ein Vergleich mit den Ergebnissen bei Verwendung skalierter Funktionen wird durchgeführt. Beide Reihen von Ergebnissen zeigen eine verbesserte Übereinstimmung zu den Energiemeßwerten der Elektronenspektroskopie. Die Änderungen des berechneten Dipolmoments bei derartigen Basisvariationen sind größer als bei früheren Methoden. Die Übereinstimmung mit dem Experiment wird, mit Ausnahme von Furan, jedoch verbessert.

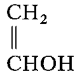
Current methods of improving linear combination of gaussian orbital (LCGO) approaches to Hartree-Fock wave functions in a single configuration are proceeding along various paths; (a) the use of extended basis sets (e.g. $11s\,7p$) [1], (b) optimisation of contraction procedures [2], (c) possibly uncontracted rather than in contracted (fixed) sets [3] representing the usual atomic orbitals, (d) improvement of small basis sets by the inclusion of polarisation orbitals [4] such as *p*- and *d*-orbitals for hydrogen and first row elements respectively. Lastly, (e) scaling of the best atomic gaussian sets, in small molecular environments [5] such that the molecular energy is minimised and the exponents thus optimal. This approach then requires that the scale factors for each atom can be transferred to a range of large molecules [6].

In our first paper [7] we reported a series of minimal basis calculations on furan (IV), pyrrole (VI) and 1,2,5-oxadiazole (VIII), using gaussian sets $7s\,3p$ for C, N and O, $3s$ for hydrogen, that were comparable with the related work by E. Clementi *et al.* [8] and G. Berthier *et al.* [9] and gave an apparently linear correlation of experimental and theoretical binding energies and orbital energies. We extended the calculations later to include polarisation functions according to (c) above and the results of these are given in the present paper. However it was immediately apparent that these very time consuming integrations over the added *p*- and *d*-orbital functions whilst having some effect on total energy and charge distribution could be duplicated by minor amounts of atomic scaling. Thus far from obtaining any improvement in electron correlation by the angular part, these calculations really only improved the radial functions by reducing the level of contraction. We thus decided to optimise the exponents using the smaller analogs I, II, III, (and also partly for IV) to the compounds V, VI, VII, (a) to test transferability in the small series and (b) to give us better functions for binding energy studies of the compounds V–VII. Our primary interest in this work is in the degree of aromaticity (if any) in simple heterocycles such as these.



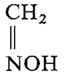
$CH_2{=}CH_2$

I



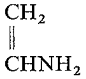
$CH_2{=}CHOH$

II



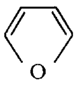
$CH_2{=}NOH$

III

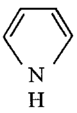


$CH_2{=}CHNH_2$

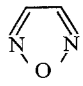
IV



V



VI



VII

The two procedures are outlined in more detail in the appendix. As in the earlier work we used the computer program IBMOL-4, on both an IBM 360/50 and Univac 1108, and a modified version of a Univac-compatible version of IBMOL-2 (the original version of which was kindly supplied by Dr. M. Krauss). The calculations on furan thus had the minimal basis (29 functions) of 7*s* 3*p* sets (for carbon and oxygen) and 3*s* for hydrogen (as detailed in Part 1) extended by up to 17 polarisation functions; pyrrole (minimal basis 30 functions) was extended by up to 15 polarisation functions; the oxadiazole (minimal basis 27 functions) was improved by up to 11 polarisation functions.

Results and Discussion

(a) *The Molecular Energies*

The results for the minimal basis calculated are detailed in Part 1, but the total energies obtained for the molecules (in the above order) were -227.79358, -208.04264 and -259.64308 a.u. respectively; the key results of the present calculations are given in Tables 1, 2 and 3.

In common with much earlier work, inclusion of polarisation *p*-functions leads to a gain in total energy, which in our case is of approximately 0.025 a.u. per hydrogen atom augmented with $p_x + p_y + p_z$. However, comparison of the minimal basis calculations with those where only a $p_\pi(p_z)$ polarisation orbital is included shows the π-effect is negligible. Thus the polarisation functions far from

