

Self-Consistent Molecular Orbital Methods. VI. Energy Optimized Gaussian Atomic Orbitals

R. DITCHFIELD, W. J. HEHRE, AND J. A. POPLE

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 14 January 1970)

Minimal basis atomic orbitals expressed as sums of N Gaussian functions are presented for hydrogen and for the first row atoms boron to fluorine. The expansion coefficients and Gaussian exponents are determined by minimizing the total calculated energy of the atomic ground state. For expansion lengths of up to six Gaussians, two sets of atomic orbitals are reported. In the first set, which we describe as unconstrained, different Gaussian exponents are used for the $2s$ and $2p$ atomic orbitals. In the second set, the $2s$ and $2p$ atomic orbitals are constrained to share the same Gaussian exponents. It is shown that this constraint, which produces a significant gain in computational speed in molecular calculations, does not seriously reduce the quality of the atomic orbitals for given N . A comparison of the contracted sets presented here with previous studies on uncontracted basis sets for the first row atoms, shows that the uncontracted Gaussian exponents are a poor approximation to those of the contracted functions.

I. INTRODUCTION

Normalized Gaussian functions of the types

$$g_s(\alpha, \mathbf{r}) = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2),$$

$$g_{px}(\alpha, \mathbf{r}) = (128\alpha^5/\pi^3)^{1/4} x \exp(-\alpha r^2), \quad (1)$$

have been widely used in basis functions for linear combination of atomic orbital self consistent field (LCAO SCF) calculations on molecules. This followed the early work of Boys¹ showing how all the necessary integrals could be evaluated. In LCAO SCF theory,² each molecular orbital ψ_i is written in the form

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}, \quad (2)$$

where ϕ_{μ} are the basis functions and the coefficients $c_{\mu i}$ are varied to minimize the total electronic energy of a molecule. Sometimes the ϕ_{μ} have been taken directly as single Gaussian functions, but more commonly, they have been taken as *fixed* linear combinations of gaussians (sometimes known as contracted Gaussians).³

At the simplest level of LCAO SCF theory, the basis ϕ_{μ} consists of a minimal set of atomic orbitals (those which are populated in the ground state of the neutral atom). For organic molecules containing atoms no heavier than fluorine, such a set consists of a $1s$ function for hydrogen and $1s$, $2s$, $2p$ functions for boron, carbon, nitrogen, oxygen and fluorine. Each such atomic orbital can be written approximately as a contracted Gaussian function

$$\phi_{1s} = \sum_{i=1}^{N_{1s}} d_{1s,i} g_s(\alpha_{1s,i}, \mathbf{r}),$$

$$\phi_{2s} = \sum_{i=1}^{N_{2s}} d_{2s,i} g_s(\alpha_{2s,i}, \mathbf{r}),$$

$$\phi_{2p} = \sum_{i=1}^{N_{2p}} d_{2p,i} g_p(\alpha_{2p,i}, \mathbf{r}). \quad (3)$$

Minimal basis sets of this type have been used by several authors.^{4,5}

Various schemes have been proposed for the choice of Gaussian exponents α and contraction coefficients d . One possibility is to obtain a least-squares fit either to

TABLE I. Atomic orbitals for hydrogen ($1S$).

N	α_{1s}	d_{1s}	E
2	1.332480(+0)	2.744085(-1)	-0.485813
	2.015287(-1)	8.212254(-1)	
3	4.500225(+0)	7.047866(-2)	-0.496979
	6.812745(-1)	4.078893(-1)	
	1.513748(-1)	6.476689(-1)	
4	1.300773(+1)	1.968761(-2)	-0.499278
	1.962079(+0)	1.379689(-1)	
	4.445290(-1)	4.783139(-1)	
	1.219492(-1)	5.011038(-1)	
5	3.405432(+1)	6.026783(-3)	-0.499810
	5.122332(+0)	4.503430(-2)	
	1.164455(+0)	2.019221(-1)	
	3.271926(-1)	5.030515(-1)	
	1.030649(-1)	3.854084(-1)	
6	8.294860(+1)	1.996848(-3)	-0.499946
	1.245470(+1)	1.527935(-2)	
	2.833203(+0)	7.530596(-2)	
	7.999973(-1)	2.563387(-1)	
	2.585797(-1)	4.976459(-1)	
	8.996358(-2)	2.967368(-1)	
∞			-0.500000

single-exponential (Slater-type) functions⁶⁻⁸ or to more accurate representations of the correct (Hartree-Fock) atomic orbitals.⁹ Another procedure which has been used is selection of linear combinations of single Gaussians which had previously been chosen on the basis of energy optimization with a larger uncontracted basis

TABLE II. Unconstrained atomic orbitals for boron (2P).

