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Simplified *ab-initio* Calculations for Molecular Systems

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A method is described for reducing a large part of the arithmetic of exact *ab-initio* SCF molecular-orbital calculations based on Slater-type-orbitals without noticeable loss of numerical accuracy. The procedure involves the transformation to Löwdin orthogonalized orbitals and then invoking the NDDO approximation. The three- and four-centre two-electron integrals required are estimated by a truncated Ruedenberg expansion. All one-electron integrals are evaluated exactly. No empirical parameters are employed. Numerical tests on CO, OF_2, O_3 and ONF show that the NDDO approximation is very accurate for Löwdin functions and that the Ruedenberg expansion is arithmetically satisfactory for the SCF MO calculations.

Eine Methode zur Reduzierung eines großen Teiles der Rechnungen ohne merklichen Verlust an numerischer Genauigkeit in der exakten *ab initio* SCF-MO-Methode, die auf Slater-Orbitalen basiert, wird beschrieben. Das Verfahren beinhaltet die Transformation zu orthogonalen Orbitalen nach Löwdin und benutzt die NDDO-Näherung. Die erforderlichen Drei- und Vier-Zentrenintegrale werden mit Hilfe der abgebrochenen Ruedenberg-Entwicklung geschätzt. Alle Ein-Elektron-Integrale werden exakt berechnet. Keine empirischen Parameter werden benutzt. Numerische Untersuchungen für CO, OF_2, O_3 und ONF zeigen, daß die NDDO-Näherung sehr genau für Löwdin-Funktionen ist, und daß die Ruedenberg-Entwicklung numerisch zufriedenstellend für die SCF-MO-Berechnungen ist.

Description d'une méthode pour réduire une grande partie des calculs numériques d'une méthode SCF *ab initio* en orbitales de Slater, sans perdre pour autant trop de précision. On utilise une orthogonalisation de Löwdin suivie d'une approximation NDDO. Les intégrales biélectroniques tri et quadricentriques sont estimées par un développement tronqué de Ruedenberg. Toutes les intégrales monoélectroniques sont évaluées exactement. Aucun paramètre empirique n'est employé. Des essais numériques sur CO, OF_2, O_3 et ONF montrent que l'approximation NDDO est très précise pour les fonctions de Löwdin et que le développement de Ruedenberg est numériquement satisfaisant pour les calculs SCF MO.

Introduction

A great variety of semi-empirical molecular orbital methods is available for theoretical studies of molecular properties [1]. However many applications have been inconclusive because the semi-empirical nature of the methods throws doubt on the reliability of numerical results. On the other hand *ab-initio* methods present formidable computing problems as soon as one proceeds beyond the smallest of molecules. The simple *ab-initio* method described here represents an attempt to reproduce with acceptable arithmetic accuracy the results of a corresponding exact *ab-initio* calculation but with considerable reduction of the computational task and without introducing any empirical parameters or procedures.

Description of Method

Procedure: An orthonormal basis set constructed from a linear combination of Slater (χ) functions is employed in this method.

$$\boldsymbol{\lambda} = \boldsymbol{\chi T} \tag{1}$$

$\boldsymbol{\chi}$ = row matrix of basis functions, where $\boldsymbol{\lambda}^{\dagger}\boldsymbol{\lambda} = \mathbf{1}$ and $\boldsymbol{T}$ is a transformation matrix which may be written as the product of three other matrices: $\boldsymbol{T} = \boldsymbol{ABS}_{\eta}^{-\frac{1}{2}}$. The matrix $\boldsymbol{A}$ transforms the non-orthogonal Slater set to an orthogonal "atomic set" ϕ for each atom by a Schmidt procedure. (For basis sets involving only 1*s*, 2*s* and 2*p* functions this matrix simply transforms the 2*s* function on each atom so that it is orthogonal to the 1*s* function on the same atom.)

The matrix $\boldsymbol{B}$ is a general transformation matrix which may be used to create a set of localized hybrid functions on each centre (if one prefers to work with hybrids), or to separate out the valence and inner shell orbitals if one wishes to consider them separately.

$\boldsymbol{S}_{\eta}^{-\frac{1}{2}}$ is the Löwdin orthogonalization matrix of the set of "general functions", η, produced from the Slater set by the operation of the matrices $\boldsymbol{A}$ and $\boldsymbol{B}$.