Table 1. Furan

	p-orbitals on hydrogen		*p*- and *d*-orbitals on all elements		Scaled optimum
	p_x, p_y, p_z	p_z only (π)	$d_{z\eta}$	d_{xy}	
E_{total} (a.u.)	–227.88891	–227.79593	–227.93702	–227.93235	–228.00447
Electron-nucleus attraction (a.u.)	–624.35673	–623.18622	–624.55858	–624.52750	–626.57157
Electron repulsion (a.u.)	235.88098	234.80346	+236.03473	236.00831	237.98026
Nuclear repulsion (a.u.)	160.58683	160.58683	+160.58683	160.58683	160.58683
Atom sum (a.u.)	–227.04202	–227.04202	–227.04202	–227.04202	—
Binding energy (a.u.) (A)	0.32511	0.23213	0.37322	0.36855	– 0.44067
(B)	0.84689	0.75391	0.89500	0.89033	– 0.96245
Orbital energies (a.u.)	A 1	A 1	A 1	A 1	A 1
	– 20.651375	– 20.681071	– 20.655219	– 20.655760	– 20.637710
	– 11.440200	– 11.477202	– 11.438181	– 11.434852	– 11.314804
	– 11.375138	– 11.415843	– 11.370089	– 11.369128	– 11.244661
	– 1.4945404	– 1.5219562	– 1.4913108	– 1.4822870	– 1.4561535
	– 1.1295396	– 1.1587933	– 1.1260078	– 1.1294091	– 1.0885647
	– 0.81449197	– 0.83269539	– 0.81169804	– 0.81759742	– 0.78007786
	– 0.76894988	– 0.79190959	– 0.76637191	– 0.76614004	– 0.74368445
	– 0.60247085	– 0.62390625	– 0.59994614	– 0.60104952	– 0.56492546
	– 0.56162365	– 0.58137598	– 0.56228328	– 0.56273641	– 0.52394021
	B 2	B 2	B 2	B 2	B 2
	– 11.440471	– 11.477630	– 11.438455	– 11.435105	– 11.315221
	– 11.374978	– 11.415964	– 11.369894	– 11.368970	– 11.244788
	– 1.0457546	– 1.0734976	– 1.0435535	– 1.043385	– 1.0035378
	– 0.82669183	– 0.84529144	– 0.82612963	– 0.82714804	– 0.7885297
	– 0.65111651	– 0.66713965	– 0.64721283	– 0.65616548	– 0.61556045
	– 0.61869699	– 0.63670517	– 0.61557737	– 0.61876420	– 0.57956975
	B 1	B 1	B 1	B 1	B 1
	– 0.67389405	– 0.70027015	– 0.66883244	– 0.66706475	– 0.64585658
	– 0.44385288	– 0.47372584	– 0.43780132	– 0.44120152	– 0.41368596
	A 2	A 2	A 2	A 2	A 2
	– 0.38359592	– 0.41467153	– 0.37599807	– 0.37857325	– 0.34425643
Dipole moment (D)	1.06	0.618	0.990	1.02	1.59
Gross populations H_α	0.8728	0.7705	0.8942	0.8705	0.812
H_β	0.8782	0.7896	0.8558	0.8545	0.828
C_α	5.9195	6.0142	5.8838	5.9341	5.911
C_β	6.1627	6.2465	6.1969	6.1934	6.193
O	8.3336	8.3221	8.33839	8.2949	8.512

leading to a redistribution of the π-electrons are working primarily on the σ-system. Since the effect is similar in the three molecules, it is not largely an effect on the "classical lone pairs" either (in the case of pyrrole these are in the π-system). Undoubtedly the effect is to provide extra flexibility to the radial functions. The calculations with added *d*-functions (one per C, N and O atom) confirm these views. The molecular energies obtained by the scaling procedure are clearly better than any of those with polarisation functions, and of course they are obtained in much less computer time.

Table 2. Pyrrole

	p-orbitals on hydrogen		Scaled optimum
	p_x, p_y, p_z	p_z-only	
E_{total} (a.u.)	−208.15734	−208.04991	−208.26263
Electron-nucleus attraction (a.u.)	−596.95133	−595.62578	−599.82388
Electron repulsion (a.u.)	227.69230	226.47417	230.45959
Nuclear repulsion (a.u.)	161.10170	161.10170	161.10167
Orbital energies (a.u.)	A 1	A 1	A 1
	− 15.711906	− 15.740782	− 15.59913
	− 11.392543	− 11.436874	− 11.25012
	− 11.347476	− 11.391613	− 11.19693
	− 1.3320757	− 1.3652375	− 1.27655
	− 1.0788309	− 1.1086674	− 1.02569
	− 0.82510294	− 0.84695972	− 0.781817
	− 0.76208659	− 0.78668500	− 0.726892
	− 0.63160944	− 0.65462207	− 0.584206
	− 0.57186894	− 0.59349368	− 0.515514
	B 2	B 2	B 2
	− 11.392695	− 11.437182	− 11.25041
	− 11.347219	− 11.391640	− 11.19694
	− 1.0151711	− 1.0445562	− 0.959742
	− 0.79973619	− 0.82191205	− 0.749721
	− 0.61841996	− 0.64033446	− 0.573106
	− 0.58627701	− 0.60638680	− 0.533074
	B 1	B 1	B 1
	− 0.62160714	− 0.65472406	− 0.583180
	− 0.39989298	− 0.43312092	− 0.350586
	A 2	A 2	A 2
	− 0.34885078	− 0.38392842	− 0.298789
Dipole moment (D)	2.01	2.26	2.01
Gross populations C_β	6.165	6.254	6.2039
C_α	6.001	6.090	6.0380
H_α	0.909	0.802	0.8465
H_β	0.894	0.807	0.8364
H_N	0.706	0.671	0.6702
N	7.354	7.421	7.4799

