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An Approximate *ab initio* SCFMO Method

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An approximate SCFMO method of calculation is presented which includes several features which are new to this type of approach. A minimal basis set of Slater type orbitals is used, and all integrals are included, but are evaluated approximately, using a series of analytical formulae which have been chosen to reproduce the rigorous values of the integrals. Results are given for the ground states of the H_2O, CH_4, BH_3, NH_3 and BeH_2 molecules, and are compared with previously calculated results.

Eine Näherungs-SCF-MO-Rechnung mit einigen neuen Abänderungen wird vorgeschlagen. Eine minimale Basis von Slater-Orbitalen wird benutzt; es werden alle Integrale berücksichtigt, jedoch nur näherungsweise berechnet, wobei eine Reihe von analytischen Formeln benutzt wird, welche die exakten Werte der Integrale möglichst reproduzieren sollen. Ergebnisse für den Grundzustand von H_2O, CH_4, BH_3, NH_3 und BeH_2 werden mit früher berechneten Ergebnissen verglichen.

Présentation d'une méthode SCF MO approchée comportant certaines caractéristiques nouvelles pour une telle méthode. On emploie une base minimale d'orbitales de Slater en ne négligeant aucune intégrale, mais en évaluant chaque intégrale d'une manière approchée au moyen d'une série de formules analytiques calibrées de manière à reproduire les valeurs exactes des intégrales. Les résultats obtenus pour les états fondamentaux de H_2O, CH_4, BH_3, NH_3 et BeH_2 sont comparés à ceux obtenus auparavant.

Introduction

Within the last ten years, a large number of molecular orbital calculations have been published for a wide variety of molecules with widely differing degrees of accuracy. Generally these fall into two main groups:

(i) *ab initio* calculations [1, 2] capable of high accuracy, but requiring a large expenditure of time and effort, and

(ii) semi-empirical calculations [3–6] of rather indefinite accuracy which may be computed rapidly.

In the present work, an attempt has been made to bridge this large gap with an approximate *ab initio* all integral method, which contains no empirical or adjustable parameters. In the early days of molecular orbital calculations when three- and four-centre integrals could not be evaluated accurately, such methods as the Mulliken [7, 8], Sklar [9], point charge [10] and uniform sphere approximations [10, 11] were discussed and widely used. However at that time, no single approximation was found that was reasonably accurate and universally applicable. The present method has been developed with the aid of accurate values for comparison, and appears likely to fulfil these two conditions, and to permit the calculation of molecular wave functions of reasonable accuracy at quite high speed.

Methods of Calculation

The essential features of the calculation method are:

A. Basis Functions

Aminimal basis set of Slater type orbitals is used. Since the aim of this work is to approximate the results of more rigorous calculations, the same orbital exponents (usually those given by Slater's rules [12]), will be used.

B. Evaluation of Integrals

All integrals are included, and are evaluated in the following way:

(i) Overlap and kinetic energy integrals are calculated exactly.

(ii) Each 2-centre overlap charge distribution $|\phi_a \phi_b\rangle$ involved in either nuclear attraction or electron repulsion integrals is replaced by a set of 1-centre charge distributions $|nS_{\mathrm{A}}\rangle$, $|nP_{\mathrm{A}}\rangle$, $|nD_{\mathrm{A}}\rangle$ with symmetry as indicated, centred at A. The points A and C are taken as the centres of charge of the overlap distributions $|\phi_a \phi_b\rangle$ and $|\phi_c \phi_d\rangle$ respectively.

$$\boldsymbol{r}_{\mathrm{A}} = (\zeta_a \boldsymbol{r}_a + \zeta_b \boldsymbol{r}_b)/(\zeta_a + \zeta_b) \tag{1}$$

where $\boldsymbol{r}_{\mathrm{A}}$, $\boldsymbol{r}_a$ and $\boldsymbol{r}_b$ are position vectors, ζ_a, ζ_b are effective weights given by

$$\zeta_a = \frac{\xi_a}{n_a - l_a}. \tag{2}$$

Here ξ, n and l are respectively the exponent and the quantum numbers of the Slater type atomic orbital (n, l, m) centred at the point a,

$$(n, l, m) = N r^{n-1}\, Y_{l,m}(\theta, \phi) \exp(-\xi r)$$

Table 1. *Magnitudes of the 1-centre charge distributions centred at* A *of given symmetry for each 2-centre overlap distribution. The atomic orbital and charge distribution classifications* σ, π, $\bar{\pi}$ *and* Σ, Π, $\bar{\Pi}$, Δ *are now defined relative to the axis* AC, *where* C *is either the nucleus (for nuclear attraction integrals) or the centre of the other charge distribution (for electron repulsion integrals)*