Hence the overall transformation may be summarized

$$\underset{\substack{\text{Slater}\\ \text{set}}}{\chi} \xrightarrow{\boldsymbol{A}} \underset{\substack{\text{atomic}\\ \text{set}}}{\phi} \xrightarrow{\boldsymbol{B}} \underset{\substack{\text{general}\\ \text{set}}}{\eta} \xrightarrow{\boldsymbol{S}_{\eta}^{-\frac{1}{2}}} \underset{\substack{\text{orthogonal}\\ \text{set}}}{\lambda} \;.$$

In the present work we have however always proceeded directly from the atomic set to the orthogonal set, i.e. we have set $\boldsymbol{B} \equiv \mathbf{1}$.

i) *One-Electron Integrals:* All overlap, kinetic energy and nuclear attraction integrals required for the SCF calculation are obtained without approximation, i.e. exactly in the Slater basis.

Thus the core matrix, $\boldsymbol{H}$, is formed *exactly* in the χ-(Slater) basis:

$$H_{ij}^{\chi} = K_{ij} - \sum_{\alpha}^{\text{atoms}} V_{ij}^{\alpha} \tag{2}$$

where

$$K_{ij} = \int \chi_i^* \left(-\tfrac{1}{2}\,\nabla^2\right) \chi_j \,\mathrm{d}\tau\,,$$

$$V_{ij}^{\alpha} = \int \chi_i^* \frac{1}{r_{\alpha}} \chi_j \,\mathrm{d}\tau\,.$$

The $\boldsymbol{H}^{\chi}$ is then transformed to the orthogonal λ-basis via the transformation:

$$\boldsymbol{H}^{\lambda} = \boldsymbol{T}^{\dagger}\boldsymbol{H}^{\chi}\boldsymbol{T}. \tag{3}$$

ii) *Two-Electron Integrals (repulsion integrals):* In the λ-basis our method invokes the NDDO (Neglect of diatomic differential overlap) approximation, i.e.

$$(\lambda_i^{\mathrm{A}}\lambda_j^{\mathrm{B}} \mid \lambda_k^{\mathrm{C}}\lambda_l^{\mathrm{D}}) = \delta_{\mathrm{AB}}\,\delta_{\mathrm{CD}}(\lambda_i^{\mathrm{A}}\lambda_j^{\mathrm{A}} \mid \lambda_k^{\mathrm{C}}\lambda_l^{\mathrm{C}}) \tag{4}$$

(where A, B, C, D refer to atomic centres).

The repulsion integrals in the λ-basis are related to the full set of integrals in the χ-basis by:

$$(\lambda_i\lambda_j \mid \lambda_k\lambda_l) = \sum_{r,s}\sum_{t,u} T_{ri}^*\,T_{sj}^*(\chi_r\chi_s \mid \chi_t\chi_u)\,T_{tk}\,T_{ul}\,. \tag{5}$$

The principal feature of the method is that this transformation is greatly simplified so that explicit calculation of multicentre (ϕ basis) integrals is unnecessary. This simplification is achieved as follows:

a) The χ-basis "NDDO" integrals $(\chi_r^{\mathrm{A}}\chi_s^{\mathrm{A}} \mid \chi_t^{\mathrm{C}}\chi_u^{\mathrm{C}})$ are transformed initially into the atomic basis ϕ:

$$(\phi_i^{\mathrm{A}}\phi_j^{\mathrm{A}} \mid \phi_k^{\mathrm{C}}\phi_l^{\mathrm{C}}) = \sum_{\mathrm{E,F}}^{\text{atoms}} \sum_{r,s}^{\mathrm{E}} \sum_{t,u}^{\mathrm{F}} A_{ri}^{*} A_{sj}^{*} (\chi_r^{\mathrm{E}}\chi_s^{\mathrm{E}} \mid \chi_t^{\mathrm{F}}\chi_u^{\mathrm{F}})\, A_{tk} A_{ul}\,. \tag{6}$$

This transformation may be carried out rapidly, since it merely involves a one-centre orthogonalization. Hence, most of the A_{ij} elements are zero and only the χ-basis "NDDO" integrals are required. These integrals are calculated by standard methods.