On this basis we can calculate the molecular binding energy by taking the molecular total energy from *either* (a) the sum of the Hartree-Fock atom energies *or* (b) the sum of the atom energies using best atom sets of same length or (c) the sum of the scaled atom energies. For small molecules course (a) is appropriate since the basis set used for the molecule should lead to an energy near the Hartree-Fock limit [1f]. For larger molecules where the latter is unlikely to be achieved at the present time (b) is probably more appropriate [5b], but in some instances a mixed system has been used; thus the total energies for various molecules studied by Snyder and Basch [1f] have been converted to atomisation energies by Ditchfield, Hehre and Pople [5a], by using atom energies of the same basis set for all

Table 3. 1,2,5-Oxadiazole

	p-orbitals	p_z-orbital	p- and d-orbitals	Scaling of hydrogen (s) functions			Scaled functions
	on H(x, y, z)	on H(π)	on H, C, N, O	$K_H = 1.414$	1.8	2.0	all atoms
E_{total}	−259.69848	−259.64443	−259.77172	−259.70170	−259.72498	−259.73034	−259.78806
Electron-nucleus attraction	−673.87335	−673.17894	−674.27810	−673.44147	−673.85148	−674.05692	−675.48550
Electron repulsion	+250.96006	+250.31971	+251.29158	+250.52499	+250.91172	+251.11179	+252.48266
Nuclear repulsion	+163.21480	+163.21480	+163.21480	+163.21479	+163.21479	+163.21479	+163.21479
Orbital energies	A1	A1	A1	A1	A1	A1	A1
	− 20.716722	− 20.735214	− 20.714792	− 20.728830	− 20.717700	− 20.711949	− 20.714373
	− 15.751462	− 15.773354	− 15.740932	− 15.767141	− 15.755036	− 15.748778	− 15.690364
	− 11.469151	− 11.493882	− 11.455980	− 11.487323	− 11.466856	− 11.455489	− 11.342890
	− 1.608508	− 1.625231	− 1.586971	− 1.620980	− 1.611418	− 1.606407	− 1.575333
	− 1.230591	− 1.249242	− 1.223136	− 1.246438	− 1.237158	− 1.232083	− 1.2024374
	− 0.903466	− 0.912985	− 0.901332	− 0.909329	− 0.901160	− 0.896781	− 0.876275
	− 0.789789	− 0.807256	− 0.783540	− 0.801822	− 0.795954	− 0.792743	− 0.771939
	− 0.619577	− 0.631982	− 0.616464	− 0.629887	− 0.622662	− 0.618704	− 0.596581
	− 0.554913	− 0.567799	− 0.554473	− 0.563421	− 0.554486	− 0.549841	− 0.529357
	B2	B2	B2	B2	B2	B2	B2
	− 15.751663	− 15.773587	− 15.741154	− 15.767381	− 15.755273	− 15.749017	− 15.690629
	− 11.468999	− 11.494058	− 11.455818	− 11.487584	− 11.467159	− 11.455806	− 11.342970
	− 1.277481	− 1.292610	− 1.263810	− 1.288791	− 1.279166	− 1.274084	− 1.239318
	− 0.884202	− 0.896852	− 0.884452	− 0.895396	− 0.888763	− 0.885122	− 0.860257
	− 0.692608	− 0.698254	− 0.693520	− 0.696842	− 0.691434	− 0.688156	− 0.664236
	− 0.522738	− 0.537614	− 0.527459	− 0.534640	− 0.526437	− 0.522144	− 0.495306
	B1	B1	B1	B1	B1	B1	B1
	− 0.737138	− 0.752263	− 0.726252	− 0.748706	− 0.740357	− 0.736013	− 0.718517
	− 0.510695	− 0.528989	− 0.501162	− 0.521843	− 0.512136	− 0.507158	− 0.485865
	A1	A1	A1	A1	A1	A1	A1
	− 0.486973	− 0.503588	− 0.476225	− 0.499397	− 490825	− 0.486374	− 0.463411
Dipole moment (D)	− 3.75	− 2.99	−3.38	− 3.07	− 3.58	− 3.79	− 4.52
Net atomic populations H	+ 0.178	+ 0.262	+ 0.198	+ 0.25693	+ 0.30430	+0.33402	+ 0.1885
C	− 0.060	− 0.161	− 0.085	− 0.14838	− 0.17959	− 0.20275	+ 0.0241
N	− 0.040	− 0.028	− 0.041	− 0.03141	− 0.04741	− 0.05265	− 0.0888
O	− 0.156	− 0.146	− 0.144	− 0.15241	− 0.15469	− 0.15726	− 0.2474

