An Optimum Minimal Basis of Exponential Atomic Orbitals

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An analysis of some of the energetic properties of the conventional minimal STO basis is used to suggest a new optimum set of exponential functions for use in molecular calculations.

Key words: Exponential AOs, optimum minimal basis of ∼

In the famous paper of 1930 [1] proposing "Slaters Rules" for the estimation of approximate self-consistent atomic orbitals, Slater made use of three pieces of information:

1) The asymptotic form for the solution of the Schrödinger equation for the hydrogen atom is

$$r^{n-1} \exp(-\zeta r)$$

for large values of r.

2) The idea of "screening" – replacing the potential generated by a "shell" of electrons by a spherical average.

3) The small amount of data on atomic calculations available at the time of writing.

Slater's qualitative conclusions have remained unchallenged for nearly half a century – only quantitative changes have been made within his general framework:

a) For reasons of computational convenience the "quantum number" n^* of

$$r^{n^*-1} \exp(-\zeta r)$$

is now almost invariably an integer [2].

b) The orbital exponents ζ can now be accurately optimized – no approximate rules are required [3].

The minimal basis of STOs provides (either explicitly or implicitly) the background for most *ab initio* or semi-empirical calculations of molecular electronic structure and so it is worthwhile to subject this basis to a careful examination.

Taking points 1) to 3) above in reverse order, clearly b) has replaced 3) as a source of information. There can be no objection to 2) since it is the only way of defining "effective" analytical approximate AOs. However the argument for the use of STOs of form $r^{n-1} \exp(-\zeta r)$ because they are the asymptotic form of the hydrogenic Schrödinger equation does not, unfortunately, stand up to close examination. In the first place the asymptotic form (r^{n-1}) takes over from the exact form $(r^l L_{n+l}^{2l+1}(r))$ at rather large values of r; there is, for example, still a 5 difference between the two $2s$ forms at 20 bohrs from the nucleus. Secondly, it is the *functional forms* $r^{n-1} \exp(-\zeta r)$ and $r^l L_{n+l}^{2l+1}(r) \exp(-\zeta r)$ which are asymptotically equivalent at large r: that is they both solve the radial differential equation at large r. But in order to use the approximate forms as *orbitals* they must be normalized, not in the asymptotic region, but in all space. Thus at $r = 100$ bohrs the two $2s$ forms are essentially identical but normalization means that the corresponding orbitals differ by a factor of $\sqrt{3}$. It goes without saying of course that these enormous distances (20–100 bohrs) are of little consequence in the atomic energy or the interpretation of bonding. Classically, the electron at such large distances from the nucleus is moving extremely slowly. Indeed the kinetic energy value for an STO of quantum numbers n, l is always less than or equal to the hydrogenic value of $\frac{1}{2}\zeta^2$, being

$$\frac{n+2l(l+1)}{2n(n-1)}\zeta^2 \leqslant \frac{1}{2}\zeta^2$$

The average value of Z/r for the STO and hydrogenic orbitals are, however, the same; $-Z\zeta/n$. These considerations suggest that the use of a minimal basis of STOs may well lead to an imbalance between kinetic and potential energy and this analysis will be carried further using the virial theorem.

Even the most casual comparison of the results of the use of a minimal basis of STOs [3] for the calculation of atomic structure with Hartree–Fock results shows some important differences. The restricted functional form of the STOs prevents the minimal basis from reproducing the Hartree–Fock total energy, of course, but the most striking difference between the two sets of calculations is in the orbital energies. In particular the minimal STO basis for the heavier members of the first transition series (Fe–Zn) gives extremely poor orbital energies (see Fig. 2), zero or positive for Ni, Cu, Zn. Thus although the computed *total* energy for the minimal basis is correct to a fraction of one per cent, the orbital energies, which in a certain sense, give an indication of the distribution of the energy are in error by anything up to 90% in this important series.

The variational method of optimizing the STO exponents in the minimal basis calculation ensures that the virial theorem for the total energy is obeyed to a high

degree of accuracy by the resulting wave function (5-figure accuracy is typical).
Thus if the total energy is a sum of kinetic (T), nuclear attraction (V_n) and electron
repulsion (V_e) terms then

$$E = T + V_n + V_e \tag{1}$$

and

$$E = -T = \tfrac{1}{2}(V_n + V_e) \tag{2}$$

thus

$$E = (-T + V_e) - V_e \tag{3}$$

But if the orbital energies are ε_i and the orbital occupation numbers are n_i then

$$E = \sum n_i \varepsilon_i - V_e \tag{4}$$

Thus to a very good approximation the sum of the orbital energies is determined by
the relative "weights" of the two essentially positive contributions to the total
energy $-T + V_e$. Now examination of the results of the minimal STO basis calcu-
lation shows that the energy term $\sum n_i \varepsilon_i$ is usually smaller than the corresponding
Hartree–Fock result, in particular it is much smaller for the transition series. Since
the total energies are comparable, this implies that the electron repulsion energy
V_e is too high in the approximate calculation; as we surmised, the kinetic and
potential energy contributions are out of balance. This situation seems likely to be
due to the use of the "higher" STOs which have low kinetic energy averages.