2-centre distributions	Magnitudes of 1-centre distributions		
	$\vert S_{\mathrm{A}}\rangle$	$\vert P_{\mathrm{A}}\rangle$	$\vert D_{\mathrm{A}}\rangle$
$\vert n s_a n' s_b\rangle$	$S_{ab}^{ss} \vert N S_{\mathrm{A}}\rangle$ [a]	0	0
$\vert 2p\sigma_s 1s_b\rangle$	$S_{ab}^{\sigma s} \vert 1S_{\mathrm{A}}\rangle$	$\frac{2}{\sqrt{3}} S_{ab}^{ss} \vert 2P\Sigma_{\mathrm{A}}\rangle$	0
$\vert 2p\pi_a 1s_b\rangle$	0	$\frac{2}{\sqrt{3}} S_{ab}^{ss} \vert 2P\Pi_{\mathrm{A}}\rangle$	0
$\vert 2p\sigma_a 2s_b\rangle$	$S_{ab}^{\sigma s} \vert 2S_{\mathrm{A}}\rangle$	$2\frac{5}{2\sqrt{3}} S_{ab}^{ss} \vert 3P\Sigma_{\mathrm{A}}\rangle$	0
$\vert 2p\pi_a 2s_b\rangle$	0	$2\frac{5}{2\sqrt{3}} S_{ab}^{ss} \vert 3P\Pi_{\mathrm{A}}\rangle$	0
$\vert 2p\sigma_a 2p\sigma_a\rangle$	$S_{ab}^{\sigma\sigma} \vert 3S_{\mathrm{A}}\rangle$	$(S_{ab}^{\sigma s} + S_{ab}^{s\sigma}) \vert 2P\Sigma_{\mathrm{A}}\rangle$	$3S_{ab}^{ss} \vert 3D\Sigma_{\mathrm{A}}\rangle$
$\vert 2p\pi_a 2p\sigma_a\rangle$	0	$S_{ab}^{s\sigma} \vert 2P\Pi_{\mathrm{A}}\rangle$	$\frac{3}{2}\sqrt{3}\, S_{ab}^{ss} \vert 3D\Pi_{\mathrm{A}}\rangle$
$\vert 2p\pi_a 2p\pi_b\rangle$	$S_{ab}^{\pi\pi} \vert 3S_{\mathrm{A}}\rangle$	0	$(-\frac{3}{2} \vert 3D\Sigma_{\mathrm{A}}\rangle + \frac{3}{2}\sqrt{3} \vert 3D\Delta_{\mathrm{A}}\rangle) S_{ab}^{ss}$
$\vert 2p\pi_a 2p\bar{\pi}_b\rangle$	0	0	$\frac{3}{2}\sqrt{3}\, S_{ab}^{ss} \vert 3D\Delta_{\mathrm{A}}\rangle$

[a] $N = (n + n' - 1)$

$S_{ab}^{ss} = (s_a | s_b) : S_{ab}^{\sigma s} = (p\sigma_a | s_b) : S_{ab}^{\sigma\sigma} = (p\sigma_a | p\sigma_b) : S_{ab}^{\pi\pi} = (p\pi_a | p\pi_b)$.

where the functions $Y_{l,m}(\theta, \phi)$ are the spherical harmonics and N is a normalisation factor.

The magnitude of these 1-centre charge distributions is given by a series of overlap integrals, as shown in Table 1. This resembles the point charge approximation, as outlined by Ellison [10], but contrasts with the recent PDDO Method of Newton, Ostlund and Pople [13].

Using a modification of Roothaan's notation, nuclear attraction and electronic repulsion integrals involving only p-type atomic orbitals are shown in (3) and (4).

$$\begin{aligned}\int \phi_a^{p\sigma*}(1)\frac{1}{r_\mathrm{C}}\,\phi_b^{p\sigma}(1)\,d\tau_1 &\equiv [\mathrm{C}|p\sigma_a p\sigma_b] \\ &= S_{ab}^{\sigma\sigma}[\mathrm{C}|3S_\mathrm{A}] + (S_{ab}^{\sigma s}+S_{ab}^{s\sigma})\,[\mathrm{C}|2P\Sigma_\mathrm{A}] + 3S_{ab}^{ss}[\mathrm{C}|3D\Sigma_\mathrm{A}]\end{aligned} \tag{3}$$