b) The transformation from the ϕ-basis to the λ-basis, which *does* require the knowledge of multicentre ϕ-basis integrals, is simplified by the use of the Ruedenberg approximation [2] for the ϕ-basis integrals. In matrix form this may be written as follows:

If

$$\boldsymbol{\Phi} = \boldsymbol{\phi}^{\dagger}\boldsymbol{\phi} \tag{7}$$

then the truncated Ruedenberg approximation may be written:

$$\langle \boldsymbol{\Phi} | \approx \tfrac{1}{2}\,[\boldsymbol{S}_{\phi}\boldsymbol{\Phi}^{0} + \boldsymbol{\Phi}^{0}\boldsymbol{S}_{\phi}]\,, \tag{8}$$

where $\boldsymbol{S}_{\phi}$ is the overlap matrix for the ϕ-basis and $\boldsymbol{\Phi}^{0}$ is a block diagonal matrix containing only one-centre overlap densities $\phi_i^{\mathrm{A}}\phi_j^{\mathrm{A}}$.

If we transform to the λ-basis:

$$\langle \boldsymbol{\Lambda} | = \langle \boldsymbol{\lambda}^{\dagger}\boldsymbol{\lambda} | = \langle \boldsymbol{X}^{\dagger}\boldsymbol{\Phi}\boldsymbol{X} | \quad \text{where} \quad \boldsymbol{X} = \boldsymbol{B}\boldsymbol{S}_{\eta}^{-\frac{1}{2}} \tag{9}$$

and make use of the Ruedenberg approximation, we have:

$$\langle \boldsymbol{\Lambda} | \approx \tfrac{1}{2}\langle \boldsymbol{X}^{\dagger}\boldsymbol{S}_{\phi}\boldsymbol{\Phi}^{0}\boldsymbol{X} + \boldsymbol{X}^{\dagger}\boldsymbol{\Phi}^{0}\boldsymbol{S}_{\phi}\boldsymbol{X} |\,. \tag{10}$$

We now define

$$\boldsymbol{u} = \boldsymbol{X}^{\dagger}\boldsymbol{S}_{\phi}\,, \tag{11}$$

$$\boldsymbol{v} = \boldsymbol{S}_{\phi}\boldsymbol{X} \tag{12}$$

so that

$$\langle \boldsymbol{\Lambda} | \approx \tfrac{1}{2}\langle \boldsymbol{u}\boldsymbol{\Phi}^{0}\boldsymbol{X} + \boldsymbol{X}^{\dagger}\boldsymbol{\Phi}^{0}\boldsymbol{v} | \tag{13}$$

hence for a λ-basis repulsion integral we may write

$$(\lambda_i^{\mathrm{A}}\lambda_j^{\mathrm{A}} \mid \lambda_k^{\mathrm{C}}\lambda_l^{\mathrm{C}}) \approx \tfrac{1}{4}\sum_{\mathrm{E}}^{\text{atoms}} \sum_{\mathrm{F}} \left[\sum_{p,q}^{\mathrm{E}} \sum_{r,s}^{\mathrm{F}} (u_{ip}^{*}X_{qj}^{*} + X_{pi}^{*}v_{qj}^{*})\,(\phi_p^{\mathrm{E}}\phi_q^{\mathrm{E}} | \phi_r^{\mathrm{F}}\phi_s^{\mathrm{F}})\,(u_{kr}X_{sl} + X_{rk}v_{sl}) \right]. \tag{14}$$

It is evident that this expansion involves only ϕ-basis "NDDO" integrals explicitly.

Because the Ruedenberg approximation for multicentre ϕ-basis integrals is included directly into the transformation, the multicentre integrals are only *implicitly* calculated during the transformation, a process requiring little extra effort or time.

F-Matrix: Because of the use of the NDDO approximation, the formation of the $\boldsymbol{F}$-matrix in the λ-basis is greatly simplified. This is due to the fact that instead of requiring a full set of about N^4 repulsion integrals for each iteration, as in a full overlap calculation, only the NDDO integrals in the orthogonal basis are used (these generally represent only a minor fraction of the full set of about N^4 integrals). Hence a considerable amount of computer time is saved.