The lowest STOs of each atomic symmetry type are identical to the hydrogenic
orbitals and therefore have kinetic energy $\tfrac{1}{2}\zeta^2$, the forms of the STOs of a given l
value are all of the same general appearance except for the $1s$ function which differs
from the other s functions in its behaviour at the origin. We have therefore used a
minimal basis of STO functions consisting of only the $1s$, $2s$, $2p$, $3d$ forms to
investigate the possibility of improving the energy distribution in atomic systems,
while retaining, if possible, the very good total energy of the "usual" STO set. Pre-
liminary exploratory work with the ground state of the sulphur atom was very
encouraging – Table 1 gives the relevant data for comparison.[1] It is readily seen
from Table 1 that the new minimal basis gives better agreement with the Hartree–
Fock orbital energies in every case. The total energy is also very slightly lower but
this is a rather trivial effect. Encouraged by these results we have performed
optimizations on the elements from the second two rows of the periodic table
since the results in [3] are already optimum for the first row. Table 2 gives the
optimum orbital exponents and total energies for these atoms and Figs. 1 and 2
show the behaviour of the valence orbital energies compared to the Hartree–Fock
and the conventional minimal basis.

There are two general points to be made about the results. Firstly there is an
improvement in orbital energies in going from the conventional minimal basis to

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[1] The last column of Table 1 verifies our conjecture about the unique nature of the $1s$ AO – total
energy is poorer although there is some improvement in some orbital energies.

Table 1 Energy quantities for the ground state of the S atom

Orbital energies	HF[a]	Best STO [3]	1s, 2s, 2p	1s, 2p
1s	−92.0046	−91.8842	−91.9346	−91.9903
2s	−9.0045	−8.7708	−8.8201	−8.4049
2p	−6.6827	−6.4362	−6.4843	−6.5985
3s	−0.8796	−0.8117	−0.8517	−0.7434
3p	−0.4374	−0.3871	−0.4335	−0.4552
Total Energy	−397.505	−396.628	−396.641	−395.345

[a] Numerical Hartree–Fock results are given in: Mann, J. B.: Technical Report LA-3690. University of California: Los Alamos Scientific Laboratory 1967, however the open-shell orbital energies differ from the analytical Roothaan–Hartree–Fock calculations given in Clementi, E.: Suppl. IBM J. Res. Develop. **9**, 2 (1965) presumably due to the arbitrariness in the definition of the open-shell Fock operator (see: McWeeny, R.: Chem. Phys. Letters **35**, 13 (1975)). The results reported here were obtained using the same formalism as the Clementi calculations, therefore in Table 1 and Figs. 1 and 2 "HF" refers to the Clementi calculations. This choice is for purposes of valid comparison and does not, of course, imply that Clementi's results obey a Koopmans' theorem or that Mann's do not.

Table 2. Optimized exponents for the 1s, 2s, 2p, 3d set[a]

Atom	1s	2s	"3s"	"4s"	2p	"3p"	"4p"	3d	Energy
Na	10.6232	3.2775	0.5636	—	3.4002	—	—	—	−161.1225
Mg	11.5993	3.6803	0.7612	—	3.9112	—	—	—	−198.8567
Al	12.5800	4.0829	0.9642	—	4.4861	0.9164	—	—	−241.1533
Si	13.5618	4.4802	1.1601	—	4.9723	0.9770	—	—	−288.0883
P	14.5435	4.8762	1.3470	—	5.4726	1.1226	—	—	−339.9072
S	15.5253	5.2721	1.5309	—	5.9719	1.2655	—	—	−396.6411
Cl	16.5066	5.6673	1.7095	—	6.4697	1.4184	—	—	−458.5577
Ar	17.4881	6.0626	1.8834	—	6.9651	1.5767	—	—	−525.8243
K	18.4688	6.4437	2.1026	0.5806	7.4629	1.8129	—	—	−598.0820
Ca	19.4480	6.8113	2.3120	0.6322	7.9613	2.0508	—	—	−675.5736
Sc	20.4300	7.2084	2.5118	0.6617	8.4627	2.2379	—	2.4621	−758.3434
Ti	21.4114	7.6054	2.6791	0.6736	8.9620	3.3992	—	2.7796	−846.7630
V	22.3939	8.0059	2.8524	0.6890	9.4606	2.5646	—	3.0484	1940.9306
Cr	23.3783	8.4086	3.0371	0.7006	9.9572	2.7275	—	3.2978	−1040.9792
Mn	24.3602	8.8100	3.2000	0.7149	10.4556	2.8839	—	3.5504	−1147.0974
Fe	25.3416	9.2072	3.3501	0.7333	10.9551	3.0434	—	3.7687	−1259.0929
Co	26.3247	9.6087	3.5140	0.7465	11.4528	3.1989	—	3.9930	−1377.4023
Ni	27.3075	10.0099	3.6726	0.7605	11.9494	3.3567	—	4.2157	−1502.0994
Cu	28.2906	10.4120	3.8314	0.7734	12.4462	3.5105	—	4.4386	−1633.3156
Zn	29.2737	10.8199	4.0033	0.8196	12.9410	3.6587	—	4.6612	−1771.2540
Ga	30.2606	11.2021	4.1915	0.9751	13.4333	3.8535	0.7539	5.0569	−1916.5290
Ge	31.2391	11.5593	4.3542	1.1215	13.9233	4.0499	0.8706	5.4412	−2068.4435
As	32.2278	11.9574	4.5888	1.2878	14.4061	4.2471	0.9044	5.8128	−2227.0823
Se	33.2068	12.3157	4.7764	1.4041	14.8916	4.4567	1.1248	6.1697	−2392.4892
Br	34.1842	12.6747	4.9326	1.5608	15.3801	4.6528	1.2401	6.5305	−2564.7889
Kr	35.1761	13.0791	5.1958	1.6421	15.8583	4.8447	1.3642	6.8815	−2744.1078
Atom	1s	2s	"3s"	"4s"	2p	"3p"	"4p"	3d	Energy

