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Extended Basis NDDO Calculations on Diatomic Molecules

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The *ab initio* NDDO method as described by Roby has been investigated for a range of diatomic species, using symmetric orthonormalization and various basis set sizes. No limiting behaviour is observed with basis set extension.

Key words: Neglect of differential overlap.

Introduction

K. R. Roby [1] has developed a theoretical framework within which the NDDO molecular orbital method [2] can be seen in relation to the conventional *ab initio* method. Each atom has a complete set of orthogonal functions centred on it, so that the full molecular basis is overcomplete. Use of the Ruedenberg expansion [3] of an orbital on one centre in terms of a complete set of orbitals on another apparently allows the derivation of a remarkable theorem. If we denote the original orthogonal basis on centre A as basis χ_A this will not in general be orthogonal to basis χ_B on centre B. One can define a canonically orthonormal basis ζ by

$$\zeta = \chi \boldsymbol{V}\boldsymbol{S}_p^{-1/2}$$

where $\boldsymbol{V}$ is a rectangular matrix which essentially removes the overcompleteness of χ on transformation into the ζ basis. $\boldsymbol{S}_p$ is the diagonal overlap matrix consisting of the non-zero eigenvalues of $\boldsymbol{S}$. Roby showed that the matrix elements of an operator $\hat{M}$ in the ζ basis are given by the matrix elements in the χ basis with the NDDO approximation applied i.e.

$$\langle \chi_i^A \hat{M} \chi_j^B \rangle = \delta_{AB} \langle \chi_i^A \hat{M} \chi_j^B \rangle.$$

King, Newton and Stanton [4], and more recently Scharfenberg [5], showed that there was a flaw in the argument for, with an over complete basis, the $\boldsymbol{S}$ matrix is infinitely degenerate and no unique transformation $\boldsymbol{V}$ exists. However, King et al. conclude that for *finite* basis sets with a *symmetrically orthogonal basis* the theorem may have some practical utility.

Thus the one electron matrix in the ζ basis, $\boldsymbol{H}^{\zeta}$, is *approximately* equal to the matrix in the χ basis with the two centre terms set equal to zero, and the two electron matrix $\boldsymbol{R}^{\zeta}$ is given by

$$\boldsymbol{R}^{\zeta} = \boldsymbol{R}_0^{\chi}$$

with

$$\boldsymbol{R}_0^{\chi} = \delta_{AB}\delta_{CD}\left\langle \mu_A \nu_B \left| \frac{1}{r_{12}} \right| \lambda_C \sigma_D \right\rangle.$$

Few numerical investigations of the Roby scheme, where the integrals are evaluated without parametrization, exist. Roby himself [1] reported a double zeta calculation on CO, which yielded an energy some 0.7 Hartree below the near Hartree–Fock result of McLean and Yoshimine [6]. Koster and Ruttink [7] studied the H_2 and H_3^+ systems at the minimum basis level, and they found good agreement with minimum basis fully *ab initio* STO calculations.

An STO-3G expansion has been utilized within Roby's framework by Chandrashekhar et al. [8] in their minimum basis studies of various systems. They scale the repulsion integrals however in a manner similar to that suggested by Cook, Hollis and McWeeny [9] in their pioneering work. More recently Chandler and Grader [10] re-examined the NDDO approximation by further consideration of the power series expansion of the overlap matrix. In so doing they point out that the method as applied to diatomic molecules, which of course have no 3 or 4 centre integrals, should be the most favourable case. Duke and Collins [11] studied the behaviour of the *ab initio* NDDO method at the minimum basis set level – using Gaussian orbital expansions – for a range of systems of complexity varying from H_2 to $(HF)_8$. They conclude that at the minimum basis level the method has little promise. The question of the behaviour of the method with respect to basis set extension in the most favourable case of diatomic molecules is still open however.

The present work uses Slater orbital bases – not Gaussian expansions – and is directed towards a resolution of the above problem.