$$\begin{aligned}&\int \phi_{ab}^{p\sigma*}(1)\,\phi_b^{p\sigma*}(1)\frac{1}{r_{12}}\,\phi_c^{p\sigma}(2)\,\phi_d^{p\sigma}(2)\,d\tau_1\,d\tau_2 \equiv [p\sigma_a p\sigma_b|p\sigma_c p\sigma_d] \\ &= S_{ab}^{\sigma\sigma}[S_{cd}^{\sigma\sigma}[3S_\mathrm{A}|3S_\mathrm{C}] + (S_{cd}^{\sigma s}+SS_{cd}^{s\sigma})\,[3S_\mathrm{A}|2P\Sigma_\mathrm{C}] + 3S_{cd}^{ss}[3S_\mathrm{A}|3D\Sigma_\mathrm{C}]] \\ &+ (S_{ab}^{\sigma s}+S_{ab}^{s\sigma})[S_{cd}^{\sigma\sigma}[2P\Sigma_\mathrm{A}|3S_\mathrm{C}] + (S_{cd}^{\sigma s}+S_{cd}^{s\sigma})[2P\Sigma_\mathrm{A}|2P\Sigma_\mathrm{C}] + 3S_{cd}^{ss}[2P\Sigma_\mathrm{A}|3D\Sigma_\mathrm{C}]] \\ &+ 3S_{ab}^{ss}[S_{cd}^{\sigma\sigma}[3D\Sigma_\mathrm{A}|3S_\mathrm{C}] + (S_{cd}^{\sigma s}+S_{cd}^{s\sigma})\,[3D\Sigma_\mathrm{A}|2P\Sigma_\mathrm{C}] + 3S_{cd}^{ss}[3D\Sigma_\mathrm{A}|3D\Sigma_\mathrm{C}]]\,.\end{aligned} \tag{4}$$

Integrals involving one or more s-type atomic orbitals are correspondingly simplified.

(iii) The resulting 1- and 2-centre integrals are evaluated approximately. Various functions have been used in previous calculations, notably those due to Ohno [15]

$$[\Phi_\mathrm{A}|\Phi_\mathrm{C}] = \frac{1}{(a^2+R_\mathrm{AC}^2)^{\frac{1}{2}}} \tag{5a}$$

and Mataga [16]

$$[\Phi_\mathrm{A}|\Phi_\mathrm{C}] = \frac{1}{a+R_\mathrm{AC}} \tag{5b}$$

for Coulomb integrals in Pariser-Parr-Pople calculations of aromatic hydrocarbons. The present work uses a generalised function of the form

$$F(R) = \frac{bR^x}{(a_1+a_2R-\frac{1}{3}a_3R^2+R^3)^{y/3}} \tag{6}$$

for both nuclear attraction and Coulomb integrals. It has the correct value at $R=0$ (or the correct first non-zero derivative if $F(0)=0$), which is determined by a_1, and has the correct dependence on R, viz. R^{x-y}, as R becomes infinite. The parameters a_2 and a_3 are chosen to give a good fit to the accurately calculated integrals for intermediate values of R. The values of these constants for the different nuclear attraction integrals are given in Table 2, and for Coulomb integrals in Table 3.

Hybrid electron repulsion integrals are given by a slightly different formula

$$F_\mathrm{H}(R) = \frac{bR^x}{(a_1+(a_2+1)R-\frac{1}{3}a_3R^2+R^3)^{y/3}} \tag{7}$$

Table 2. *Values of the parameters in Eq. (6) for nuclear attraction integrals involving different charge distributions*

Integral	x	y	a_1	a_2	a_3	b
1-centre						
$[C\|nS_A]$	0	1	$[(n+1)/2]^3$	1.0	$(n+1)/2$	1.0
$[C\|2P\Sigma_A]$	1	3	3.0	2.0	1.5	1.0
$[C\|3P\Sigma_A]$	1	3	7.5	2.0	2.0	1.0
$[C\|3D\Sigma_A]$	2	5	$(22.5)^{3/5}$	3.0	2.0	1.0
2-centre						
$[C\|nS_A]$	0	1	$[(n+1)/2]^3$	1.5	1.5	1.0
$[C\|2P\Sigma_A]$	1	3	3.0	1.5	1.5	1.0
$[C\|3P\Sigma_A]$	1	3	7.5	2.0	1.5	1.0
$[C\|3D\Sigma_A]$	2	5	$(22.5)^{3/5}$	3.0	1.5	1.0

Table 3a. *Values of the parameters in Eq. (6) for Coulomb integrals involving different charge distributions*

Integral	x	y	a_1	a_2	a_3	b
$[nS_A\|mS_C]$	0	1	see Table 3b	1.5	1.5	1.0
$[nP\Sigma_A\|mS_C]$	1	3		3.0	3.0	$\frac{1}{1+\tau}$
$[nP\Pi_A\|mP\Pi_C]$	0	3		3.0	2.0	$\frac{1}{(1-\tau^2)}$
$\Delta(nP\|mP)^a$	2	5		4.0	3.0	
$[3D\Sigma_A\|nS_C]$	2	5		4.0	3.0	$\frac{1}{(1+\tau)^2}$
$[3D\Pi_A\|nP\Pi_C]$	1	5		4.0	3.0	$\frac{1}{(1+\tau)^2(1-\tau)}$
$\Delta(3D\|nP)^b$	3	7		5.0	4.0	
$[3D\Delta_A\|3D\Delta_C]$	0	5		4.0	3.0	$\frac{1}{(1-\tau^2)^2}$
$\Delta_1(3D\|3D)^c$	2	7		5.0	4.0	
$\Delta_2(3D\|3D)^d$	4	9		6.0	5.0	

