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The Use of Population Optimized Basis Functions. 1. Determination of Optimum Basis Functions and Their Use in a Semiempirical Method for Atomic State Energies

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Abstract: Direct optimization of the exponents in minimum Slater type orbital basis sets on atoms with fractional closed shell populations provided a series of optimum exponents for atoms in molecule-like states. These optimum exponents were very well fit by an empirical linear relation based on the populations themselves. The calculated optimum exponents were used in a new semiempirical atomic orbital method to calculate the energies of a large number of states of atoms and ions.

(I) Introduction

Atomic orbital basis sets are very widely used in molecular orbital methods because they provide a simple uniform foundation for these methods. It is clear that regardless of the form used to represent atomic orbitals, the "size" of an orbital will vary with the effective nuclear charge. Changes in molecular electronic distribution affect the apparent nuclear charge, so the optimum mathematical representation of atomic orbitals varies with the distribution of electrons in any molecule.

Variation of atomic orbital size with electronic distribution is included implicitly in extended basis set LCAO-MO calculations[1] and has been included explicitly in minimum basis set calculations by direct minimization[2,3] or by the use of a modified form of Slater's rules[4] to predict optimum exponents[5] for Slater orbital basis sets.

Table I. Ranges of Populations Used for Optimization of Orbital Exponents

Atom	No. of populations used	Ranges of valence shell populations	
		s	Total p
Li	15	0.15-0.55	0.15-0.30
Be	138	0.50-1.35	0.15-1.35
B	158	1.00-1.70	0.15-2.40
C	212	1.00-1.80	1.05-3.45
N	161	1.40-1.90	2.10-4.05
O	69	1.50-2.00	4.20-5.40
F	24	1.75-2.00	5.10-6.00
Ne	1	2.00	6.00
Si	53	1.00-1.80	1.20-3.30
P	46	1.20-1.90	2.10-4.20
S	19	1.60-2.00	4.20-5.40
Cl	7	1.80-2.00	5.40-6.00
Total	903		

Table II. Effect of Optimizing Core Exponents on Optimum Valence Shell Exponents and Energy for Carbon

q_{2s}	q_{2p}	Status of ζ_{1s}	Exponents			E, au
			1s	2s	2p	
1.00	1.00	Constant	5.6738	1.5856	1.4336	−36.708 704
1.00	1.00	Optimized	5.6738	1.5856	1.4336	−36.708 704
2.00	0.66	Constant	5.6738	1.6457	1.3732	−37.247 869
2.00	0.66	Optimized	5.6743	1.6457	1.3732	−37.247 870
1.00	1.33	Constant	5.6738	1.5247	1.2599	−36.680 926
1.00	1.33	Optimized	5.6774	1.5245	1.2599	−36.680 938
2.00	1.00	Constant	5.6738	1.5970	1.1532	−37.166 331
2.00	1.00	Optimized	5.6789	1.5967	1.1532	−37.166 355
1.00	0.66	Constant	5.6738	1.6756	1.6072	−36.397 090
1.00	0.66	Optimized	5.6714	1.6758	1.6073	−36.397 096
2.00	0.33	Constant	5.6738	1.7285	1.5620	−37.006 064
2.00	0.33	Optimized	5.6695	1.7289	1.5620	−37.006 081
RMS error[a]			0.0032	0.0002	0.0000	0.000 013[b]

[a] Root mean square error between values for varied ζ_{1s} and values for constant ζ_{1s}. [b] Corresponds to an energy difference of 0.0082 kcal/mol.

Table III. Regression Coefficients for Population Optimized Valence Shell Exponents

Coefficient	Valence orbital a				
	1s	2s	2p	3s	3p
n_a	1.000 000	2.497 12	1.774 12	3.294 14	2.780 18
$b_{a,1s}$	0.156 250	0.682 478	1.042 126	0.858 092	0.974 378
$b_{a,2s}$		0.055 165	0.421 994	0.677 161	0.825 430
$b_{a,2p}$		0.209 948	0.318 755	0.798 092	0.930 904
$b_{a,3s}$				0.107 820	0.396 515
$b_{a,3p}$				0.225 119	0.279 550
RMS error	Exact	7.0×10^{-3}	7.0×10^{-3}	3.2×10^{-3}	3.2×10^{-3}
Corr coeff		0.9999	0.9998	0.9999	0.9998