Computational Methods

The essential features of the calculations are as follows:

a) The Slater orbitals on each centre are Schmidt orthogonalized.

b) The core Hamiltonian matrix is calculated exactly in the Schmidt (χ) basis, and then transformed into the symmetrically orthonormal basis ζ using

$$\boldsymbol{H}^{\zeta} = \boldsymbol{S}^{-1/2}\boldsymbol{H}^{\chi}\boldsymbol{S}^{-1/2}.$$

c) All NDDO repulsion integrals

$$\boldsymbol{R}_{\mu\nu,\,\sigma\lambda} = \delta_{AB}\delta_{CD}\left\langle \mu_A\nu_B \frac{1}{r_{12}} \sigma_C\lambda_D \right\rangle$$

are calculated exactly in the Schmidt basis, and are assumed equal to the corresponding integrals in the symmetrically orthonormal basis.

The integrals are evaluated using the Fourier convolution technique of Silverstone, Kay and Todd [12]. Slater orbitals up to principal quantum number 5 and up to angular momentum quantum number 4 could be introduced with the programme, which was kindly provided by Dr. H. D. Todd. The package has been extensively checked against the Stevens integral routines [13].

Results

The following species have been studied: H_2, Be_2, C_2, OH^-, N_2, BH, F_2, LiH, CH^+, HF, CN^-, CO, BF and LiF. For BH, BF, CO, HF and H_2 extended basis set calculations have been performed. Only a limited selection of results will be presented here. The full set of results, and the full listing of the programme used, are available in F. W. McConkey's Ph.D. thesis [14]. Copies of the programme are available on request however.

Table 1. Geometry and exponent optimised minimum basis results

Molecule (R_e/a.u.)	ΔR_{opt}(a.u.)	$-\langle V\rangle/\langle T\rangle$ final	$E_{initial}$	E_{final}	$\tilde{\nu}/cm^{-1}$ calc.	$\tilde{\nu}_{obs}/cm^{-1}$
BF (2.385)	−0.703	2.00002	−124.4755	−125.3095	3750	1410
CO (2.132)	−0.440	2.00002	−112.8909	−113.7821	3480	2140
HF (1.733)	−0.443	2.00001	−99.7371	−100.2194	8050	5050
N_2 (2.068)	−0.178	2.0003	−108.3189	−109.2318	2820	2358
LiH (3.015)	−1.152	2.006	−7.9679	−8.6600	3530	1521
LiF (2.850)	−1.415	2.0005	+107.1807	−108.8221	5000	895
F_2 (2.680)	−0.701	2.0002	−197.7820	−198.7546	2510	602

Table 2. Geometry optimised double ζ results[a]

Molecule (R_e/a.u.)	ΔR_{opt}(a.u.)	$-\langle V\rangle/\langle T\rangle$ final	$E_{initial}$	E_{final}	$\tilde{\nu}/cm^{-1}$ calc.	$\tilde{\nu}_{obs}/cm^{-1}$
BF (2.385)	−0.366	2.018	−125.7007	−125.8101	2040	1410
CO (2.132)	−0.258	1.979	−114.4054	−114.4842	2420	2140
HF (1.733)	−0.348	1.990	−100.9722	−100.9722	5530	5050
N_2 (2.068)	−0.220	1.997	−110.5616	−110.6354	2680	2358
LiH (3.015)	+0.360	2.0004	−8.0172	−8.0237	1130	1521
LiF (2.853)	−0.146	1.994	−107.4451	−107.4505	1250	895
F_2 (2.680)	−0.010	1.997	−199.0874	−199.0875	1345	602

[a] Double zeta basis sets used the Clementi-Roetti exponents. [Clementi, E., Roetti, C.: J. Chem. Phys. **60**, 4725 (1974)]

Table 3. Eigenvalues and eigenvectors for CO; basis set of Huo [15][a]