atoms except hydrogen [1a]. The third course (c) is likely to lead to spurious correlations since it represents the difference between two inadequately determined levels. This is evident from the results of Moskowitz and Harrison [10] where the atomisation energy of ethylene is substantially greater than experiment for small basis sets (the Hartree-Fock limit appears to give about 75% of the experimental value). Fortuitously, procedure (c) applied to the present bases leads to atomisation energies for methane and ethylene virtually in complete agreement with experiment. At this point it is appropriate to compare our results for furan with those of the extended basis set $(9s\,5p)_{C,O}\,(4s\,1p)_H$ calculation by P. Siegbahn [11], the only molecule of this trio where such a large basis has been used. His molecular energy is about 0.5 a.u. (0.2%) better than the present scaled results, while the binding energy based on method *B* is about 7% better.

(b) Ionisation Potentials

(i) *Experimental Results*

In the previous paper (1) we reported data on the He^I photoelectron spectra, together with some data for furan using He^{II}. A much more detailed spectrum for this molecule is cited by P. Siegbahn [11], in which assignments of the bands to each of the four symmetry types is given. We are uncertain as to how these detailed assignments have been obtained, and are thus treating them with caution. The same paper reports X-ray electron spectra of the core electrons in the furan molecule in the gas phase, while similar studies for pyrrole, kindly supplied by K. Siegbahn [12] are reported in Table 4. (One of us has confirmed these last results on a prototype electron spectrometer at Manchester University.) We have obtained the solid state electron spectra of the core levels for each molecule, and in the case of furan we have also obtained the valency shell ionisation potentials.

Table 4. Experimental and calculated binding energies of electrons

		Calculated				Measured	
		Minimal	Scaled	Extended[a]	Extended[b]	Solid state[e]	Gas phase[e]
Furan[d]	$1s_O$	562.7	561.6	562.0	561.2	535.1	539.4
	$1s_C(\alpha)$	312.2	307.9	311.2	307.8	287.55	291.4
	$1s_C(\beta)$	310.6	306.0	309.4	306.3	285.75	290.3
Pyrrole	$1s_N$	427.9	424.5	427.5	—	401.2	—
	$1s_C(\alpha)$	311.4	306.1	310.0	—	284.9	289.9[c]
	$1s_C(\beta)$	309.8	304.7	308.8	—	285.7	290.88
1,2,5-Oxadiazole	$1s_O$	564.2	563.7	563.7	—	535.6	—
	$1s_N$	429.2	427.0	428.3	—	401.9	—
	$1s_C$	312.8	308.6	311.7	—	287.1	—

[a] Present work, P_{xyz}-orbitals on hydrogen, $d_z2(\sigma-)$ on carbon and oxygen.

[b] K. Seigbahn, U. Gelius *et al*: cited in Ref. [4].

[c] K. Seigbahn *et al.*: Personal communication.

[d] The valency shell ionisation potentials determined by X-ray excitation are as follows: 9.6, 14.0, 15.5 (sh), 19.2, 24.0 (sh), 24.6, 34.4 eV (sh = shoulder).

[e] The differences between solid state and gas phase spectra are as expected on the basis of work function in the former series.