N	α_{1s}	d_{1s}	α_{2s}	d_{2s}	α_{2p}	d_{2p}	E
2	3.140545(+1)	2.679579(-1)	4.514556(+0)	-7.204728(-2)	9.003765(-1)	3.305632(-1)	-23.794512
	4.493601(+0)	8.298996(-1)	1.892696(-1)	1.015312(+0)	1.638776(-1)	8.087126(-1)	
3	1.058307(+2)	7.027108(-2)	3.653065(+0)	-8.271356(-2)	2.548906(+0)	1.065666(-1)	-24.373007
	1.584172(+1)	3.941004(-1)	2.831874(-1)	6.098679(-1)	5.120810(-1)	4.581013(-1)	
	3.340571(+0)	6.659628(-1)	9.309538(-2)	4.655954(-1)	1.219411(-1)	6.307460(-1)	
4	3.042257(+2)	1.991855(-2)	1.575423(+1)	-9.642981(-3)	5.991286(+0)	3.547125(-2)	-24.491268
	4.585941(+1)	1.365792(-1)	3.257995(+0)	-9.446299(-2)	1.237401(+0)	1.982711(-1)	
	1.017633(+1)	4.611131(-1)	2.975132(-1)	5.808782(-1)	3.349874(-1)	5.057953(-1)	
	2.662993(+0)	5.256799(-1)	9.663106(-2)	5.023628(-1)	9.494719(-2)	4.788884(-1)	
5	7.894903(+2)	6.166626(-3)	1.075114(+1)	-1.445036(-2)	1.200029(+1)	1.318902(-2)	-24.519014
	1.187842(+2)	4.567576(-2)	2.807117(+0)	-9.445252(-2)	2.601383(+0)	8.026531(-2)	
	2.691899(+1)	1.984598(-1)	3.622380(-1)	3.917444(-1)	7.443944(-1)	2.779839(-1)	
	7.378115(+0)	4.869539(-1)	1.486747(-1)	5.230337(-1)	2.375202(-1)	5.045675(-1)	
	2.225609(+0)	4.118871(-1)	6.294368(-2)	1.808806(-1)	7.668705(-2)	3.523579(-1)	
∞							-24.529050

set.¹⁰⁻¹² A more satisfactory and direct procedure based on the calculation of a total atomic energy would be to use the atomic orbitals (3) directly and vary the α and d parameters until the energy is minimized. Such atomic orbitals exist for hydrogen¹³ and some transition metals,¹⁴ but no such study appears to have been published for first row atoms. (Closely related work by Whitten¹⁵ is concerned with a slightly larger set of ϕ functions). One of the purposes of the present paper is to present energy optimized forms of the atomic orbitals (3), each containing N Gaussian functions ($N_{1s} = N_{2s} =$

$N_{2p} = N$). Since each atomic orbital ϕ must be normalized, this involves minimization of the calculated energy with respect to $6N-3$ variables.

It has been noted previously⁷ that the efficiency of integral evaluation in molecular calculations is considerably improved if a p -basis function ϕ_p shares common Gaussian α exponents with one of the s -basis functions ϕ_s . This reduces the number of distinct error functions to be calculated and permits other improvements in computer program efficiency. For a minimal basis of atomic orbitals, sharing of Gaussian exponents

TABLE III. Unconstrained atomic orbitals for carbon (3P).

N	α_{1s}	d_{1s}	α_{2s}	d_{2s}	α_{2p}	d_{2p}	E
2	4.610255(+1)	2.669850(-1)	7.441596(+0)	-7.193301(-2)	1.531474(+0)	3.376222(-1)	-36.576765
	6.653506(+0)	8.300199(-1)	2.948745(-1)	1.014602(+0)	2.746815(-1)	8.051966(-1)	
3	1.552622(+2)	6.960382(-2)	5.793223(+0)	-8.215337(-2)	4.152398(+0)	1.124423(-1)	-37.453062
	2.328926(+1)	3.936907(-1)	4.472592(-1)	6.034712(-1)	8.464664(-1)	4.657363(-1)	
	4.948442(+0)	6.658730(-1)	1.440200(-1)	4.736710(-1)	1.981786(-1)	6.227623(-1)	
4	4.466221(+2)	1.967742(-2)	2.444207(+1)	-9.937562(-3)	9.428069(+0)	3.811267(-2)	-37.631716
	6.734026(+1)	1.355229(-1)	5.114090(+0)	-9.477617(-2)	1.997720(+0)	2.096638(-1)	
	1.498591(+1)	4.615983(-1)	4.688586(-1)	5.783725(-1)	5.439079(-1)	5.090003(-1)	
	3.944722(+0)	5.252413(-1)	1.486947(-1)	5.071269(-1)	1.511528(-1)	4.683674(-1)	
5	1.157968(+3)	6.092928(-3)	1.639284(+1)	-1.503645(-2)	1.867211(+1)	1.406610(-2)	-37.673560
	1.742169(+2)	4.521420(-2)	4.359020(+0)	-9.440515(-2)	4.123790(+0)	8.707472(-2)	
	3.950940(+1)	1.976763(-1)	5.829277(-1)	3.752337(-1)	1.197237(+0)	2.905790(-1)	
	1.086781(+1)	4.882354(-1)	2.382709(-1)	5.252502(-1)	3.818039(-1)	5.012192(-1)	
	3.292347(+0)	4.107026(-1)	9.805799(-2)	1.985425(-1)	1.205754(-1)	3.427061(-1)	
∞							-37.688612

TABLE IV. Unconstrained atomic orbitals for nitrogen (4S).