[a] The columns labelled "3s", "4s" refer to 2s-type STO's; those labelled "3p", "4p" to 2p STO's.
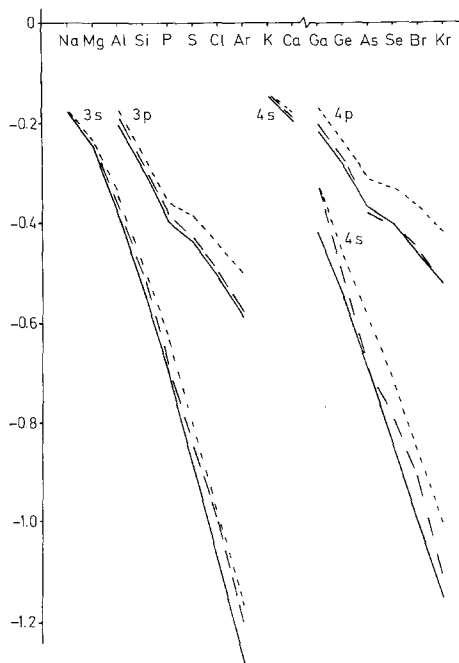
Fig. 1. Orbital energies for the "valance orbitals" of the elements Na to Kr (excluding the transition series). Full line Hartree–Fock (see Footnote to Table 1), broken line this work, dotted line results of Ref. [3]
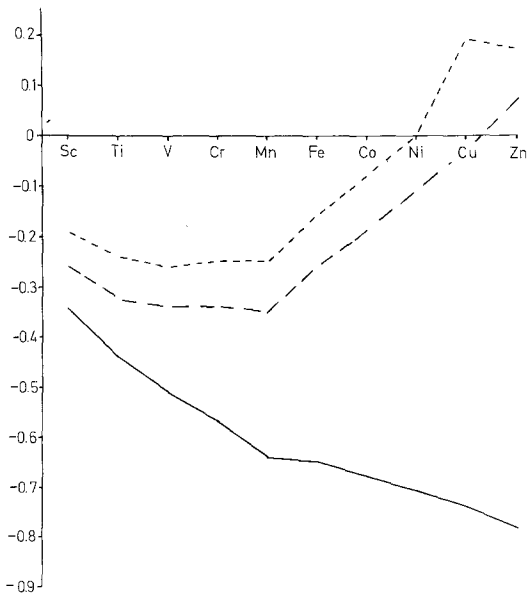
Fig. 2. Orbital energies of the 3d orbital in the first transition series (Sc to Zn). The lines are described in Fig. 1. (The 4s orbital energies are omitted as they are scarcely distinguishable on the scale used)

the 1s, 2s, 2p, 3d basis – this improvement being most dramatic in the case of the 3d energies of the first transition series. Secondly the total energies of the two minimal bases are essentially the same: sometimes the result computed here is the lower, sometimes the result of [3] is lower, the difference being very small indeed. Notwithstanding the first of these conclusions, the 3d orbital energies of the first transition series are, absolutely speaking, still in extremely poor agreement with the HF values as can be seen from Fig. 2. (It is also incidentally the case that the Hartree–Fock orbital energies for these systems are in very poor agreement with experiment – they are generally a factor of 2 too tightly bound in the Hartree–Fock model.) Thus the use of a minimal basis of 3d STOs for these atoms in a molecular calculation is almost guaranteed to give misleading results. Examination of the change in orbital energy with atomic number (for the minimal basis 3d energies) shows that even the wrong trends are given for changes in the population of the 3d levels. Preliminary work with the cobalt atom shows that the use of the 1s, 2s, 2p, 3d minimal basis plus one extra 3d function gives orbital energies within one or two per cent of the Hartree–Fock values for all orbitals with a total energy two hartrees better than the minimal 1s, 2s, 2p, 3d basis. The choice of optimum small bases of exponential functions for transition elements will be the subject of a later note.

Finally it is perhaps worth noting that the molecular energy integrals involving the "lower" STOs are rather simpler to compute than the orbitals of higher n; so that there are considerable economies to be obtained by the use of the 1s, 2s, 2p, 3d basis. For example, existing $n=2$ programs for CNDO, INDO etc. can be used without further modification for second row atoms.

References

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