Our spectra were determined on an AEI ES 100 spectrometer, calibrated with the oxygen 1*s* of water (533.2 eV) and hexane (285.0 eV) carbon 1*s* levels. The figures obtained are shown in Table 4; the doublets expected from the α- and β-carbon 1*s* electrons of furan and pyrrole are not resolved under these conditions, but the peak widths (half height) are 2.6, 2.5 and 1.6 eV for furan, pyrrole and the oxadiazole respectively, thus suggesting a separation of near 1.0 eV in each of the first two cases. The unpublished figures obtained by K. Siegbahn [12] are 1.2 eV and 0.9 eV respectively.

(ii) *Comparison of Calculated and Experimental Results (Using Koopmans' Theorem).*

Agreement between the observed and calculated ionisation potentials is much better for the extended sets and scaled functions than for the minimal basis sets. For the *valency shell* there are clearly linear relationships between calculated and experimental data (irrespective of whether this relationship is theoretically valid). The data for furan (13 points) using P. Siegbahn's assignments [11] are: scaled set $(\text{I.P.})_{\text{Exptl.}} = 0.8234\,(\text{I.P.})_{\text{Calc.}} + 1.102$ eV (standard error in slope 0.028 eV, in intercept 0.610 eV); for extended set *D*, $(\text{I.P.})_{\text{Exptl.}} = 0.8236\,(\text{I.P.})_{\text{Calc.}} + 0.426$ eV (standard error in slope 0.021 eV, in intercept 0.45 eV); the Siegbahn 11*s* 7*p* set gives, $(\text{I.P.})_{\text{Exptl.}} = 0.8029\,(\text{I.P.})_{\text{Calc.}} + 1.398$ eV (standard error in slope 0.028 eV, in intercept 0.596 eV). For pyrrole and the oxadiazole (7 points in each case) the corresponding data is more scattered (and also no complete assignment of the A1 and B2 lines has been reported); the figures are pyrrole (*p*-orbitals on hydrogen) $(\text{I.P.})_{\text{Exptl.}} = 0.773\,(\text{I.P.})_{\text{Calc.}} + 3.42$ eV (errors 0.06 and 0.76 eV), pyrrole (scaled) $(\text{I.P.})_{\text{Exptl.}} = 0.940\,(\text{I.P.})_{\text{Calc.}} + 1.22$ eV (errors 0.06 and 0.74 eV); 1,2,5-oxadiazole (extended), $(\text{I.P.})_{\text{Exptl.}} = 0.936\,(\text{I.P.})_{\text{Calc.}} + 1.18$ (errors 0.09 and 1.23), and scaled $(\text{I.P.})_{\text{Exptl.}} = 0.915\,(\text{I.P.})_{\text{Calc.}} + 0.29$ eV (errors 0.05 and 0.76 eV). A significant feature is the near identity of orbital energies obtained between the 11*s* 7*p* set of Siegbahn [11] and the scaled and expanded sets of the present work for furan. There is again excellent agreement between the experimental and calculated ordering of the first three ionisation potentials for the three molecules, both in the extended and scaled series. A feature not previously reported (which is also applicable to the minimal basis set calculation) is that the third ionisation potential of 1,2,5-oxadiazole is predicted to be from the 6 B2 orbital in contrast to 9 A1 for the other two molecules (the first two ionisations are of π-type in each case). This observation fits well with the high degree of localisation of the 6 B2 on the $2p_x$ antisymmetric combination for nitrogen (see also Paper 1), the classical lone pair.

The 1*s* levels are not significantly effected by changes from 7*s* 3*p* to 9*s* 5*p* or addition of polarisation functions or molecular scaling, the $1s_{\text{O}}$ levels being calculated at about 27 eV higher binding energy than the electron spectra indicate. The corresponding figures for $1s_{\text{N}}$ and $1s_{\text{C}}$ are about 26 and 24 eV larger than experiment. In any event it seems doubtful whether Koopmans' Theorem has any validity to such deep seated orbitals. None the less, the separation of the 1*s* levels for carbon are predicted to be larger for furan (1.9 eV for scaled or extended bases) than pyrrole (1.4 eV scaled basis) and this is consistent with the separations obtained with electron spectroscopy. Further the relative placings of the carbon, nitrogen and oxygen 1*s* levels are correctly reproduced for the three molecules.