Table IV. Regression Coefficients for Population Optimized Core Shell Exponents

Coefficient	Core orbital			
	2nd row	3rd row		
	1s	1s	2s	2p
n_a	1.004 17	1.011 87	2.510 94	1.953 71
$b_{a,1s}$	0.306 240	0.270 479	0.587 420	0.902 930
$b_{a,2s}$			0.202 067	0.288 876
$b_{a,2p}$			0.213 045	0.388 496
No. of pop. used	16	8	16	16
RMS error	5.7×10^{-3}	1.45×10^{-2}	6.0×10^{-3}	3.0×10^{-3}
Corr coeff	1.0000	0.9998	0.9998	1.0000

Table V. Values of Parameters, a_x, for First-Row Atoms

Integral type: x	a_x
Kinetic energy	1.243 134
Nuclear attraction	1.253 502
Electron repulsion	1.095 968

Table VI. Values of Parameters, a_x, for Second-Row Atoms

Integral type: x	a_x for orbital type	
	2s	2p
Kinetic energy	1.349 98	0.884 010
Nuclear attraction	0.909 416	0.858 762
Repulsion (s,s)	1.030 01	
Repulsion (p,p)		0.783 744
Repulsion (s,p)	1.494 35	0.630 547
Repulsion (p,p′)		0.791 076
Core repulsion	0.881 494	0.786 654

Table VII. Values of Parameters, a_x, for Third-Row Atoms

Integral type: x	a_x for orbital type	
	3s	3p
Kinetic energy	3.430 70	1.945 31
Nuclear attraction	1.579 53	1.358 96
Repulsion (s,s)	0.842 895	
Repulsion (p,p)		1.043 89
Repulsion (s,p)	1.081 47	1.566 84
Repulsion (p,p′)		1.094 42
Core repulsion	1.397 61	1.259 09

Semiempirical calculations do not use explicit basis sets so semiempirical integrals have no simple physical significance, but Freed has shown that these integrals correspond to, "The matrix elements of $\mathcal{H}$ in the N-electron basis set of chemical sea states," where $\mathcal{H}$ is the, "true effective Hamiltonian".[6] Inclusions of forms for semiempirical integrals which mimic the variation of these matrix elements with electron distribution will probably allow semiempirical methods to better predict experimental energies and electron distributions. The improvement will be especially important in species with unusual electron distributions such as polyfluorinated compounds (which have large charge separations), strained ring organics (which have unusually high p/s population ratios), and in calculations of electronic transitions (in which population changes are important).

As an initial step in the development of a semiempirical molecular orbital method which includes charge distribution effects, we have determined how the optimum exponents, for a set of Slater atomic orbitals, vary with atomic populations, using populations similar to those found on atoms in molecules. The exponent variation was found to be fit extremely well by a linear function with the same form as that originally proposed by Slater.[7]