[a] $[nP\Sigma_A|mP\Sigma_C] = [nP\Pi_A|mP\Pi_C] - 3\Delta(nP|mP)$.
[b] $[3D\Sigma_A|nP\Sigma_C] = [3D\Pi_A|nP\Pi_C] + 5\Delta(3D|nP)$.
[c] $[3D\Pi_A|3D\Pi_C] = [3D\Delta_A|3D\Delta_C] + 5\Delta_1(3D|3D)$.
[d] $[3D\Sigma_A|3D\Sigma_C] = [3D\Delta_A|3D\Delta_C] - 6.1\Delta_1(3D|3D) + 11.1\Delta_2(3D|3D)$.

where the parameters are the same as for the analogous Coulomb integrals.

Exchange integrals, especially 2-centre integrals, are overestimated by either the above approximations A better result is obtained by taking the mean of the value given by the first approximation (6) and the value given by the Mulliken [7] approximation (8).

$$[\phi_a\phi_b|\phi_c\phi_d] \cong \frac{S_{ab}S_{cd}}{4}\left[[\phi_a\phi_a|\phi_c\phi_c] + [\phi_a\phi_a|\phi_d\phi_d] + [\phi_b\phi_b|\phi_c\phi_c] + [\phi_b\phi_b|\phi_d\phi_d]\right]. \tag{8}$$

(iv) There are a small number of exceptions and modifications to the general procedures that are necessary to obtain more accurate results.

Table 3b. *Values of the parameter* a_1 *in Eq. (6) for Coulomb integrals involving different charge distributions* $[\tau = (\xi_a - \xi_b)/(\xi_a + \xi_b)]$

Integral	a_1
$[1S_A \vert 1S_C]$	$[8/(1-\tau^2)(5-\tau^2)]^3$
$[2S_A \vert 1S_C]$	$[48/(1-\tau^2)(25+7\tau-5\tau^2-3\tau^3)]^3$
$[2S_A \vert 2S_C]$	$[24/(1-\tau^2)(11-4\tau^2+\tau^4)]^3$
$[2P\Sigma_A \vert 1S_C]$	$48/(1-\tau^2)^3(5+3\tau)$
$[2P\Sigma_A \vert 2S_C]$	$48/(1-\tau^2)^3(3-\tau-2\tau^2)$
$[2P\Sigma_A \vert 3S_C]$	$192/(1-\tau^2)^3(7-9\tau-3\tau^2+5\tau^3)$
$[2P\Pi_A \vert 2P\Pi_C]$	$96/(1-\tau^2)^2(7-3\tau^2)$
$[3P\Pi_A \vert 2P\Pi_C]$	$960/(1-\tau^2)^2(49+27\tau-21\tau-15\tau^3)$
$[3P\Pi_A \vert 3P\Pi_C]$	$960/(1-\tau^2)^2(37-30\tau^2+9\tau^4)$
$[3D\Sigma_A \vert 1S_C]$	$[360(1-\tau)/(1-\tau^2)^5(3+2\tau)]^{3/5}$
$[3D\Sigma_A \vert 2S_C]$	$[1080(1-\tau)/(1-\tau^2)^5(4-4\tau-5\tau^2)]^{3/5}$
$[3D\Sigma_A \vert 3S_C]$	$[1440(1-\tau)/(1-\tau^2)^5(2-7\tau+5\tau^3)]^{3/5}$
$[3D\Pi_A \vert 2P\Pi_C]$	$[1440/(1-\tau^2)^5(7+5\tau)]^{3/5}$
$[3D\Pi_A \vert 3P\Pi_C]$	$[1440/(1-\tau^2)^5(4-\tau+3\tau^2)]^{3/5}$
$[3D\Delta_A \vert 3D\Delta_C]$	$[2880/(1-\tau^2)^5(9-5\tau^2)]^{3/5}$
$[3S_A \vert 1S_C]$	$[32/(1-\tau^2)(14+7\tau-\tau^2-3\tau^3-\tau^4)]^3$
$[3S_A \vert 2S_C]$	$[192/(1-\tau^2)(77+19\tau-28\tau^2-16\tau^3+7\tau^4+5\tau^5]^3$
$[3S_A \vert 3S_C]$	$[256/(1-\tau^2)(93-47\tau^2+23\tau^4-5\tau^6)]^3$
$[3P\Sigma_A \vert 1S_C]$	$120/(1-\tau^2)^3(8+9\tau+3\tau^2)$
$[3P\Sigma_A \vert 2S_C]$	$240/(1-\tau^2)^3(11+3\tau-9\tau^2-5\tau^3)$
$[3P\Sigma_A \vert 3S_C]$	$960/(1-\tau^2)^3(29-18\tau-36\tau^2+10\tau^3+15\tau^4)$
$\Delta(2P \vert 2P)$	$[120/(1-\tau^2)^5]^{5/3}$
$\Delta(3P \vert 2P)$	$[240/(1-\tau^2)^5(1+\tau)]^{5/3}$
$\Delta(3P \vert 3P)$	$[400/(1-\tau^2)^5(1-\tau^2)]^{5/3}$
$\Delta(3D \vert 2P)$	$2520^{3/7}$
$\Delta(3D \vert 3P)$	$6300^{3/7}$