	Eigenvalues 1σ		2σ		3σ		4σ		5σ	
	AI	NDDO	AI	NDDO	AI	NDDO	AI	NDDO	AI	NDDO
Coeffs	−20.66123	−20.61965	−11.35927	−11.29145	−1.51920	−1.53454	−0.80235	−0.84840	−0.55304	−0.41895
$1s$	0.00002	−0.00084	−0.91928	0.91458	−0.12135	0.08248	−0.13073	−0.12902	−0.11115	−0.10491
$1s'$	−0.00000	0.00045	−0.08724	0.08754	−0.00239	0.00735	−0.00552	0.01511	−0.01163	−0.01436
$2s$	0.00070	−0.04193	0.00045	−0.03331	−0.00418	−0.20089	0.11105	0.02561	0.68860	0.63437
C $3s$	0.00002	0.00922	−0.00484	−0.00900	0.19832	−0.12219	0.26508	0.40355	0.21163	0.34468
$2p\sigma$	0.00055	−0.04777	0.00050	−0.00808	−0.03822	−0.21728	−0.07028	−0.20842	−0.21623	−0.20496
$2p\sigma'$	0.00005	0.01611	−0.00202	−0.01090	0.19795	−0.04372	0.13200	0.39450	−0.33496	−0.34952
$2p\sigma''$	0.00002	−0.00133	−0.00096	0.00338	0.00428	−0.01618	0.00164	−0.01004	−0.01234	−0.02424
$3d\sigma$	0.00010	−0.01121	−0.00104	0.00054	0.02907	0.00587	0.01291	0.10428	−0.02098	−0.00630
$1s$	0.92173	−0.91665	0.00074	0.00200	−0.20517	0.24617	0.10223	0.06245	0.01435	−0.01437
$1s'$	0.08281	−0.08364	−0.00001	0.00017	−0.00411	0.00553	0.00434	0.00380	0.00051	0.00886
$2s$	−0.00135	0.05650	0.00038	0.06100	0.58501	−0.25900	−0.42530	−0.36788	−0.06762	−0.34314
O $3s$	0.00606	−0.02505	−0.00076	−0.03334	0.26224	−0.50656	−0.14013	−0.08963	−0.01853	0.21563
$2p\sigma$	−0.00034	−0.01083	0.00073	−0.06969	0.09840	−0.06298	0.36668	−0.20586	−0.20817	0.19021
$2p\sigma'$	0.00029	−0.00530	−0.00128	0.04543	0.13062	0.11831	0.35823	−0.45391	−0.17850	0.08920
$2p\sigma''$	0.00117	0.00352	0.00003	−0.01004	0.00975	0.00364	0.03985	−0.04231	−0.02008	0.04987
$3d\sigma$	0.00022	0.00230	−0.00015	0.01267	0.03134	0.01795	0.03566	−0.01281	−0.02167	−0.16599

		Eigenvalues 1π	
		AI	NDDO
	Coeffs	−0.63771	−0.65625
C	$2p\pi$	0.32617	0.42858
	$2p\pi'$	0.05288	0.03050
	$2p\pi''$	—	0.02137
	$3d\pi$	0.06070	0.09090
O	$2p\pi$	0.44164	0.26340
	$2p\pi'$	0.37506	0.52154
	$2p\pi''$	0.04463	0.02287
	$3d\pi$	0.03871	0.01506

[a] At experimental geometry, $R_e = 2.132$ a.u.

Table 4. Eigenvalues and eigenvectors for CO; McLean, Yoshimine basis [6][a]