Table VIII. Valence State Energies Used for Parameterization of Second-Row Atoms

Atom	Configuration				Energy	$E_{\text{exptl}} - E_{\text{calcd}}$		
(Charge)	2s	2p	2p	2p	obsd, eV	Ours	Oleari's	Best STO
Be(1+)	1	0	0	0	−18.21	0.29	0.37	−0.23
Be(0)	1	1	0	0	−24.17	0.06	0.25	−0.80
Be(1−)	2	1	0	0	−26.93	−0.30	−0.35	−0.83
Be(1−)	1	1	1	0	−24.33	0.02	−0.10	−0.03
Be(1−)	1	2	0	0	−23.69	0.15	−0.40	−2.21
B(1+)	2	0	0	0	−63.07	−0.24	0.42	−2.09
B(1+)	1	1	0	0	−57.32	0.15	−0.40	−1.05
B(0)	2	1	0	0	−71.36	−0.51	0.02	−2.63
B(0)	1	1	1	0	−65.84	0.10	0.02	−2.42
B(0)	1	2	0	0	−64.59	0.25	0.02	−2.87
B(1−)	2	1	1	0	−71.42	0.21	0.24	−4.23
B(1−)	2	2	0	0	−70.72	0.06	−0.31	−4.84
B(1−)	1	1	1	1	−66.91	−0.39	0.28	−5.19
B(1−)	1	2	1	0	−66.16	−0.55	−0.22	−5.75
C(1+)	2	1	0	0	−136.72	0.03	0.16	−3.24
C(1+)	1	1	1	0	−128.30	0.05	0.02	−2.65
C(1+)	1	2	0	0	−126.38	0.26	0.39	−3.22
C(0)	2	1	1	0	−147.67	0.02	0.04	−4.59
C(0)	2	2	0	0	−146.30	−0.06	−0.14	−5.43
C(0)	1	1	1	1	−139.84	−0.01	0.04	−5.38
C(0)	1	2	1	0	−138.29	0.03	0.04	−6.02
C(1−)	2	1	1	1	−148.95	0.15	0.06	−7.89
C(1−)	2	2	1	0	−147.97	−0.13	−0.51	−8.76
C(1−)	1	2	1	1	−140.30	−0.43	0.06	−10.04
N(1+)	2	1	1	0	−251.86	0.12	0.00	−5.10
N(1+)	2	2	0	0	−249.80	0.13	0.32	−6.04
N(1+)	1	1	1	1	−240.70	−0.37	0.00	−5.65
N(1+)	1	2	1	0	−238.31	−0.08	0.65	−6.22
N(0)	2	1	1	1	−265.70	0.40	0.00	−7.58
N(0)	2	2	1	0	−263.96	0.28	0.00	−8.53
N(0)	1	2	1	1	−252.65	0.53	0.00	−9.88
N(1−)	2	2	1	1	−266.56	0.21	0.00	−13.37
N(1−)	1	2	2	1	−254.23	−0.15	−0.87	−16.67
O(1+)	2	1	1	1	−417.80	−0.05	0.05	−8.05
O(1+)	2	2	1	0	−415.34	−0.05	−0.06	−9.06
O(1+)	1	2	1	1	−400.26	−0.19	−0.10	−10.30
O(1+)	1	2	2	0	−397.48	0.07	0.11	−10.97
O(0)	2	2	1	1	−432.55	0.50	−0.02	−12.94
O(1−)	2	2	2	1	−435.24	−0.51	0.02	−21.42
F(1+)	2	2	1	1	−640.67	−0.30	−0.21	−13.25
F(1+)	1	2	2	1	−618.57	−0.19	0.28	−16.77
F(0)	2	2	2	1	−658.74	0.43	0.00	−20.08
F(0)	1	2	2	2	−637.78	0.40	−0.28	−25.80
F(1+)	2	2	2	0	−637.85	−0.34	0.36	−14.39
F(1−)	2	2	2	2	−662.38	−0.21	0.18	−20.44
Root mean square error						0.27	0.27	10.54

Using the assumption that semiempirical integrals vary with population in a similar manner to that of Hartree–Fock integrals over Slater functions, a simple semiempirical method incorporating population optimized atomic orbital basis function was developed. Calculations employing this method resulted in values of atomic state energies for a wide variety of electron distributions, which were very close to experimental values.

(II) Determination of Optimum Exponents

To determine the optimum exponents at various populations, a total of 903 populations of valence shell orbitals for 12 atoms were selected. The number of populations for each atom type, and the range of populations used in each valence shell orbital on that atom, are given in Table I. The total p orbital population was, in all cases, divided equally among the three p orbitals, because it can be shown that, for any set of three equivalent p orbitals with arbitrary populations, a unitary transformation exists which transforms the p orbitals into an equivalent set with equal populations.[8]

The valence shell fractional populations were assumed to be without spin. For any orbital the population was therefore considered to contain equal fractional α and β parts. This procedure mimics atomic orbital populations in closed shell molecules.

The total Hartree–Fock energies of atoms with the above fractional populations, using orthogonalized Slater type orbitals, were minimized with respect to the orbital exponents, using the Flecher–Powell algorithm.[9] Initial calculations, on six sets of populations for carbon, showed that the optimum core orbital exponent was essentially independent of valence shell electron distribution. This agrees with the work done by Weltin[10] on open shell atomic systems. These results are given in Table II. For all other calculations, the optimum core orbital exponent for each atom was obtained by direct optimization of all exponents for one population (that of the neutral atom).