(a) If the parameter $\tau = (\xi_a - \xi_b)/(\xi_a + \xi_b)$ is large (i.e. if 1*s* atomic orbitals on the heavy atom (N) are involved), the value of the integral is determined less by the charge in the region of large overlap A given by (1) than by the charge closer to the nucleus N. This may be approximated by moving A closer to N to A′ where

$$r_{A'} - r_N = (1 - \tau^2)(r_A - r_N). \tag{9}$$

(b) Three-centre integrals of the type $[C \vert \phi_a \phi_b]$ or $[\phi_c \phi_c \vert \phi_a \phi_b]$ where $R_{AC} < 0.25\,(R_{ac} + R_{bc})$ are overestimated by these approximations. A better result is obtained by taking the mean of the normal result and the value given by the Mulliken approximation (8). Examples of these integrals are those involving orbitals on two H atoms, and the nucleus or orbitals of the central atom in such molecules as H_2O and CH_4.

C. Determination of Molecular Orbitals

Once the integrals have been calculated, the normal Roothaan [2] procedure is used to calculate the closed shell Hamiltonian matrix elements, and to solve the pseudo-eigenvalue equation iteratively until a self-consistent result is obtained.

Table 4a. *Number of integrals of magnitude I whose error lies in the range E*

H_2O-*nuclear attraction integrals*

Magnitude of integral (a.u.) (I)	Error range % (*E*)						Total
	$E=0$	$0<E<1$	$1<E<2$	$2<E<5$	$5<E<10$	$E>10$	
$I>1.0$	8	11					19
$0.1<I<1.0$	2	10	10	6	2		30
$0.01<I<0.1$		4	2	4	2		12
$I<0.01$							0
$I=0$	23						23
Total	33	25	12	10	4	0	84

Electron repulsion integrals

Magnitude of integral (a.u.) (I)	$E=0$	$0<E<1$	$1<E<2$	$2<E<5$	$5<E<10$	$E>10$	Total
$I>0.5$	18	2					20
$0.1<I<0.5$	10	34	8	17	5		74
$0.01<I<0.1$	11	16	16	15	10	25	93
$I<0.01$			2	4	6	29	41
$I=0$	178						178
Total	217	52	26	36	21	54	406

Table 4b. *Number of integrals of magnitude I whose error lies in the range E*

CH_4-*nuclear attraction integrals*

Magnitude of integral (a.u.) (*I*)	Error % (*E*)						Total
	$E=0$	$0<E<1$	$1<E<2$	$2<E<5$	$5<E<10$	$E>10$	
$I\geqq 1.0$	10	14		4			28
$0.1<I<1.0$	8	44	24	36			112
$0.01<I<0.1$		12		64			76
$I<0.01$							0
$I=0$	9						9
Total	27	70	24	104	0	0	225

Electron repulsion integrals

Magnitude of integral (a.u.) (*I*)	$E=0$	$0<E<1$	$1<E<2$	$2<E<5$	$5<E<10$	$E>10$	Total
$I\geqq 0.5$	19						19
$0.1<I<0.5$	8	118	52	36			214
$0.01<I<0.1$	10	58	78	106	112	135	499
$I<0.01$				12	36	114	162
$I=0$	141						141
Total	178	176	130	154	148	249	1035

Initial molecular orbital coefficients of the correct symmetry and approximately correct magnitude are obtained by using the eigenvectors of the matrix of overlap integrals.

Accuracy of Integral Approximations

The accuracy of this method is difficult to assess, because the error in a particular integral varies with the internuclear distance, and with the relative magnitudes of the orbital exponents. Table 4 shows a summary of a comparison of the ap-

Table 5

H_2O	$R(O\text{–}H)=0.958$ Å, $H\hat{O}H=105$ degrees
Exponents	$1s(H)=1.0$, $1s(O)=7.7$, $2s(O)=2p(O)=2.275$
Geometry	$H_1=(0.760008, 0.0, 0.583169)$, $H_2=(-0.760008, 0.0, 0.583169)$ $O=(0.0, 0.0, 0.0)$