N	α_{1s}	d_{1s}	α_{2s}	d_{2s}	α_{2p}	d_{2p}	E
2	6.357953(+1)	2.663950(-1)	1.101003(+1)	-7.195049(-2)	2.304868(+0)	3.423681(-1)	-52.803260
	9.230158(+0)	8.300462(-1)	4.216567(-1)	1.014200(+0)	4.094001(-1)	8.028147(-1)	
3	2.141064(+2)	6.913578(-2)	8.394697(+0)	-8.165721(-2)	6.085492(+0)	1.164253(-1)	-54.062880
	3.215723(+1)	3.934835(-1)	6.465681(-1)	5.980757(-1)	1.252070(+0)	4.705657(-1)	
	6.866035(+0)	6.657830(-1)	2.050868(-1)	4.802935(-1)	2.896766(-1)	6.176643(-1)	
4	6.156398(+2)	1.952993(-2)	3.480423(+1)	-1.017511(-2)	1.353789(+1)	3.990437(-2)	-54.319468
	9.284316(+1)	1.349016(-1)	7.363335(+0)	-9.477406(-2)	2.913618(+0)	2.172447(-1)	
	2.070341(+1)	4.621335(-1)	6.764089(-1)	5.760407(-1)	7.954953(-1)	5.106687(-1)	
	5.470375(+0)	5.246789(-1)	2.108459(-1)	5.110324(-1)	2.179462(-1)	4.619019(-1)	
5	1.594665(+3)	6.050395(-3)	2.310313(+1)	-1.548375(-2)	2.659179(+1)	1.469339(-2)	-54.379474
	2.399168(+2)	4.495261(-2)	6.229139(+0)	-9.410243(-2)	5.940534(+0)	9.186051(-2)	
	5.443689(+1)	1.973501(-1)	8.537230(-1)	3.638343(-1)	1.739756(+0)	2.989269(-1)	
	1.501177(+1)	4.892996(-1)	3.472534(-1)	5.274011(-1)	5.540904(-1)	4.986211(-1)	
	4.559641(+0)	4.095034(-1)	1.398734(-1)	2.101657(-1)	1.722309(-1)	3.365790(-1)	
∞							-54.4.0910

between ϕ_{2s} and ϕ_{2p} is clearly reasonable since they have their largest values in similar regions of space. We shall therefore also consider a constrained set of atomic orbitals as (3) but with

$$\alpha_{2s_i} = \alpha_{2p_i} = \alpha_{2_i}. \quad (4)$$

The number of independent variables is then $5N-3$. We shall find that this constraint leads to compara-

tively little reduction in the quality of the atomic orbitals for given N . These functions, with the constraint (4), will be used in future molecular orbital studies.

II. METHOD

Given a minimal set of normalized basis functions as in Eq. (3), the total electronic energies of the atomic ground states may be calculated by standard proce-

TABLE V. Unconstrained atomic orbitals for oxygen (3P).

N	α_{1s}	d_{1s}	α_{2s}	d_{2s}	α_{2p}	d_{2p}	E
2	8.387674(+1)	2.618666(-1)	7.684635(-1)	6.761316(-1)	3.124534(+0)	3.530503(-1)	-72.602782
	1.228656(+1)	8.327590(-1)	2.474365(-1)	3.743843(-1)	5.394050(-1)	7.981834(-1)	
3	2.824431(+2)	6.877755(-2)	1.146494(+1)	-8.185136(-2)	8.093693(+0)	1.232504(-1)	-74.339560
	4.246874(+1)	3.931957(-1)	8.861834(-1)	5.980639(-1)	1.674014(+0)	4.755688(-1)	
	9.102204(+0)	6.658253(-1)	2.780659(-1)	4.813791(-1)	3.726591(-1)	6.150747(-1)	
4	8.130415(+2)	1.938375(-2)	4.691855(+1)	-1.042172(-2)	1.768271(+1)	4.301817(-2)	-74.696249
	1.226090(+2)	1.342522(-1)	1.001681(+1)	-9.538896(-2)	3.849817(+0)	2.290162(-1)	
	2.737847(+1)	4.621860(-1)	9.249654(-1)	5.786946(-1)	1.043857(+0)	5.090129(-1)	
	7.253830(+0)	5.247734(-1)	2.851133(-1)	5.096893(-1)	2.746995(-1)	4.602311(-1)	
5	2.104034(+3)	6.008518(-3)	3.091170(+1)	-1.593431(-2)	3.441632(+1)	1.595186(-2)	-74.779711
	3.165679(+2)	4.468078(-2)	8.424138(+0)	-9.451388(-2)	7.741046(+0)	9.981647(-2)	
	7.185795(+1)	1.968250(-1)	1.180484(+0)	3.584750(-1)	2.277938(+0)	3.106153(-1)	
	1.985250(+1)	4.897749(-1)	4.795308(-1)	5.292388(-1)	7.147004(-1)	4.912530(-1)	
	6.041781(+0)	4.092444(-1)	1.895890(-1)	2.156312(-1)	2.136278(-1)	3.359744(-1)	
∞							-74.809360