The one- and two-centre $\boldsymbol{F}^{\lambda}$ elements are given by:

$$(F_{\mu\nu}^{\mathrm{AA}})^{\lambda} = H_{\mu\nu}^{\lambda} + \sum_{\lambda,\sigma}^{\mathrm{A}} P_{\lambda\sigma}\{(\lambda_\mu \lambda_\nu \mid \lambda_\lambda \lambda_\sigma) - \tfrac{1}{2}(\lambda_\mu \lambda_\lambda \mid \lambda_\nu \lambda_\sigma)\},$$

$$(F_{\mu\nu}^{\mathrm{AB}})^{\lambda} = H_{\mu\nu}^{\lambda} - \sum_{\lambda}^{\mathrm{A}} \sum_{\sigma}^{\mathrm{B}} P_{\lambda\sigma}(\lambda_\mu \lambda_\lambda \mid \lambda_\sigma \lambda_\nu).$$

Numerical Performance

To examine the numerical performance of the method a series of trial calculations have been performed on small molecules, chosen because limited-basis-set STO *ab-initio* calculations are available for comparative purposes [3, 4]. Here we report results for CO, F_2O and O_3 and ONF. To facilitate comparisons, eigenvalues and expectation values for several one-electron operators are listed (Tables 1–6). The coordinate systems and geometries set out in [4] were used in the present calculations.

As an additional comparison, corresponding calculations have been carried through without transforming to the λ-basis and invoking the NDDO simplification in the case of CO and F_2O. These "full overlap" calculations will be seen to yield numerical results very close to the orthogonal basis results, demonstrating that *the* NDDO *approximation for a λ-basis is arithmetically acceptable.* There appears to have been no previous direct numerical evidence on this point. The agreement for all one-electron operators and for the total energy is so good that for virtually all applications the NDDO simplification introduces no arithmetic error of practical significance.

A comparison of the results obtained by our simplified method with the arithmetically exact calculations indicates that the numerical error stemming from the use of the Ruedenberg integral approximation is acceptably small. Total energies agree to within about 0.2% except in the case of CO where it seems likely that the abnormally small internuclear distance and correspondingly larger overlap integrals lead to slightly poorer performance of the Ruedenberg approximation.

Some indication of the shapes of the various individual molecular orbitals may be gained by inspecting the one-electron operator mean values. It is noticeable that for valence shell molecular orbitals there are sometimes sizeable differences between the orbitals computed by our method and by the exact procedure. However the sum of mean values over orbitals belonging to the same irreducible representation remains in close agreement with the exact value (see Table 6). Moreover when there is only one orbital of a given symmetry type, e.g. $1a_2$ for OF_2, good agreement between the two procedures is observed. This suggests that in cases where the energy separation between two or more orbitals of the same

Table 1. *Total electronic energies and expectation values of one-electron operators*

	CO			F_2O			O_3		ONF	
	Simplified		Exact	Simplified		Exact	Simplified	Exact	Simplified	Exact
	(1)[h]	(2)[i]		(1)	(2)		(1)		(1)	
E (a.u.)	−112.75	−112.75	−112.33	−272.52	−272.52	−272.43	−223.93	−223.48	−228.24	−227.71
$\langle 1/r \rangle$ (a.u.)	18.335[a] 25.094[b]	18.356[a] 25.091[b]	18.274[a] 24.856[b]	31.639[a] 29.013[b]	31.641[a] 29.013[b]	31.566[a] 28.838[b]	27.538[a] 28.871[b]	27.501[a] 28.629[b]	30.831[a] 27.758[b] 25.249[c]	30.890[a] 27.517[b] 24.909[c]
$\langle z \rangle$ (a.u.)[d]	17.310	17.224	16.823	29.581	29.589	29.542	20.074	20.432	24.343 6.982[e]	24.511 7.305[e]
$\langle r^2 \rangle$ (a.u.)[f]	37.36	37.28	39.18	119.61	119.58	122.19	103.30	107.55	110.73	105.42
$\langle x^2 \rangle$ (a.u.)[f]	7.23	7.24	7.05	86.80	86.80	88.52	75.53	79.24	80.35	77.68
$\langle y^2 \rangle$ (a.u.)[f]	7.23	7.24	7.05	9.28	9.28	9.28	9.31	9.31	9.31	9.13
$\langle z^2 \rangle$ (a.u.)[f]	22.89	22.80	25.09	23.53	23.50	24.40	18.45	19.00	21.07	18.62
$\mu(D)$	−0.64	−0.43	0.59	0.19	0.17	0.29	0.43	−0.47	0.78	0.32
σ_d ppm[g]	325.4[a] 445.5[b]	325.8[a] 445.4[b]	324.4[a] 441.2[b]	561.6[a] 515.0[b]	561.6[a] 515.0[b]	560.3[a] 511.9[b]	488.8[a] 512.5[b]	488.3[a] 508.2[b]	547.3[a] 492.7[b] 448.2[c]	543.3[a] 488.4[b] 442.1[c]