Hamiltonian matrix

	H_1	H_2	O_{1s}	O_{2s}	O_{2pz}	O_{2px}	O_{2py}
H_1	−0.697						
H_2	−0.456	−0.697					
O_{1s}	−1.368	−1.368	−20.576				
O_{2s}	−1.154	−1.154	− 5.063	−2.388			
O_{2pz}	−0.367	−0.367	− 0.030	−0.110	−0.401		
O_{2px}	−0.341	0.341	—	—	—	−0.278	
O_{2py}	—	—	—	—	—	—	−0.413

	Present work	*Exact integral calculation* [18]
E (total)	− 75.7226	−75.6812
E (kin)	76.2836	
E (pot)	−152.0062	

Molecular orbitals

E	−20.579	−1.3068	−0.6337	−0.4802	−0.4128	−20.481	−1.3015	−0.6387	−0.4590	−0.4204
Symm.	a_1	a_1	b_1	a_1	b_2	a_1	a_1	b_1	a_1	b_2

Coefficients

H_1	−0.0016	−0.1798	0.5626	0.2221	—	−0.0042	0.1719	0.5236	0.2112	—
H_2	−0.0016	0.1798	−0.5626	0.2221	—	−0.0042	0.1719	−0.5236	0.2112	—
O_{1s}	0.9964	−0.2201	—	0.0920	—	0.9960	−0.2202	—	0.0940	—
O_{2s}	0.0158	0.7931	—	−0.4986	—	0.0188	0.7999	—	0.4981	—
O_{2pz}	0.0022	0.1251	—	0.8322	—	0.0034	0.1446	—	0.8377	—
O_{2px}	—	—	0.5264	—	—	—	—	0.5716	—	—
O_{2py}	—	—	—	—	1.0	—	—	—	—	1.0

Population analysis

	Present work	*Exact integral calculation* [18]
H	0.901	0.828
O_{1s}	1.999	1.998
O_{2s}	1.724	1.747
O_{2pz}	1.593	1.616
O_{2px}	0.881	0.984
O_{2py}	2.000	2.000
O–H	0.559	0.562

proximate integrals with the accurately calculated values for the H_2O and CH_4 molecules[1].

However the best means of checking the accuracy of the present method lies in a comparison of the wavefunctions with previously reported results. One of the

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[1] We are grateful to Prof. R. M. Pitzer for supplying the list of exact integrals for H_2O and CH_4.

Table 6

CH_4	$R(C\text{–}H) = 1.0935$ Å
Exponents	$1s(H) = 1.2$, $1s(C) = 5.7$, $2s(C) = 2p(C) = 1.625$
Geometry	$H_1 =$ (0.631352, 0.631352, 0.631352), $H_2 =$ (0.631352, −0.631352, −0.631352), $H_3 =$ (−0.631352, 0.631352, −0.631352), $H_4 =$ (−0.631352, −0.631352, 0.631352), $C =$ (0.0, 0.0, 0.0)

Hamiltonian matrix

			H_1	H_2	H_3	H_4	C_{1s}	C_{2s}	C_{2p}
H_1	−0.575		−0.507	−0.274	− 0.274	−0.274	− 0.730	−0.787	±0.253
H_2	−0.273	−0.575		−0.507	− 0.274	−0.274	− 0.730	−0.787	±0.253
H_3	−0.273	−0.273	−0.575		− 0.507	−0.274	− 0.730	−0.787	±0.253
H_4	−0.273	−0.273	−0.273	−0.575		−0.507	− 0.730	−0.787	±0.253
C_{1s}	−0.732	−0.732	−0.732	−0.732	−11.444		−11.268	−2.640	—
C_{2s}	−0.793	−0.793	−0.793	−0.793	− 2.678	−1.434		−1.432	—
C_{2p}	±0.247	±0.247	±0.247	±0.247	—	—	−0.360		−0.349

Wavefunction

	Present work	*Exact integral calculation* [17]
E (total)	−40.0776	−40.1141
E (kin)	39.3224	39.9045
E (pot)	−79.4000	−80.0185

Molecular orbitals

E	−11.4531	−1.0098	−0.5616	−11.2714	−0.9320	−0.5418
Symm.	a_1	a_1	t_1	a_1	a_1	t_1

Coefficients

H	−0.0165	0.1941	±0.3110	−0.0057	0.1590	±0.2850
C_{1s}	0.9932	−0.1856	—	0.9953	−0.2012	—
C_{2s}	0.0489	0.5782	—	0.0257	0.6644	—
C_{2p}	—	—	0.5479	—	—	0.5943

Population analysis

	Present work	*Exact integral calculation* [17]
H	0.988	0.867
C_{1s}	1.988	1.996
C_{2s}	1.108	1.274
C_{2p}	0.984	1.088
C–H	0.792	0.780

most complete collections of information on some SCF calculations for a number of small molecules remains that of Palke and Lipscomb [17], and an attempt was made to reproduce some of their results in detail, using the same orbital exponents. In Tables 5–9, the geometries and orbital exponents are given, and a comparison is made of the Hamiltonian matrix, wave function and population analysis. (Where the Hamiltonian matrix is available for comparison, it is given in the upper triangle, and that of the present work is in the lower triangle.)