The optimum exponents determined by direct minimization were found to be excellently represented by a function, identical in form with that used with Slater's rules to determine

Table IX. Valence State Energies Used for Parameterization of Third-Row Atoms

Atom (Charge)	Configuration 3s	3p	3p	3p	Energy obsd, ev	$E_{\text{exptl}} - E_{\text{calcd}}$ Ours	Oleari's
Mg(1+)	1	0	0	0	−15.03	−0.69	0.09
Mg(0)	2	0	0	0	−22.67	−0.32	0.00
Mg(0)	1	1	0	0	−19.55	0.10	0.11
Mg(1−)	2	1	0	0	−22.37	0.12	−0.02
Al(1+)	2	0	0	0	−47.26	0.44	0.17
Al(1+)	1	1	0	0	−41.92	−0.42	−0.07
Al(0)	2	1	0	0	−53.25	−0.02	−0.01
Al(0)	1	1	1	0	−48.34	0.53	0.35
Al(0)	1	2	0	0	−47.50	0.52	0.46
Al(1−)	2	1	1	0	−53.74	0.32	0.06
Al(1−)	2	2	0	0	−53.20	0.12	−0.13
Al(1−)	1	2	1	0	−50.08	0.44	−0.53
Si(1+)	2	1	0	0	−94.93	0.21	−0.57
Si(1+)	1	1	1	0	−87.87	−0.15	−0.71
Si(1+)	1	2	0	0	−86.66	−0.10	−0.46
Si(0)	2	1	1	0	−102.87	−0.02	−0.01
Si(0)	2	2	0	0	−101.93	−0.12	−0.03
Si(0)	1	1	1	1	−96.86	0.41	0.15
Si(0)	1	2	1	0	−96.24	−0.04	−0.19
Si(1−)	2	1	1	1	−104.79	−0.21	0.22
Si(1−)	2	2	1	0	−104.05	−0.42	0.00
Si(1−)	1	2	1	1	−100.28	−0.60	−0.73
P(1+)	2	1	1	0	−165.87	0.23	0.29
P(1+)	2	2	0	0	−164.55	0.22	0.41
P(1+)	1	1	1	1	−157.48	0.32	0.56
P(1+)	1	2	1	0	−156.36	0.07	0.48
P(0)	2	1	1	1	−176.47	−0.34	−0.02
P(0)	2	2	1	0	−175.31	−0.43	−0.06
P(0)	1	2	1	1	−169.16	−0.79	−0.35
P(1−)	2	2	1	1	−177.76	0.03	0.34
P(1−)	1	2	2	1	−171.58	0.19	0.56
S(1+)	2	1	1	1	−265.30	0.00	−0.08
S(1+)	2	2	1	0	−263.78	−0.04	0.10
S(1+)	1	2	1	1	−255.22	−0.47	−0.02
S(0)	2	2	1	1	−276.27	0.06	0.02
S(0)	1	2	2	1	−267.19	0.45	0.65
S(1−)	2	2	2	1	−278.98	0.17	−0.18
Cl(1+)	2	2	1	1	−395.58	−0.13	−0.02
Cl(1+)	2	2	2	0	−393.86	−0.18	0.03
Cl(1+)	1	2	2	1	−383.68	0.45	0.01
Cl(0)	2	2	2	1	−408.94	0.05	0.06
Cl(0)	1	2	2	2	−400.13	−0.62	−0.68
Cl(1−)	2	2	2	2	−412.76	0.39	0.05
Root mean square error						0.34	0.33

Slater exponents:

$$\zeta_a = \frac{1}{n_a}\left(Z - \sum_c b_{ac}q_c\right) \tag{1}$$

where ζ_a is the approximate optimum exponent of valence shell orbital a, n_a an effective principal quantum number for that orbital, Z is the nuclear charge, q_c is the population of orbital c, and b_{ac} is a constant. For the single occupied 1s Slater orbital on hydrogen and helium the optimum exponent is exactly that calculated from eq 1 with $n_{1s} = 1$ and $b_{1s,1s} = 5/32$. For the core orbitals, which were not forced to be spin free, a similar formula was used but with unit charge subtracted from the total charge in the orbital of interest, thus neglecting the screening of an electron on itself:

$$\zeta_a = \frac{1}{n_a}\left[Z - \sum_{c \neq a} b_{ac}q_c - b_{aa}(q_a - 1)\right] \tag{2}$$

The values of the parameters n_a and b_{ac} were determined by a multiple linear regression procedure and are summarized in Tables III and IV. Included in the valence shell exponent regressions were 20 sets of exponents optimized for states with subvalence-shell holes. Unlike the valence-shell populations, the unit core populations were calculated with unit spin to mimic atomic orbitals in molecular states resulting from core ionization (as in x-ray photoelectron spectroscopy).