[a] Origins: C in CO; F in F_2O; end O in O_3; F in ONF.

[b] Origin: O in CO, F_2O and ONF, centre O in O_3.

[c] Origin: N in ONF.

[d] Origins: C in CO; O in F_2O; central O in O_3; N in ONF.

[e] $\langle x \rangle$.

[f] Origin is centre of mass.

[g] $\sigma_d = 17.7497 \langle 1/r \rangle$ [5].

[h] (1) Calculations with the NDDO approximation for a λ-basis.

[i] (2) Calculation *without* transforming to the λ-basis and invoking the NDDO simplification.

Table 2. *Eigenvalues (a.u.)*

CO				OF$_2$				O$_3$			ONF		
Orbital	Simplified		Exact	Orbital	Simplified		Exact	Orbital	Simplified	Exact	Orbital	Simplified	Exact
	(1)	(2)			(1)	(2)			(1)			(1)	
1σ	−20.685	−20.699	−20.812	$1b_1$	−26.342	−26.340	−26.395	$1a_1$	−20.779	−20.960	$1a$	−26.388	−26.312
2σ	−11.457	−11.462	−11.444	$1a_1$	−26.342	−26.341	−26.395	$1b_1$	−20.630	−20.677	$2a$	−20.663	−20.797
3σ	− 1.570	− 1.534	− 1.534	$2a_1$	−20.654	−20.654	−20.760	$2a_1$	−20.629	−20.677	$3a$	−15.720	−15.863
4σ	− 0.980	− 0.932	− 0.760	$3a_1$	− 1.520	− 1.527	− 1.638	$3a_1$	− 1.454	− 1.668	$4a$	− 1.541	− 1.634
1π	− 0.556	− 0.546	− 0.612	$2b_1$	− 1.520	− 1.513	− 1.527	$2b_1$	− 1.299	− 1.336	$5a$	− 1.471	− 1.475
5σ	− 0.617	− 0.616	− 0.507	$4a_1$	− 1.272	− 1.270	− 1.170	$4a_1$	− 1.260	− 1.006	$6a$	− 1.208	− 0.902
				$1b_2$	− 0.535	− 0.534	− 0.653	$5a_1$	− 0.608	− 0.712	$7a$	− 0.648	− 0.709
				$3b_1$	− 0.545	− 0.545	− 0.632	$1b_2$	− 0.461	− 0.680	$8a$	− 0.575	− 0.652
				$5a_1$	− 0.536	− 0.535	− 0.631	$3b_1$	− 0.702	− 0.673	$1b$	− 0.565	− 0.648
				$1a_2$	− 0.537	− 0.536	− 0.558	$4b_1$	− 0.469	− 0.441	$9a$	− 0.560	− 0.496
				$4b_1$	− 0.499	− 0.498	− 0.518	$6a_1$	− 0.462	− 0.418	$2b$	− 0.486	− 0.491
				$6a_1$	− 0.467	− 0.466	− 0.484	$1a_2$	− 0.381	− 0.350	$10a$	− 0.412	− 0.374
				$2b_2$	− 0.477	− 0.477	− 0.423						

Table 3. *Values of $\langle 1/r \rangle$ for each molecular orbital*[a] *(a.u.)*