TABLE VI. Unconstrained atomic orbitals for fluorine (2P).

N	α_{1s}	d_{1s}	α_{2s}	d_{2s}	α_{2p}	d_{2p}	E
2	1.069555(+2)	2.614652(-1)	1.012207(+0)	6.693948(-1)	4.117613(+0)	3.573589(-1)	-96.449075
	1.572906(+1)	8.327857(-1)	3.248267(-1)	3.818536(-1)	7.004697(-1)	7.966763(-1)	
3	3.600420(+2)	6.853762(-2)	1.499656(+1)	-8.182856(-2)	1.050044(+1)	1.271087(-1)	-98.777363
	5.418639(+1)	3.930858(-1)	1.160913(+0)	5.968600(-1)	2.179919(+0)	4.788136(-1)	
	1.164656(+1)	6.657464(-1)	3.611721(-1)	4.833816(-1)	4.761736(-1)	6.127027(-1)	
4	1.037534(+3)	1.927719(-2)	6.076760(+1)	-1.059666(-2)	2.266343(+1)	4.484988(-2)	-99.257259
	1.564542(+2)	1.337938(-1)	1.306672(+1)	-9.563705(-2)	4.973936(+0)	2.357679(-1)	
	3.497088(+1)	4.623238(-1)	1.209514(+0)	5.795819(-1)	1.344952(+0)	5.087200(-1)	
	9.282866(+0)	5.247396(-1)	3.694688(-1)	5.097516(-1)	3.465366(-1)	4.579636(-1)	
5	2.680829(+3)	5.984398(-3)	3.978542(+1)	-1.628430(-2)	4.387073(+1)	1.666684(-2)	-99.369582
	4.032891(+2)	4.454388(-2)	1.093554(+1)	-9.457739(-2)	9.923604(+0)	1.044586(-1)	
	9.156451(+1)	1.966839(-1)	1.556231(+0)	3.544462(-1)	2.929595(+0)	3.172419(-1)	
	2.533452(+1)	4.903453(-1)	6.298499(-1)	5.314300(-1)	9.126815(-1)	4.875688(-1)	
	7.721834(+0)	4.085528(-1)	2.454083(-1)	2.189360(-1)	2.669034(-1)	3.344735(-1)	
∞							-99.409285

dures.¹⁶ First, the ϕ_{2s} in (3) is replaced by a modified function which is orthogonal to ϕ_{1s} ,

$$\phi_{2s}' = (1 - S)^{2-1/2} [\phi_{2s} - S\phi_{1s}], \quad (5)$$

where S is the overlap integral between ϕ_{1s} and ϕ_{2s} . Then we note that the ground states of all atoms considered are spin multiplets and we treat the component with maximum S_z , that is the maximum number of α

electrons. The electronic energy is then

$$E = \sum_i^{\alpha+\beta} H_{ii} + \frac{1}{2} \sum_i^{\alpha+\beta} \sum_j^{\alpha+\beta} J_{ij} - \frac{1}{2} \left(\sum_i^{\alpha} \sum_j^{\alpha} + \sum_i^{\beta} \sum_j^{\beta} \right) K_{ij}. \quad (6)$$

TABLE VII. Constrained atomic orbitals for boron (2P).