(c) Population Analysis and Dipole Moment

The dipole moment in the minimal basis set calculation for furan was (perhaps fortuitously) virtually identical with the experimental value (0.67*D*), while those for pyrrole and 1,2,5-oxadiazole were about 15% too high and too low respectively. Thus for furan almost any change produced by the addition of polarisation orbitals or by scaling was expected to lead to a worsening in agreement with experiment. All of the changes led to a positive increase in the dipole moment, the scaling by a larger factor than the polarisation functions. It is worth noting that Siegbahn's [11] value is also poor, lying between that for the most extensive set and the scaled set. For the oxadiazole, the most extended set gave exact agreement with experiment (3.38 Debye), while scaling gave too large a value. This last result probably shows the sensitivity of the dipole moment to the scaling procedure most clearly, and to the oxygen scale factors in particular. For pyrrole the values from both the scaling and extended basis are nearer to the experimental value (1.80 Debye); in view of the dependence of much of the dipole moment on the polarity of the N–H bond this is particularly satisfactory.

Conclusions

It is well established that the use of scaled functions, where the scaling factors are determined from molecular energy optimisation on related but smaller molecules, leads to molecular energies substantially closer to the Hartree-Fock limit, for small basis sets. In the present series of compounds this also leads to a considerable improvement in the ionisation potentials predicted by Koopmans' Theorem. The core levels however are not greatly changed in this process, or indeed by increasing the basis set; this reflects the inadequacy of Koopmans' Theorem as much as other factors. Small changes in core ionisation potentials between related molecules are however reproduced in order, but the extent is magnified.

The use of polarisation functions does lead to much the same improvement over the best atom basis, but of course at the expense of much more computer time. It is worth noting again that the total energy improvements resulting from both polarisation functions and scaling procedures occur by very different mechanisms. Thus there is in all cases an increase in electron-electron repulsion which is outweighed by an increase in electron-nucleus attraction; these terms however mask the fact, evident from the population analysis (and the exponents themselves), that the electrons are more concentrated in the viscinity of the atoms in scaled calculations, and more in the internuclear region for the expanded basis sets of polarisation functions; that is, there is a larger overlap population in the latter series of calculations. To a certain extent therefore errors in charge distributions resulting from equipartition of the overlap population are worse in the expanded series than the scaled ones. In general the addition of polarisation functions to hydrogen increases the population on these atoms, while the addition of polarisation functions on oxygen, nitrogen and carbon have comparatively small and variable effects, such that it is not universally true that addition of a basis function to a centre increases the population at that centre (see furan for example). In general we favour the use of scaled functions, but for very polar molecules this will mean that the dipole moment in particular will be very sensitive to small changes in the scaling parameters. The use of an average set as proposed by Ditchfield, Hehre and Pople [5a] is unlikely to be satisfactory in these cases; we propose to always attempt an optimisation of the molecular energy on a related smaller molecule as a necessary first step.This process breaks down for molecules with systems which cannot be described in terms of simple structures with well-defined bonds[1].

Appendix

Polarisation Orbitals

For hydrogen atoms these took the form of a further contracted function of two terms with exponents 0.5 and 0.1 but with *p*-orbital symmetry; while on carbon nitrogen and oxygen we used *d*-orbital types with a single function of exponent 0.63, 0.95 and 1.33 respectively, following the recommendation by Roos and Siegbahn [4d] and others. Although we have noted that polarisation functions on hydrogen are usually incorporated along an axis to allow interaction with either an adjacent π-system or "long pair", we preferred to incorporate the function in all three planes to test the extent of interaction.

The Scaling Procedure

The valency shell atomic orbitals of the minimal basis (Part 1) were replaced by Eq. (1), where all functions in a given contracted basis orbital had the same scaling factor (k_i). The optimal scale factors were determined by parabolic minimisation within a two dimensional array of molecular energy against scale factor. No subsidiary minima were noted for any of the model compounds used, namely ethylene (I), vinyl alcohol (II), formaldoxime (III) or vinylamine (IV). The final optimum scaling factors are shown in

$$\Phi_i = A_i \exp(-k_i \alpha_i r^2) \tag{1}$$

Table 4. These gave total energies (unscaled in parentheses) as follows:

$$\text{I} \ -77.8531 \text{ a.u. } (-77.6893 \text{ a.u.}); \ \text{II} \ -152.4748 \text{ a.u. } (-151.7322 \text{ a.u.});$$
$$\text{III} \ -168.3647 \text{ a.u. } (-168.2245 \text{ a.u.}); \ \text{IV} \ -132.5415 \text{ a.u. } (-132.5315 \text{ a.u.}).$$

The curvature of the scaled energy surface with respect to oxygen parameters is particularly marked in vinyl alcohol; it seems that this is related to the polarity of the C—O and O—H bonds particularly, for the energy is also particularly sensitive to changes in k_H, which decreases in the series O—H, N—H, C—H.

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[1] We are grateful to a referee for suggesting the addition of this last point.

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