CO				OF$_2$				O$_3$			ONF		
Orbital	Simplified		Exact	Orbital	Simplified		Exact	Orbital	Simplified	Exact	Orbital	Simplified	Exact
	(1)	(2)			(1)	(2)			(1)			(1)	
1σ	0.938	0.938	0.938	$1b_1$	8.862	8.863	8.861	$1a_1$	0.895	0.828	$1a$	17.250	17.247
2σ	11.304	11.304	11.306	$1a_1$	8.863	8.862	8.861	$1b_1$	7.878	7.877	$2a$	0.484	0.484
3σ	1.125	1.104	1.248	$2a_1$	0.749	0.749	0.749	$2a_1$	7.811	7.876	$3a$	0.696	0.696
4σ	1.669	1.665	1.108	$3a_1$	1.682	1.582	1.409	$3a_1$	0.855	0.941	$4a$	2.806	0.828
5σ	1.146	1.190	1.526	$2b_1$	1.713	1.713	1.654	$2b_1$	1.557	1.202	$5a$	0.651	2.479
1π	1.077	1.077	1.073	$4a_1$	0.790	0.794	1.075	$4a_1$	1.549	1.095	$6a$	0.665	0.794
				$1b_2$	1.507	1.507	1.166	$5a_1$	0.875	1.239	$7a$	0.674	0.830
				$3b_1$	1.521	1.520	1.250	$1b_2$	1.066	0.962	$8a$	1.153	0.860
				$5a_1$	1.504	1.503	1.273	$3b_1$	0.988	1.428	$1b$	2.536	0.791
				$1a_2$	1.512	1.512	1.512	$4b_1$	1.365	1.372	$9a$	2.122	2.360
				$4b_1$	1.138	1.131	1.471	$6a_1$	1.343	1.335	$2b$	0.571	2.275
				$6a_1$	1.074	1.085	1.222	$1a_2$	1.356	1.357	$10a$	1.222	1.246
				$2b_2$	0.722	0.722	1.063						

[a] Origin is: C in CO, F in OF$_2$; end O in O$_3$, F in CNF.

Table 4. *Values of* $\langle z \rangle$ *for each molecular orbital*[a] *(a.u.)*

CO				OF$_2$				O$_3$			ONF		
Orbital	Simplified		Exact	Orbital	Simplified		Exact	Orbital	Simplified	Exact	Orbital	Simplified	Exact
	(1)	(2)			(1)	(2)			(1)			(1)	
1σ	4.264	4.264	4.264	$1b_1$	3.295	3.295	3.295	$1a_1$	0.024	0.000	$1a$	3.287	3.287
2σ	0.001	0.001	0.001	$1a_1$	3.295	3.295	3.295	$1b_1$	2.531	2.530	$2a$	2.444	2.443
3σ	3.440	3.442	3.149	$2a_1$	0.000	0.000	0.000	$2a_1$	2.506	2.530	$3a$	0.000	0.001
4σ	1.236	1.530	3.958	$3a_1$	3.110	3.091	2.445	$3a_1$	0.376	1.138	$4a$	3.143	1.745
5σ	2.328	1.950	−0.629	$2b_1$	3.244	3.248	3.081	$2b_1$	2.460	1.796	$5a$	2.112	2.889
1π	3.020	3.018	3.041	$4a_1$	0.335	0.350	1.266	$4a_1$	2.438	1.555	$6a$	0.917	1.572
				$1b_2$	3.295	3.295	1.948	$5a_1$	0.076	0.879	$7a$	0.721	1.724
				$3b_1$	3.265	3.264	2.448	$1b_2$	1.357	0.883	$8a$	2.236	1.416
				$5a_1$	3.306	3.298	2.172	$3b_1$	0.697	2.151	$1b$	3.256	1.474
				$1a_2$	3.318	3.312	3.295	$4b_1$	2.514	2.380	$9a$	2.978	3.072
				$4b_1$	1.728	1.696	3.013	$6a_1$	2.564	2.059	$2b$	1.432	3.123
				$6a_1$	1.363	1.415	1.939	$1a_2$	2.531	2.531	$10a$	1.817	1.765
				$2b_2$	0.027	0.028	1.344						

[a] Origins: C in CO, O in OF$_2$, central O in O$_3$, N in ONF.