(III) Calculations of Atomic State Energies

A critical and important test of any method which can be used to calculate semiempirical atom energies is the comparison of calculations with the experimental valence state atom energies of Pritchard[11] and Moore.[12] These energies were used by Oleari[13] to determine the one-center integrals which are now extensively used in semiempirical methods.[14] Oleari assumed that the atomic basis set was independent of charge or state for each type of atom and expanded the Hartree–Fock expression for energy as a continuous distribution of occupation numbers to obtain:

$$E = C + \sum_i n_iU_i + ½ \sum_{i \neq j} n_in_jg_{ij} + ½ \sum_i n_i(n_i - 1)g_{ii} \tag{3}$$

where n_i is the population of the ith orbital, $g_{ii} = (ii,ii)$, $g_{ij} = (ii,jj) - ½(ij,ij)$, $U_i = \langle i| - ½\nabla^2 - Zr^{-1}| i\rangle$, and C is a constant required by the expansion. Least-squares fits of energies calculated from eq 3 to experimental energies provided the best values for a total of parameters: C, U_{S}, U_{p}, g_{ss}, g_{pp}, g_{sp}, and g_{pp}, for each element (for the 12 second and third period elements treated).

It is evident that even with optimum exponents, Hartree–Fock calculations of the energies of the various atoms and ions involved cannot approach experimental values because the calculations do not include electron correlation. In semiempirical methods, correlation energy is implicitly included through the use of empirically derived functions in place of each type of integral used in the Hartree–Fock formalism. For one-center integrals the functions used are usually constants, often those derived by Oleari as described above.

The optimum parameters which represent one-center integrals in semiempirical methods may be regarded either as approximations to Hartree–Fock integrals or as complex integrals of an effective Hamiltonian over many-electron functions. The major assumption is here made that the best one-center semiempirical integrals will vary, with electron distribution, in a manner similar to that of the corresponding Hartree–Fock integrals over optimum Slater functions.

For a particular electron distribution each integral will have an optimum numerical value. This numerical value can be reproduced by evaluating the corresponding integral over a Slater function, but the Slater function required to give the same numerical value as a semiempirical integral will differ, depending on what integral is to be evaluated.

Thus, in semiempirical methods a basis is implied. The integrals over this implicit basis can be represented by integrals over Slater functions but different Slater functions must be used for each integral.

Both the value of a semiempirical integral and that of an integral over an optimum Slater function, which might be used to represent it, will vary with population (the Slater integral in the manner derived in section II above). It is reasonable to assume that the value of each semiempirical integral will vary with population in the same manner as that integral over optimum Slater functions varies with population. One can then write for each semiempirical integral:

$$I_x = I_x'(a_x\zeta_{\text{opt}}) \tag{4}$$

where I_x is the semiempirical integral (type x), I_x' is the equivalent integral over Slater functions with exponents $(a_x\zeta_{\text{opt}})$, ζ_{opt} is the population optimized Slater exponent calculated using eq 1, and a_x is a scaling constant. In this manner

Table X. Valence State Energies for Highly Charged States of Second-Row Atoms

Atom (Charge)	Configuration				Energy obsd, eV	$E_{\text{exptl}} - E_{\text{calcd}}$		
	2s	2p	2p	2p		Ours	Oleari's	Best STO
B(2+)	1	0	0	0	−37.92	1.09	2.45	−0.44
B(2+)	0	1	0	0	−31.92	−0.17	−0.05	−0.28
C(3+)	1	0	0	0	−64.48	2.36	12.13	−0.74
C(2+)	2	0	0	0	−112.34	1.80	4.18	−2.87
C(2+)	1	1	0	0	−104.30	0.40	2.93	−1.35
C(2+)	0	1	1	0	−95.02	−0.13	1.68	−1.31
N(3+)	2	0	0	0	−175.31	4.74	15.15	−3.82
N(3+)	1	1	0	0	−165.01	0.79	14.59	−1.72
N(2+)	2	1	0	0	−222.74	1.25	4.04	−3.98
N(2+)	1	1	1	0	−211.54	−0.30	4.23	−3.01
N(2+)	1	2	0	0	−208.79	0.15	5.24	−3.50
O(3+)	2	1	0	0	−329.35	3.05	18.15	−4.90
O(3+)	1	1	1	0	−315.40	−0.92	15.86	−3.46
O(2+)	2	1	1	0	−383.64	0.49	5.01	−5.80
O(2+)	2	2	0	0	−380.93	0.55	5.15	−6.85
O(2+)	1	1	1	1	−369.08	−1.31	3.89	−5.94
O(2+)	0	2	1	1	−348.63	0.42	3.74	−7.50
F(3+)	2	1	1	0	−542.89	1.06	15.38	−6.72
F(3+)	1	1	1	1	−525.07	−3.07	13.10	−6.48
F(3+)	1	2	1	0	−521.28	−2.57	14.64	−7.14
F(2+)	2	1	1	1	−604.28	−0.57	3.44	−8.66
F(2+)	2	2	1	0	−601.13	−0.46	4.34	−9.74
F(2+)	1	2	1	1	−582.15	−1.83	3.59	−10.64
F(2+)	0	2	2	1	−556.60	0.91	5.44	−13.22
Root mean square error						1.68	9.08	6.05