N	α_{1s}	d_{1s}	α_{2sp}	d_{2s}	d_{2p}	E
2	3.140736(+1)	2.650226(-1)	1.046062(+0)	-1.942415(-2)	2.999362(-1)	-23.780993
	4.500669(+0)	8.319466(-1)	1.853321(-1)	1.011627(+0)	8.330214(-1)	
3	1.055221(+2)	7.033583(-2)	2.277343(+0)	-1.099655(-1)	1.249312(-1)	-24.367747
	1.579294(+1)	3.944299(-1)	4.595619(-1)	3.628715(-1)	4.669353(-1)	
	3.346104(+0)	6.651698(-1)	1.245991(-1)	7.451286(-1)	5.943895(-1)	
4	3.059242(+2)	1.974240(-2)	4.139308(+0)	-7.236250(-2)	5.306589(-2)	-24.490328
	4.610635(+1)	1.355665(-1)	1.022637(+0)	-4.185294(-2)	2.152849(-1)	
	1.026651(+1)	4.581864(-1)	3.134664(-1)	5.905279(-1)	4.783977(-1)	
	2.680133(+0)	5.295643(-1)	9.613404(-2)	5.150757(-1)	4.669701(-1)	
5	7.880088(+2)	6.181648(-3)	1.090269(+1)	-1.600439(-2)	1.442356(-2)	-24.518805
	1.185756(+2)	4.577285(-2)	2.561946(+0)	-1.078546(-1)	7.900701(-2)	
	2.687508(+1)	1.987729(-1)	7.557046(-1)	7.818702(-2)	2.682473(-1)	
	7.360178(+0)	4.878824(-1)	2.503916(-1)	6.338602(-1)	4.792736(-1)	
	2.220012(+0)	4.105983(-1)	8.339601(-2)	3.974152(-1)	3.828827(-1)	
6	1.895409(+3)	2.081410(-3)	1.562811(+1)	-7.684427(-3)	8.521376(-3)	-24.526040
	2.846858(+2)	1.586529(-2)	3.902706(+0)	-6.582900(-2)	4.120506(-2)	
	6.475071(+1)	7.692983(-2)	1.345239(+0)	-7.611211(-2)	1.322743(-1)	
	1.817658(+1)	2.511023(-1)	4.914418(-1)	2.782199(-1)	3.284504(-1)	
	5.744942(+0)	4.836360(-1)	1.806782(-1)	6.171486(-1)	4.552737(-1)	
	1.923256(+0)	3.224145(-1)	6.703335(-2)	2.398980(-1)	2.648007(-1)	
∞						-24.529050

TABLE VIII. Constrained atomic orbitals for carbon (3P).

N	α_{1s}	d_{1s}	α_{2sp}	d_{2s}	d_{2p}	E
2	4.610789(+1)	2.636678(-1)	1.602488(+0)	-7.074384(-3)	3.281618(-1)	-36.557336
	6.672552(+0)	8.322659(-1)	2.869303(-1)	1.004286(+0)	8.121822(-1)	
3	1.543460(+2)	6.991845(-2)	3.766137(+0)	-1.105435(-1)	1.269707(-1)	-37.443557
	2.314469(+1)	3.952336(-1)	7.854455(-1)	3.264866(-1)	4.692911(-1)	
	4.941932(+0)	6.638258(-1)	2.000463(-1)	7.813513(-1)	5.990386(-1)	
4	4.494023(+2)	1.949184(-2)	7.160910(+0)	-6.659190(-2)	5.191113(-2)	-37.629626
	6.773945(+1)	1.344861(-1)	1.722269(+0)	-5.668624(-2)	2.258677(-1)	
	1.514323(+1)	4.574048(-1)	5.089629(-1)	5.809462(-1)	4.931223(-1)	
	3.980903(+0)	5.303019(-1)	1.500178(-1)	5.343484(-1)	4.517697(-1)	
5	1.157401(+3)	6.098023(-3)	1.728474(+1)	-1.611350(-2)	1.532730(-2)	-37.673222
	1.741360(+2)	4.524664(-2)	3.998293(+0)	-1.094827(-1)	8.856041(-2)	
	3.950136(+1)	1.976585(-1)	1.185257(+0)	8.456425(-2)	2.883773(-1)	
	1.085467(+1)	4.891760(-1)	3.877309(-1)	6.361284(-1)	4.861347(-1)	
	3.285545(+0)	4.098040(-1)	1.258553(-1)	3.931382(-1)	3.546724(-1)	
6	2.751605(+3)	2.082879(-3)	3.397107(+1)	-4.100587(-3)	5.468952(-3)	-37.684090
	4.132890(+2)	1.588389(-2)	8.127950(+0)	-4.735284(-2)	3.296395(-2)	
	9.401787(+1)	7.717846(-2)	2.577665(+0)	-1.014565(-1)	1.263351(-1)	
	2.637295(+1)	2.540942(-1)	8.842232(-1)	2.226487(-1)	3.295291(-1)	
	8.353770(+0)	4.865640(-1)	3.106437(-1)	6.307756(-1)	4.654348(-1)	
	2.812598(+0)	3.151894(-1)	1.085403(-1)	2.868040(-1)	2.780369(-1)	
∞						-37.688612

Here $\sum^\alpha$, $\sum^\beta$, and $\sum^{\alpha+\beta}$ indicate summation over α , β and all spin-orbitals, respectively. H_{ii} is the diagonal matrix element of the core Hamiltonian and J_{ij} and K_{ij} are the usual Coulomb and exchange integrals. These integrals are all easily evaluated,¹ so that E is obtained as a function of the parameters α and d of Eq. (3).