	Eigenvalues 1σ		2σ		3σ		4σ		5σ	
	AI	NDDO	AI	NDDO	AI	NDDO	AI	NDDO	AI	NDDO
Coeffs	−20.66430	−20.82804	−11.35972	−11.59564	−1.52097	−1.63203	−0.80383	−1.04509	−0.55437	−0.71829
$1s$	−0.00019	−0.01650	0.91055	−0.88530	−0.09028	0.16820	+0.08909	−0.02113	0.11561	0.02263
$1s'$	0.00009	0.00729	0.09217	−0.10280	−0.01739	−0.03280	0.02560	−0.02963	0.00844	0.07198
$2s$	−0.00028	−0.01360	0.00448	0.04323	0.23893	−0.07345	−0.34372	0.25053	−0.29941	−0.86190
$2s'$	0.00011	0.01055	0.00403	−0.02012	−0.04782	−0.04428	0.06494	−0.06874	0.02303	0.15033
$2s''$	0.00023	−0.05447	−0.00168	0.02270	−0.05641	−0.17089	−0.05006	−0.21576	−0.65367	−0.15561
C $2p\sigma$	−0.00013	−0.18200	−0.00411	0.05493	−0.02523	−0.10124	0.03874	1.08528	0.13151	0.13919
$2p\sigma'$	0.00015	0.13666	0.00474	−0.02837	0.18993	−0.07524	−0.13125	−0.50786	0.26512	0.16190
$2p\sigma''$	0.00023	0.00624	0.00065	−0.01117	−0.00750	−0.08232	0.01898	−0.52513	0.15054	0.09780
$2p\sigma'''$	0.00002	−0.00569	0.00075	−0.00137	0.00395	−0.00875	−0.00161	0.03457	0.01000	0.02673
$3d\sigma$	0.00002	−0.01783	0.00088	0.00021	0.02793	0.00244	−0.01454	0.08990	0.01900	−0.02322
$4f\sigma$	−0.00006	−0.02294	0.00022	−0.00287	0.00683	−0.00784	−0.00575	−0.00551	−0.00139	−0.03133
$1s$	0.93449	−0.93362	−0.00072	0.01838	−0.19038	0.18198	−0.10067	0.02283	−0.01544	−0.07747
$1s'$	0.04114	−0.03924	0.00003	−0.00907	−0.00490	0.02561	−0.00135	0.02897	0.00083	0.02602
$2s$	0.00296	−0.02734	0.00022	0.06312	0.43239	−0.73016	0.24339	−0.36009	0.01820	−0.06577
$2s'$	0.03527	−0.02603	−0.00003	−0.03133	−0.09028	0.17990	−0.04225	0.12042	−0.00052	0.06609
$2s''$	0.00003	0.08770	0.00095	−0.08533	0.47112	−0.13233	0.36792	−0.08584	0.09935	0.28069
O $2p\sigma$	0.00049	−0.03576	−0.00076	−0.01291	−0.15791	0.11331	0.39555	−0.65037	−0.19713	−0.69737
$2p\sigma'$	−0.00098	0.01319	−0.00054	−0.00497	−0.07530	0.13004	0.25922	−0.22575	−0.13007	0.20974
$2p\sigma''$	−0.00041	−0.01161	−0.00028	0.06519	−0.01254	−0.05295	0.09757	0.16254	−0.11207	0.50969
$2p\sigma'''$	−0.00065	−0.00067	−0.00001	−0.00084	−0.00520	−0.00160	0.01343	−0.02395	−0.00692	−0.02575
$3d\sigma$	0.00038	0.01236	0.00063	−0.02057	0.04446	−0.03247	−0.04611	0.06077	0.03046	0.23062
$4f\sigma$	−0.00016	−0.00279	−0.00041	0.01755	−0.01207	0.01725	0.00956	−0.01033	−0.00578	−0.10422

		Eigenvalues 1π	
		AI	NDDO
	Coeffs	−0.63947	−0.76156
C	$2p\pi$	0.26215	0.05686
	$2p\pi'$	0.11378	0.10574
	$2p\pi''$	−0.01605	0.27369
	$2p\pi'''$	0.00429	0.00354
	$3d\pi$	0.04727	0.04214
	$4f\pi$	0.00854	0.03560
O	$2p\pi$	0.46192	0.55605
	$2p\pi'$	0.25685	0.26811
	$2p\pi''$	0.14780	0.01403
	$2p\pi'''$	0.01328	0.01464
	$3d\pi$	−0.04970	0.00788
	$4f\pi$	0.01106	0.00809

[a] At experimental geometry, $R_e = 2.132$ a.u.

Geometry and exponent optimized minimum basis calculations are presented in Table 1; the corresponding geometry optimized (only) double zeta calculations appear in Table 2. As a representative of the extended basis heteronuclear calculations the CO molecule is taken; Table 3 presents the eigenvalues and eigenvectors for the Huo [15] basis set, and Table 4 the equivalent output for the McLean–Yoshimine basis [6]. The results of geometry variation for *fixed* bases for BF and CO are presented in Table 5. Finally Table 6 presents the results of a range of calculations on H_2. All energies are in Hartree, all distances in Bohr unless otherwise stated.