the semiempirical integral is linked to the optimum Slater function and changes with population as does the integral over Slater functions but, because the exponent is scaled by a_x, has numerical value which accurately reproduces experimental energies in the semiempirical calculation.

The constants a_x were determined by an empirical fit of the Hartree-Fock energy of the 45 second row and 43 third row atomic states, used by Oleari for his parameterization, to experimental values of the energies. In this fit a modified form of eq 4 was used:

$$E = \sum_i n_i U_i + \frac{1}{2} \sum_{i \neq j} n_i n_j g_{ij} + \frac{1}{2} \sum_i n_i (n_i - 1) g_{ii} + \sum_c \sum_i n_c n_i g_{ci} \quad (5)$$

where c is the index of a core orbital. This form is more correct than eq 3 for the present case because core-valence repulsion should vary with the effective valence shell exponent even in the case where the core exponent is constant. Each integral in eq 5 was calculated over Slater functions with exponents, $a_x \zeta_{\text{opt}}$, the values of a_x being adjusted to give maximum agreement between calculated and experimental energies. Similar constants were determined for the three integrals required for first row atom calculations from the experimental ionization potentials of H and He (13.605, 24.481, and 54.403 eV)[10] and the calculated electron affinity of H (0.747 eV).[14] It was found that no significant improvement resulted from using different constants for repulsion and exchange integrals over the same type functions so these values were assumed equal. The integrals were calculated using nonorthogonalized Slater type orbitals. It was found that repeating the calculation with core and valence shell orbitals orthogonalized to one another did not significantly improve the accuracy of the fit, though the complexity of the calculation, particularly for third row elements, increased greatly. The resulting parameters, a_x (3 for first row atoms and 11 each for second and third row atoms), are presented in Tables V, VI and VII.

Table XI. Valence State Energies for Highly Charged States of Third-Row Atoms

Atom (Charge)	Configuration				Energy obsd, eV	$E_{\text{exptl}} - E_{\text{calcd}}$	
	3s	3p	3p	3p		Ours	Oleari's
Al(2+)	1	0	0	0	−28.44	−0.50	1.32
Si(3+)	1	0	0	0	−45.13	−0.09	3.28
Si(2+)	2	0	0	0	−78.59	1.58	0.92
Si(2+)	1	1	0	0	−71.11	−0.36	−0.15
Si(2+)	0	1	1	0	−62.74	2.22	−1.10
P(3+)	2	0	0	0	−116.63	2.66	6.63
P(2+)	2	1	0	0	−146.52	1.07	1.91
P(2+)	1	1	1	0	−137.26	0.09	1.37
P(2+)	1	2	0	0	−135.65	0.25	1.78
S(3+)	2	1	0	0	−207.82	2.26	6.90
S(2+)	2	1	1	0	−242.42	0.73	1.83
S(2+)	2	2	0	0	−240.77	0.74	2.14
S(2+)	1	1	1	1	−231.88	0.41	2.12
S(2+)	1	2	1	0	−230.14	0.48	2.52
Cl(3+)	1	1	1	1	−319.03	1.09	4.25
Cl(3+)	1	2	1	0	−316.84	1.31	4.77
Cl(2+)	2	1	1	1	−371.05	0.26	1.44
Cl(2+)	2	2	1	0	−369.20	0.26	1.62
Cl(2+)	1	2	1	1	−358.17	−0.09	0.13
Root mean square error						1.16	3.07

The use of only 22 second and third row parameters allowed calculation of the energies of the 88 atomic energies used by Oleari to derive his 84 parameters and resulted in an accuracy comparable to that of his calculations. These results, along with the deviations of Hartree-Fock energies (best Slater orbitals) from experimental values for second row atoms, are presented in Tables VIII and IX.