Table 5. *Values of* $\langle r^2 \rangle$ *for each molecular orbital*[a] *(a.u.)*

CO				OF$_2$				O$_3$			ONF		
Orbital	Simplified		Exact	Orbital	Simplified		Exact	Orbital	Simplified	Exact	Orbital	Simplified	Exact
	(1)	(2)			(1)	(2)			(1)			(1)	
1σ	9.200	9.200	9.191	1b_1	14.342	14.342	14.340	1a_1	0.216	0.104	1a	16.584	16.584
2σ	0.191	0.192	0.191	1a_1	14.342	14.342	14.341	1b_1	11.773	11.770	2a	9.226	9.241
3σ	8.785	8.804	8.304	2a_1	0.104	0.104	0.104	2a_1	11.661	11.769	3a	0.138	0.139
4σ	8.096	8.184	13.762	3a_1	15.779	15.661	11.445	3a_1	3.087	5.697	4a	17.700	8.909
5σ	12.023	11.640	7.423	2b_1	16.094	16.152	15.525	2b_1	13.594	10.851	5a	9.657	16.233
1π	10.229	10.225	10.258	4a_1	3.364	3.424	9.559	4a_1	14.127	12.371	6a	6.471	3.762
				1b_2	16.471	16.468	10.891	5a_1	5.632	9.558	7a	9.081	10.156
				3b_1	16.656	16.633	13.103	1b_2	9.094	6.924	8a	12.365	9.668
				5a_1	16.534	16.513	13.033	3b_1	6.780	13.449	1b	18.689	9.242
				1a_2	16.582	16.582	16.582	4b_1	14.795	14.817	9a	16.834	17.951
				4b_1	10.281	10.113	15.984	6a_1	14.589	12.888	2b	8.704	17.757
				6a_1	9.577	9.786	12.134	1a_2	14.738	14.740	10a	12.151	12.769
				2b_2	3.122	3.126	8.703						

[a] Origin is: C in CO, O in OF$_2$, central O in O$_3$, N in ONF

Table 6. *Sums of* $\langle 1/r \rangle$, $\langle z \rangle$ *and* $\langle r^2 \rangle$ *for orbitals of each symmetry type*[a]

CO					OF$_2$							
	$\Sigma n\sigma$		$\Sigma 1\pi$		Σna_1		Σnb_1		Σnb_2		1a_2	
	(1)	Exact	(1)	Exact	(1)	Exact	(1)	Exact	(1)	Exact	(1)	Exact
$\langle 1/r \rangle$	16.181	16.127	2.153	2.147	14.666	14.589	13.234	13.237	2.229	2.229	1.512	1.512
$\langle z \rangle$	11.269	10.742	6.041	6.081	11.408	11.117	11.585	11.837	3.292	3.292	3.295	3.295
$\langle r^2 \rangle$	38.29	38.87	20.46	20.52	59.70	60.62	57.37	58.95	19.59	19.59	16.58	16.58

O$_3$									ONF			
	Σna_1		Σnb_1		1b_2		1a_2		Σna		Σnb	
	(1)	Exact	(1)	Exact	(1)	Exact	(1)	Exact	(1)	Exact	(1)	Exact
$\langle 1/r \rangle$	13.327	13.314	11.789	11.879	1.066	0.962	1.356	1.357	27.724	27.824	3.107	3.066
$\langle z \rangle$	7.985	8.162	8.202	8.857	1.357	0.883	2.531	2.531	19.655	19.914	4.688	4.597
$\langle r^2 \rangle$	49.31	52.39	46.94	50.89	9.09	6.92	14.74	14.74	110.21	105.42	27.39	27.00

[a] Origins as in Tables 3, 4 and 5.

symmetry type is small the effect of the Ruedenberg integral approximation on the off-diagonal ***F*** elements has a noticeable effect on the eigenvectors. Resultant total electronic expectation values are little affected however.

Since the Ruedenberg approximation becomes more accurate the more extensive the basis set used in (8), we expect the present simple SCF method to show an even more satisfactory performance in calculations using bases more extended than the present minimal basis sets. We hope to report on this indue course. But even for minimal basis sets the present simple procedure, much more economical of computer time than the corresponding exact calculation, gives results of very adequate accuracy and offers a more palateable path to STO calculations on larger molecules. The use of the Löwdin-orbital-based NDDO simplification also leads to considerable reduction in the magnitude of configuration-interaction calculations.

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