Table 5. McLean–Yoshimine basis [6]; variation of geometry for CO, BF

	R/Bohr	Charge on C	$-\langle V\rangle/\langle T\rangle$	E_{tot}/Hartree
CO	2.3	0.084	2.0078	−113.95709
	2.1	−0.108	2.0000	−113.96145
	2.015	−0.069	1.9971	−113.95840
	1.8	−0.332	1.9873	−113.93977
BF	2.39	−0.414	1.9937	−125.6851
	2.00	−0.757	1.9799	−125.8343
	1.60	−1.725	1.9542	−126.0151

Table 6. Representative calculations on H_2 ($R = 1.4$ a.u.)

Basis set[a]	Number of orbitals	$-\varepsilon_{1\sigma}$	$-\langle V\rangle/\langle T\rangle$	$-E_{\text{total}}$(SCF)*
A (minimal)	2	0.5948	1.993	+1.1303
B (double ζ)	4	0.6431	—	+1.1765
C (triple $\zeta+2s$)	8	0.6413	2.001	+1.1825
D (triple $\zeta+2s+2p$)	14	0.5986	1.984	+1.1416
E (triple $\zeta+2s+2p+2p'+3s+3p+4s$)	30	0.6058	1.992	+1.1486
F (triple $\zeta+2s+2p+2p'+3d$)	30	0.6032	—	+1.1460
G (triple $\zeta+2s+2p+2p'+3s+3p+3d+3d'+3d''+4d$)	68	0.5990	1.996	+1.1396
H (*spdf*)	44	0.6030	1.987	+1.1459
I (*spdfg*)	62	0.6031	1.987	+1.1460
**Ab initio* [16]	—	0.5946	2.0067	+1.1336

[a] Basis set A: $\zeta_{1s}=1.2$; Basis set B: $\zeta_{1s}=0.9$, $\zeta_{1s'}=1.4$. Basis set C: $\zeta_{1s}=0.7$, $\zeta_{1s'}=1.3$, $\zeta_{1s''}=2.0$, $\zeta_{2s}=1.16$. Basis set D: Basis set $C+\zeta_{2p}=1.4$. Basis set E: Basis set $D+\zeta_{2p'}=2.0+\zeta_{3s}=1.3+\zeta_{3p}=1.5$. Basis set F: Basis set $C+\zeta_{2p}=1.4+\zeta_{2p'}=2.0+\zeta_{3d}=1.3$. Basis set G: Basis set $E+\zeta_{3d}=1.2+\zeta_{3d'}=1.7+\zeta_{3d''}=2.4+\zeta_{4d}=1.9+\zeta_{3p}+1.5$. Basis set H: Basis set $D+\zeta_{2p'}=2.0+\zeta_{3d}=1.3+\zeta_{4f}=1.0$. Basis set I: Basis set $H+\zeta_{5g}=1.5$.

Discussion of Results

At the minimum basis level geometry optimization showed a pronounced tendency for the more electronegative centre to draw a considerable amount of electronic charge away from the other centre. Considerable bond shortening occurred also, as described by Duke and Collins [11]. Geometry and exponent optimized studies converged to virial ratios ($-\langle V\rangle/\langle T\rangle$) very close to 2, but with disastrous effects on the total energy and charge separation (see Table 1). Vibrational frequencies calculated with respect to the minimum energy configuration were much too high. No problems were encountered in the integral and SCF stages between 0.2 a.u. and 4 a.u. Exponent optimization gave small changes in the core orbital exponents but very large changes in the outer shell exponents. In passing it is worth commenting that the exponent and geometry optimization (R first and then zeta) for H_2 and H_3^+ performed by Koster and Ruttink [7] is reproduced by this work exactly, but *only* for this order of optimization.