Table 7

BH_3 R(B–H) = 1.190637 Å, $H\hat{B}H$ – 120 degrees
Exponents 1*s*(H) = 1.2, 1*s*(B) = 4.7, 2*s*(B) = 2*p*(B) = 1.3
Geometry H_1 = (1.190637, 0.0, 0.0), H_2 = (−0.595319, 1.031122, 0.0)
H_3 = (−0.595319, −1.031122, 0.0), B = (0.0, 0.0, 0.0)

Hamiltonian matrix

			H_1	H_2	H_3	B_{1s}	B_{2s}	B_{2px}	B_{2py}	B_{2pz}
H_1	−0.488		−0.465	−0.176	−0.176	−0.584	−0.569	−0.406	—	—
H_2	−0.169	−0.488		−0.465	−0.176	−0.584	−0.569	0.203	−0.352	—
H_3	−0.169	−0.169	−0.488		−0.465	−0.584	−0.569	0.203	0.352	—
B_{1s}	−0.508	−0.508	−0.508	−7.718		−7.677	−1.719	—	—	—
B_{2s}	−0.571	−0.571	−0.571	−1.733	−0.946		−0.969	—	—	—
B_{2px}	−0.421	0.210	0.210	—	—	−0.352		−0.345	—	—
B_{2py}	—	−0.364	0.364	—	—	—	−0.352		−0.345	—
B_{2pz}	—	—	—	—	—	—	—	0.109		0.114

Wavefunction

	Present work	*Exact integral calculation* [17]
E (total)	−26.4259	−26.3377
E (kin)	25.8953	26.1784
E (pot)	−52.3212	−52.5161

Molecular orbitals

E	−7.7277	−0.7358	−0.5300		−7.6795	−0.7120	−0.5104	
Symm.	a_1'	a_1'	e'		a_1'	a_1'	e'	

Coefficients

H_1	−0.0026	0.2803	0.4790	—	−0.0048	0.2457	0.4614	—
H_2	−0.0026	0.2803	−0.2395	0.4148	−0.0048	0.2457	−0.2307	0.3996
H_3	−0.0026	0.2803	−0.2395	−0.4148	−0.0048	0.2457	−0.2307	−0.3996
B_{1s}	0.9935	−0.1749	—	—	0.9960	−0.1902	—	—
B_{2s}	0.0547	0.5307	—	—	0.0233	0.5932	—	—
B_{2px}	—	—	0.5312	—	—	—	0.5545	—
B_{2py}	—	—	—	0.5312	—	—	—	0.5545
B_{2pz}	—	—	—	—	—	—	—	—

Population analysis

	Present work	*Exact integral calculation* [17]
H	1.017	0.943
B_{1s}	1.987	1.997
B_{2s}	0.998	1.121
B_{2px}	0.982	1.027
B_{2pz}	0.0	0.0
B–H	0.832	0.837

Computation Times

It is difficult to make a meaningful estimate of computation times based on the molecules studied, because of their small size and close similarity. Total times for calculating all integrals for H_2O and CH_4 were approximately 0.20 and

Table 8

NH_3 R(N–H) = 1.012 Å, $H\hat{N}H$ = 106.7 degrees

Exponents 1s(H) = 1.2, 1s(N) = 6.7, 2s(N) = 2p(N) = 1.95

Geometry H_1 = (0.937110, 0.0, 0.380856), H_2 = (−0.468555, 0.811561, 0.380856),
H_3 = (−0.468555, −0.811561, 0.380856), N = (0.0, 0.0, 0.0)

Hamiltonian matrix

			H_1	H_2	H_3	N_{1s}	N_{2s}	N_{2pz}	N_{2px}	N_{2py}
H_1	−0.629		−0.563	−0.348	−0.348	−1.008	−0.887	−0.221	−0.434	—
H_2	−0.346	−0.629		−0.563	−0.348	−1.008	−0.887	−0.221	0.217	−0.375
H_3	−0.346	−0.346	−0.629		−0.563	−1.008	−0.887	−0.221	0.217	0.375
N_{1s}	−0.973	−0.973	−0.973	−15.681		−15.519	−3.742	−0.025	—	—
N_{2s}	−0.962	−0.962	−0.962	−3.779	−1.854		−1.859	−0.119	—	—
N_{2pz}	−0.204	−0.204	−0.204	−0.023	−0.097	−0.406		−0.356	—	—
N_{2px}	−0.379	0.189	0.189	—	—	—	−0.333		−0.328	—
N_{2py}	—	−0.328	0.328	—	—	—	—	−0.333		−0.328