It was found convenient to select an initial set α^0 and d^0 and then to define new variables $x_1, x_2, \dots$ according to

$$\begin{aligned}\alpha &= \alpha^0 x, \\ d &= d^0 + x,\end{aligned}\quad (7)$$

so that for Gaussian exponents x is a multiplicative factor and for coefficients it is an additive variable. For the coefficients, it is not necessary to vary the last one in an atomic orbital expansion since the normalization provides one constraint. In this way we define E as a function of the x variables which number $6N-3$ or $5N-3$ if the Gaussian $2s$ and $2p$ exponents are constrained to be equal.

The minimization of $E(x_i)$ was carried out using the pattern search technique of Hooke and Jeeves.^{17,18} All x_i were varied in small steps δ until the minimal conditions

$$\begin{aligned}0 &\leq E(x_1, x_2, \dots, x_i + \delta, \dots) - E(x_1, x_2, \dots, x_i, \dots), \\ 0 &\leq E(x_1, x_2, \dots, x_i - \delta, \dots) - E(x_1, x_2, \dots, x_i, \dots),\end{aligned}\quad (8)$$

are satisfied for all i . The procedure was then repeated with reduced δ until it was at least as small as 10^{-6} .

The right hand sides of Eq. (8) were then all less than 2×10^{-6} hartree. The α and d parameters corresponding to the final stage of this search are those listed in the tables of the next section.

To check that the stationary point found is not a saddle point, the complete second-derivative matrix was evaluated from the approximate formulas

$$\begin{aligned}\partial^2 E / \partial x_i^2 &= [E(x_i + \delta) + E(x_i - \delta) - 2E(x_i)] / \delta^2, \\ \partial^2 E / \partial x_i \partial x_j &= [E(x_i + \delta, x_j + \delta) - E(x_i + \delta, x_j) \\ &\quad - E(x_i, x_j + \delta) + E(x_i, x_j)] / \delta^2.\end{aligned}\quad (9)$$

In all cases this matrix was found to have all positive eigenvalues, indicating that the energy found is a strict local minimum. Similar estimates of the first derivatives can be made from

$$\partial E / \partial x_i = [E(x_i + \delta) - E(x_i - \delta)] / 2\delta, \quad (10)$$

and a new minimum can then be projected by fitting a quadratic surface to the derivatives (9) and (10). These projections were not used for the final values because of roundoff problems, but they led to the general conclusion that the parameters quoted are all within about one part per thousand of their optimum values.

It should be emphasized that this nonlinear optimization procedure only serves to find and establish a *local* minimum. It cannot be ruled out that other lower local minima exist in other parts of the parameter space. Some attempts were made to find other minima by starting with different α^0 and d^0 but these all led back to the same point.

TABLE IX. Constrained atomic orbitals for nitrogen (4S).

N	α_{1s}	d_{1s}	α_{2sp}	d_{2s}	d_{2p}	E
2	6.361295(+1)	2.627935(-1)	2.326571(+0)	-3.052822(-3)	3.409803(-1)	-52.776769
	9.269296(+0)	8.324378(-1)	4.133914(-1)	1.001846(+0)	8.037850(-1)	
3	2.123527(+2)	6.964027(-2)	5.646244(+0)	-1.097734(-1)	1.274825(-1)	-54.048270
	3.188619(+1)	3.958639(-1)	1.185736(+0)	3.055042(-1)	4.724609(-1)	
	6.841401(+0)	6.628737(-1)	2.912856(-1)	8.008609(-1)	6.007528(-1)	
4	6.187593(+2)	1.937471(-2)	1.100147(+1)	-6.256882(-2)	5.058171(-2)	-54.315944
	9.327268(+1)	1.341008(-1)	2.601504(+0)	-6.620673(-2)	2.306138(-1)	
	2.090657(+1)	4.575132(-1)	7.528397(-1)	5.700696(-1)	4.995621(-1)	
	5.525325(+0)	5.298312(-1)	2.158594(-1)	5.512909(-1)	4.472937(-1)	
5	1.597130(+3)	6.040601(-3)	2.486487(+1)	-1.625472(-2)	1.593593(-2)	-54.378977
	2.402330(+2)	4.490061(-2)	5.736882(+0)	-1.099794(-1)	9.446715(-2)	
	5.451058(+1)	1.970287(-1)	1.706735(+0)	8.777936(-2)	2.997873(-1)	
	1.501285(+1)	4.901702(-1)	5.544043(-1)	6.354726(-1)	4.873502(-1)	
	4.553173(+0)	4.090673(-1)	1.766751(-1)	3.933173(-1)	3.413672(-1)	
6	3.782966(+3)	2.072366(-3)	4.902871(+1)	-4.049933(-3)	5.554115(-3)	-54.394501
	5.681556(+2)	1.581254(-2)	1.163786(+1)	-4.843178(-2)	3.539460(-2)	
	1.292557(+2)	7.697836(-2)	3.656996(+0)	-1.007911(-1)	1.366781(-1)	
	3.627330(+1)	2.547597(-1)	1.257385(+0)	2.303805(-1)	3.401913(-1)	
	1.151474(+1)	4.879549(-1)	4.403168(-1)	6.272573(-1)	4.606595(-1)	
	3.883581(+0)	3.127025(-1)	1.513487(-1)	2.851525(-1)	2.650905(-1)	
∞						-54.400910