Double zeta calculations gave less error in the core orbital energies, and may therefore be useful for ESCA studies (average error about 0.5%). Geometry optimisation (Table 2) shows less dramatic changes in R_e than with minimum basis calculations. Vibrational frequencies are considerably improved at the double zeta level also. Amazing charge distribution effects are observed in the heteronuclear systems; it appears that the electronegative species acquires charge "quickly", such that the outer electrons prefer to be on the *less* electronegative partner in the more diffuse orbitals, resulting in a reversal of the conventional dipole moment.

At the very large basis set level (Huo [15], Cade/Huo [16], McLean–Yoshimine [6]) it is clear that the results are markedly basis set dependent. Thus a good basis in the *ab initio* realm is not necessarily a good basis for NDDO (Tables 3, 4, 5). Cade/Huo basis set [16] calculations on BH and LiH, with only 6 and 4 electrons respectively, were however quite accurate for the eigenvalues and eigenvectors.

	$-\varepsilon_{1\sigma}$		$-\varepsilon_{2\sigma}$		$-\varepsilon_{3\sigma}$		$-E_{\mathrm{tot/Hartree}}$	
Molecule	NDDO	AI	NDDO	AI	NDDO	AI	NDDO	AI
LiH	+2.479	+2.445	+0.299	+0.302	−0.02	−0.02	+8.027	+7.987
BH	+7.689	+7.686	+0.647	+0.648	+0.380	+0.348	+25.300	+25.131

It appears that the level of agreement depends both on the number of electrons and on the electronegativity difference. In general the outer eigenvalues are subject to large errors, which also influence the charge distribution. Total energies are too negative, as expected. Variation of geometry for a given fixed extended basis produces severe charge distortions; anomalous dipole moments are encountered also.

In the case of the H_2 study we see that augmentation of the *s* basis dramatically worsens the energy from the minimum basis value. Higher angular momentum functions begin to bring back the energy into the correct region, but the introduction of *f* and *g* functions destroy the apparent trend. However it should be noted that computer store limitations prevented us from expanding the *f* and *g* calculations from the *spd* limit, which would have given a "cleaner" result. The Löwdin orthogonalisation procedure broke down in only one case for the basis $H_1 = H_2(1s, 1s', 1s'', 2s, 2p, 2p', 3s, 3p, 4s, 4p, 5s, 5p)$ i.e. 7 *s* functions and 5 *p* functions on each centre. The numerical stability broke down at the SCF stage, due to two near zero roots of the *S* matrix. The formation of $S^{-1/2}$ was therefore subject to very large errors.

The consistent tendency for total energies to be too negative shows that the expectation value of the approximate Hamiltonian $\hat{H}_{\mathrm{NDDO}}$ need bear little relation to the fully *ab initio* value. In itself this does not imply that the variation theorem for the *approximate* $\hat{H}$ is invalid. Numerical inaccuracies in the evaluation of the expectation value may however produce truly non-variational behaviour. The calculations presented show that the extension of basis set size does not necessarily bring improvement in energy, eigenvalues and charge distribution. Brown et al. [17], in their study of basis set extension using the 'simplified *ab initio* method' similarly found disappointing results. Thiel [18], in a recent paper on a semiempirical NDDO scheme using a 4-31G basis, found minimum basis calculations to be more satisfactory, a conclusion with which we agree. (Non geometry optimised calculations at the minimum basis level show a much better general correlation with *ab initio* results, *at that level* [14]). It seems that a more profitable use of the NDDO scheme may be along the lines indicated by Cook [19], where the neglect of repulsion integrals is compensated for by a change in the core Hamiltonian matrix elements. Finally it should be pointed out that extensive Schmidt orthogonalization with large bases can be very time consuming; it may well consume the time saved in using a shorter integral list i.e. the highly efficient *ab initio* packages now available may be cheaper to use.

In conclusion we find that basis set extension does not lead to improved results, indeed rather the converse. It is perhaps possible that we are still far from the limiting situation, but in any case for computations with practicable basis sets the Roby scheme does not appear to offer any advantages over conventional *ab initio* theory.

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