It would be expected that calculations on highly charged ions would be better represented by the present formalism, because the variation of integrals with population is included, and this prediction is verified by the data in Tables X and XI.

(IV) Conclusions

It is evident from the above results that the use of population optimized basis functions can result in a method which, compared to the methods presently used for one-center integrals in most semiempirical methods, requires fewer parameters but predicts with equal or better accuracy the energies of atoms and ions in a wide variety of states. The absence of parameters which depend on atom type may open the path to a semiempirical molecular orbital method which will be relatively easy to parameterize for a wide variety of atoms.

The accuracy of the atomic energy predictions will probably be improved by development of a modified form of eq 1 involving spin populations. Such a form should be used in open shell molecular orbital calculations and, of course, in the above calculations of valence shell atomic energies, as few of the states calculated were closed shell. The improvement such a modification would make, however, must be no larger than the relatively small error in the present calculations.

An additional path for improvement is the inclusion of external coulombic effects on the orbital optimization. This additional effect may well be necessary in future molecular calculations using population optimized basis functions.

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Ground States of Molecules. 38.[1] The MNDO Method. Approximations and Parameters

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Abstract: The basic approximations of the MNDO (modified neglect of diatomic overlap) method are described including a semiempirical model for the two-center repulsion integrals. Parametric functions for the various terms in the MNDO Fock matrix are then chosen which contain atomic parameters only (no bond parameters). Using a nonlinear least-squares iterative optimization technique, numerical values of the parameters are determined for the elements H, C, N, O. Finally, the main differences between the MNDO and MINDO methods are discussed.

(I) Introduction

The primary objective of the work reported in this series of papers has been the development of a quantitative treatment of molecular properties accurate enough, reliable enough, and cheap enough to be of practical value in chemistry, in particular in areas where experimental data are lacking or where current experimental procedures fail. For reasons that have been discussed in detail elsewhere,[2] we have always felt that the only hope of success lay in a parametric approach and our efforts have accordingly been directed to such semiempirical versions of the Roothaan[3]-Hall[4] (RH) SCF-LCAO-MO method.

In order to keep the cost of the calculations within bounds, it is necessary to simplify the RH treatment. Our previous work has been based on the simplified versions developed by Pople et al.,[5] in particular INDO.[6] Here the number of electron repulsion integrals is greatly reduced by using the core approximation, together with a minimum basis set of valence shell AO's, and by neglecting all integrals involving differential overlap except for the one-electron core resonance integrals ($\beta_{\mu\nu}$) and one-center exchange integrals ($\mu\nu$, $\mu\nu$).

The core approximation is certainly reasonable and the neglect of electron repulsion integrals involving diatomic differential overlap can also be justified.[7] These are the assumptions made in the NDDO approximation.[6,8] The further neglect of electron repulsion integrals involving one-center overlap, as in INDO, is, however, unjustifiable,[7] so NDDO would seem the logical basis for a semiempirical treatment. In previous studies we have nevertheless used INDO because the problems of parametrization are much simpler and because less computation is involved.

In the CNDO[5,9] and INDO[5,6] approximations, the repulsion integrals ($\mu\mu$, $\nu\nu$) between any AO ϕ_μ of atom A and any AO ϕ_ν of atom B are set equal ($=\gamma_{AB}$), regardless of whether ϕ_μ and ϕ_ν are of s, pσ, or pπ type. This simplification is essential if the results of the calculation are to be invariant for rotation of the coordinate axes.[5,8] The integrals are not in fact equal and in NDDO they are not assumed to be equal. Moreover in NDDO there are a number of additional bicentric integrals to be considered, which involve one-center differential overlap and are consequently neglected in CNDO or INDO. For a given pair of dissimilar first-row atoms, there are 22 distinct bicentric NDDO integrals to be determined instead of just one in the simple treatments.

In the NDDO calculations so far reported (e.g., ref 10–13) the electron repulsion integrals were found by direct quadra-