Wavefunction

	Present work	*Exact integral calculation* [17]
E (total)	−55.8722	−56.0052
E (kin)	55.7152	56.3959
E (pot)	−111.5874	−112.4011

Molecular orbitals

E	−15.585	−1.1573	−0.5628		−0.3989	−15.523	−1.1014	−0.5824		−0.3661
Symm.	a_1	a_1	e		a_1	a_1	a_1	e		a_1

Coefficients

H_1	−0.0098	0.1967	0.5496	—	0.0578	−0.0050	0.1554	0.5034	—	0.1247
H_2	−0.0098	0.1967	−0.2748	0.4756	0.0578	−0.0050	0.1554	−0.2517	0.4359	0.1247
H_3	−0.0098	0.1967	−0.2748	−0.4756	0.0578	−0.0050	0.1554	−0.2517	−0.4359	0.1247
N_{1s}	0.9949	−0.1977	—	—	0.0611	0.9957	−0.2096	—	—	0.0830
N_{2s}	0.0294	0.6645	—	—	−0.2987	0.0225	0.7390	—	—	−0.4506
N_{2pz}	0.0062	0.0908	—	—	0.9492	0.0041	0.1375	—	—	0.8921
N_{2px}	—	—	0.5414	—	—	—	—	0.5901	—	—
N_{2py}	—	—	—	0.5414	—	—	—	—	0.5901	—

Population analysis

	Present work	*Exact integral calculation* [17]
H	0.955	0.845
N_{1s}	1.999	1.997
N_{2s}	1.361	1.598
N_{2pz}	1.883	1.760
N_{2px}	0.946	1.056
N–H	0.743	0.677

0.35 minutes respectively (0.10 and 0.15 minutes for 1-electron integrals, 0.10 and 0.20 minutes for 2-electron integrals). Approximately 10 iterations were necessary to get each m.o. energy correct to 4 figures and approximately 0.03 and 0.04 minutes respectively were required for each SCF iteration. All times refer to an IBM 360/50 programmed in Fortran.

Table 9

BeH_2	R(Be–H) = 1.4166 Å, $\mathrm{H\hat{B}eH}$ = 180 degrees
Exponents	1s(H) = 1.0, 1s(Be) = 3.7, 2s(Be) = 2p(Be) = 1.0
Geometry	H^1 = (0.0, 0.0, 1.416600), H_2 = (0.0, 0.0, −1.416600), Be = (0.0, 0.0, 0.0)

Hamiltonian matrix

	H_1	H_2	Be_{1s}	Be_{2s}	Be_{2pz}	Be_{2px}	Be_{2py}
H_1	−0.446						
H_2	−0.107	−0.446					
Be_{1s}	−0.348	−0.348	−4.760				
Be_{2s}	−0.412	−0.412	−1.039	−0.548			
Be_{2pz}	−0.318	0.318	—	—	−0.335		
Be_{2px}	—	—	—	—	—	0.087	
Be_{2py}	—	—	—	—	—	—	0.087

Wavefunction

	Present work	*Exact integral calculation* [19]
E (total)	−15.7586	−15.7123
E (kin)	15.3330	15.6362
E (pot)	−31.0916	−31.3485

Molecular orbitals

E	−4.7654	−0.5194	−0.4502	−4.7701	−0.4980	−0.4373
Symm.	σ_g	σ_g	σ_u	σ_g	σ_g	σ_u

Coefficients

H_1	−0.0284	0.4875	0.4156
H_2	−0.0284	0.4875	−0.4156
Be_{1s}	0.9945	−0.1506	—
Be_{2s}	0.0468	0.3634	—
Be_{2pz}	—	—	0.4825

Population analysis

	Present work
H	1.228
Be_{1s}	1.988
Be_{2s}	0.642
Be_{2pz}	0.914
Be–H	0.792

Times quoted by Aung, Pitzer, and Chan [20] for H_2O (4 minutes on IBM 7094) suggest that the present method is faster than methods for exact calculation of integrals by at least an order of magnitude.

Summary

As shown in Tables 5–9, the accuracy of this calculation method varies for different molecules. The errors in the total energy, although large in absolute magnitude, are comparatively small, with a maximum value near 0.3 %. The wave functions, as shown by the population analysis, are reasonable, with molecular orbital energies accurate to approximately 5%. There is a consistent tendency to place too much charge (up to 0.1 of an electron) on the hydrogen atoms, but the bond overlap populations (with one exception) are correct to within 0.01 of an electron.

The advantage of this method, compared with an accurate *ab initio* calculation is the fast speed of computation, at the price of reduced accuracy. The advantage compared with a semi-empirical calculation is the increased credibility through inclusion of all integrals and the neglect of empirical parameters, at the price of reduced speed and simplicity. A further advantage is the possibility of using the present method for the calculation of approximate potential energy surfaces for molecules and chemical reactions. This is currently under investigation and preliminary results are encouraging.

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