TABLE X. Constrained atomic orbitals for oxygen (3P).

N	α_{1s}	d_{1s}	α_{2sp}	d_{2s}	d_{2p}	E
2	8.386993(+1)	2.622575(-1)	3.194226(+0)	5.664311(-3)	3.470050(-1)	-72.556655
	1.228273(+1)	8.324877(-1)	5.526740(-1)	9.966066(-1)	8.023262(-1)	
3	2.796271(+2)	6.941046(-2)	7.652621(+0)	-1.117596(-1)	1.318187(-1)	-74.316623
	4.202916(+1)	3.962640(-1)	1.619163(+0)	3.211956(-1)	4.710119(-1)	
	9.052787(+0)	6.622110(-1)	3.827091(-1)	7.914684(-1)	6.054923(-1)	
4	8.162436(+2)	1.925310(-2)	1.496339(+1)	-6.343957(-2)	5.230954(-2)	-74.690563
	1.230449(+2)	1.336015(-1)	3.498837(+0)	-6.349163(-2)	2.411618(-1)	
	2.763183(+1)	4.574244(-1)	9.967102(-1)	6.002459(-1)	4.956271(-1)	
	7.327384(+0)	5.298755(-1)	2.757914(-1)	5.231617(-1)	4.495582(-1)	
5	2.103633(+3)	6.011702(-3)	3.260035(+1)	-1.757950(-2)	1.703002(-2)	-74.778776
	3.164701(+2)	4.471285(-2)	7.523394(+0)	-1.133416(-1)	1.023229(-1)	
	7.184040(+1)	1.968243(-1)	2.235212(+0)	1.105251(-1)	3.124862(-1)	
	1.981765(+1)	4.911408(-1)	7.131792(-1)	6.629696(-1)	4.801244(-1)	
	6.023608(+0)	4.079325(-1)	2.194564(-1)	3.507522(-1)	3.395969(-1)	
6	4.974284(+3)	2.066493(-3)	6.091908(+1)	-4.863690(-3)	6.415253(-3)	-74.800446
	7.471157(+2)	1.577138(-2)	1.442993(+1)	-5.600062(-2)	4.139720(-2)	
	1.699676(+2)	7.690691(-2)	4.548575(+0)	-9.391438(-2)	1.547385(-1)	
	4.772500(+1)	2.551914(-1)	1.571215(+0)	2.807970(-1)	3.534578(-1)	
	1.519641(+1)	4.881327(-1)	5.431318(-1)	6.359805(-1)	4.471526(-1)	
	5.138837(+0)	3.116110(-1)	1.813283(-1)	2.297043(-1)	2.544630(-1)	
∞						-74.809360

TABLE XI. Constrained atomic orbitals for fluorine (3P).

N	α_{1s}	d_{1s}	α_{2sp}	d_{2s}	d_{2p}	E
2	1.069193(+2)	2.618664(-1)	4.195122(+0)	1.017299(-2)	3.521510(-1)	-96.386545
	1.571946(+1)	8.325094(-1)	7.159301(-1)	9.939347(-1)	8.001107(-1)	
3	3.561218(+2)	6.923553(-2)	1.003901(+1)	-1.124382(-1)	1.340847(-1)	-98.745011
	5.356475(+1)	3.966070(-1)	2.128919(+0)	3.257471(-1)	4.728066(-1)	
	1.156849(+1)	6.616981(-1)	4.909967(-1)	7.897130(-1)	6.061565(-1)	
4	1.039663(+3)	1.918958(-2)	1.969760(+1)	-6.321431(-2)	5.300144(-2)	-99.249027
	1.567420(+2)	1.333847(-1)	4.578027(+0)	-6.352451(-2)	2.469308(-1)	
	3.525278(+1)	4.575930(-1)	1.290010(+0)	6.118574(-1)	4.963153(-1)	
	9.374258(+0)	5.295208(-1)	3.485629(-1)	5.135313(-1)	4.484569(-1)	
5	2.680691(+3)	5.986544(-3)	4.172542(+1)	-1.827662(-2)	1.774231(-2)	-99.368179
	4.032824(+2)	4.455585(-2)	9.641212(+0)	-1.148294(-1)	1.073497(-1)	
	9.158373(+1)	1.965777(-1)	2.866989(+0)	1.219525(-1)	3.201291(-1)	
	2.529671(+1)	4.917936(-1)	9.059159(-1)	6.737311(-1)	4.777047(-1)	
	7.698515(+0)	4.072868(-1)	2.725275(-1)	3.326010(-1)	3.356827(-1)	
6	6.329421(+3)	2.061440(-3)	7.707169(+1)	-5.178209(-3)	6.763396(-3)	-99.397372
	9.506127(+2)	1.573793(-2)	1.822026(+1)	-5.903586(-2)	4.445214(-2)	
	2.162597(+2)	7.683586(-2)	5.735813(+0)	-9.033551(-2)	1.643591(-1)	
	6.074609(+1)	2.555594(-1)	1.981144(+0)	3.019378(-1)	3.597739(-1)	
	1.937936(+1)	4.885010(-1)	6.795145(-1)	6.363388(-1)	4.406576(-1)	
	6.562300(+0)	3.105741(-1)	2.222028(-1)	2.093229(-1)	2.491585(-1)	
∞						-99.409285

All refinement calculations were performed in double precision (72-bit word) on a UNIVAC 1108 computer system.

III. RESULTS AND DISCUSSION

The hydrogen atomic orbitals and energies for $N=2-6$ are presented in Table I. For $N=2$ and 3 the results are in reasonable agreement with those of Huzinaga.¹³ However, optimization of the larger sets gives different exponents and lower energies than those previously reported.

The unconstrained atomic orbitals and energies for boron, carbon, nitrogen, oxygen and fluorine are reported in Tables II-VI. Exponents, coefficients and energies for the constrained ($\alpha_{2s_i} = \alpha_{2p_i}$) atomic orbitals for B to F are presented in Tables VII-XI.

The following points may be noted:

(1) The sharing of Gaussian exponents between s and p functions which results in a significant gain in computational speed for molecular calculations, does not seriously affect the calculated energy. For the values of N considered here, the constrained N -Gaussian set produces lower energies than the unconstrained ($N-1$)-Gaussian set for comparable computational effort.

(2) For $N=6$, the calculated energies of the constrained sets are in close agreement with the Hartree-Fock values.

(3) Comparison of the unconstrained atomic orbitals with the uncontracted basis sets reported by Whitman and Hornback¹⁹ for the first row atoms, shows that the exponents for the contracted sets are smaller than those

for the uncontracted functions. Our own studies of uncontracted sets with $\alpha_{2s_i} = \alpha_{2p_i}$ show that this is also true for the constrained sets. Thus the exponents for the uncontracted sets are a poor approximation to those of the contracted functions.

ACKNOWLEDGMENT

This research was supported by National Science Foundation Grant GP 9338.

- ¹ S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950).
- ² C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
- ³ E. Clementi and D. R. Davis, J. Chem. Phys. **45**, 2593 (1966); J. Comput. Phys. **2**, 223 (1967).
- ⁴ E. Clementi, H. Clementi, and D. R. Davis, J. Chem. Phys. **46**, 4725 (1967).
- ⁵ J. R. Hoyland, J. Chem. Phys. **49**, 1908 (1969); **49**, 2563 (1969).
- ⁶ K. O-Ohata, H. Taketa, and S. Huzinaga, J. Phys. Soc. (Japan) **21**, 2306 (1966).
- ⁷ W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969).
- ⁸ R. F. Stewart, J. Chem. Phys. **52**, 431 (1970).
- ⁹ R. F. Stewart, J. Chem. Phys. **50**, 2485 (1969).
- ¹⁰ J. M. Schulman, J. W. Moskowitz, and C. Hollister, J. Chem. Phys. **46**, 2759 (1967).
- ¹¹ H. Basch, M. B. Robin, and N. A. Kuebler, J. Chem. Phys. **47**, 1201 (1967).
- ¹² L. C. Snyder and H. Basch, J. Am. Chem. Soc. **91**, 2189 (1969).
- ¹³ S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).
- ¹⁴ H. Basch, C. J. Hornback, and J. W. Moskowitz, J. Chem. Phys. **51**, 1311 (1969).
- ¹⁵ J. L. Whitten, J. Chem. Phys. **44**, 359 (1966); **51**, 256 (1969).
- ¹⁶ J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954).
- ¹⁷ R. Hooke and T. A. Jeeves, J. Assoc. Computing Machinery **8**, 212 (1961).
- ¹⁸ D. J. Wilde, *Optimum Seeking Methods* (Prentice-Hall, Englewood Cliffs, N.J., 1964), p. 145.
- ¹⁹ D. R. Whitman and C. J. Hornback, J. Chem. Phys. **51**, 398 (1969).