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Consistent Approximate Wavefunctions for all Elements of the Periodic Table

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A consistent set of exponents for all elements of the periodic table, suitable for semiempirical molecular orbital and other calculations is presented. These exponents were calculated by fitting analytical functions to numerical Herman-Skillman results. The new exponents compare well with existing exponents.

Introduction

One-electron radial wavefunctions for atomic systems can be obtained numerically by solution of the Hartree-Fock [1] or Hartree-Fock-Slater equations [2]. Alternatively, analytical solutions may be found using Roothaan's self-consistent field (SCF) method [3]. Radial functions, either numerical or analytic, obtained by these methods provide an excellent starting basis for further molecular orbital calculations. However for approximate comparative calculations (SCCC or CNDO formalisms) where high accuracy is not required, simpler expressions for the radial wavefunctions are needed.

Slater [4], long ago, recognised this need and proposed the use of an exponential function to describe the radial part of each atomic orbital,

$$R(r) = Nr^{n^*-1}\exp(-\zeta r) \qquad \zeta = (Z - s)/n^*. \qquad (1)$$

Values for n^* and rules for calculating the screening constant s were given. These functions (Slater orbitals) can be calculated for all elements of the periodic table but give poor approximations for $n^* = 3$ and upwards [5–7]. Subsequent workers retained the form of eqn. (1), often as a linear combination, and used a variety of methods to obtain the optimum orbital exponent ζ. Such functions become known as Slater type orbitals (STOs). Both single parameter and double-zeta radial functions with optimised ζ values were obtained by Clementi and Raimondi for elements up to the first transition series [8, 9]. Their method, using a minimal basis of STOs, minimises the energy through a modified Roothaan SCF atomic program. These functions are widely used in MO calculations [10–13]. Burns also obtained single parameter functions by fitting the moments $\langle r^q \rangle$ with accurate Hartree-Fock numerical functions [14]. A recipe was then obtained and ξ values calculated. For the first transition series the multi-parameter radial wavefunctions due to Richardson *et al.* are commonly employed in routine MO calculations [15, 16]. These were obtained by maximising the overlap with the more accurate analytic functions of Watson [17] over a wide range of configurations. Comparable radial wavefunctions are not available for the second and third row transition series. Functions for both these series were obtained by Basch and Gray by fitting multi-parameter STOs to numerical Hartree-Fock functions [18]. However, these functions are resticted to the +1 ions only with fixed configurations of $4d^{n-3}5s^1 5p^1$ and $5d^{n-3}6s^1 6p^1$. Functions for the important neutral states are omitted and due to the importance of transition metal chemistry this restriction in published radial wavefunctions is a serious omission. Ground state electronic properties which are sensitive to the quality of the basis set used have been calculated using these various radial wavefunctions for the 3d, 4d and 5d orbitals of the first, second and third transition series [19]. It was found that the Watson and Richardson functions were adequate for the first series while those of Basch and Gray were suitable for the remaining transition metals.

A limiting factor in accurate ab-initio MO calculations remains the evaluation of many-centre molecular integrals over a basis of STOs. To overcome this, Boys [20] originally suggested the use of Gaussian-type orbitals (GTOs) as an approximation to the radial wavefunction,

$$R_g(r) = \sum N r^{n_g-1}\exp(-\zeta r^2).$$

Although this introduces additional integrals as well as the already multidimensional integrals, the fact that integrals over GTOs are simpler to evaluate than those over STOs more than compensates for the extra computation. Using the integral transform from exponentials to Gaussians allows a basis of STOs to be converted to one of corresponding GTOs. A frequently used conversion is the STO-3GTO expansion due to Stewart [21].

Notwithstanding this wide availability of radial wavefunctions the choice of which basis to use for a

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MO calculation is always a major problem. Computational considerations may dictate both the type, STO or GTO, and size, single or multi-parameter, of the basis functions. Compounding this is the fact that these basis functions often suffer from the defect of limited set availability both within a molecule and between members of a series. If a MO calculation requires bases outside this range recourse to other authors becomes necessary. Since these separate sets are usually obtained by different optimisation techniques non-compatibility is immediately introduced. Though unavoidable, this introduces unsatisfactory features. The present work aims to remedy this situation by providing a compatible basis set for all elements of the periodic table which will be suitable for the more approximate SCCC and CNDO techniques.

Routine applications of MO theory normally use a semiempirical approach, usually within the SCCC-MO or CNDO formalisms. These do not require extensive or highly accurate basis functions. However a consistent set within and between members of a series is most desirable. Typically only single exponents for the valence orbitals are required. Due to the coupling of orbitals with the same *l* value but different n, the total radial wavefunction, given by

$$Tn, l = \sum_{k=l+1}^{n} C_{nk}R_k(\zeta) \tag{2}$$

where,

$$R_k(\zeta) = (2\zeta)^{k+1/2}((2k)!)^{-1/2}r^{k-1}\exp(-\zeta r)$$

is a normalised STO, and the coefficients are completely determined by the Schmidt orthogonalisation procedure. Since only one exponent is actually required for a semiempirical calculation the summation in eqn. (2) was dropped and each radial wavefunction was represented by a single STO. However each radial wavefunction displays oscillatory behaviour and for a given n and *l* value has $n - l - 1$ radial nodes, whereas a single STO has the property of being both nodeless and positive. Consequently fitting the radial wavefunction is only possible when $n - l - 1 = 0$, *i.e.* for 1s, 2p, 3d and 4f orbitals. This difficulty can be overcome, and the single STO representation retained, by considering instead the radial distribution function (RDF), $r^2R^2{}_n(\zeta)$, which although still displaying oscillatory behaviour, is always positive. The occurrence of zeroes in the RDF is confined to a region near the nucleus. Thus the possibility of neglecting such zeroes and approximating only the outermost maximum of the RDF arises. Although the analytic RDF cannot represent this inner behaviour adequately, the above possibility was considered undesirable as the inner part of the radial wavefunction has an important role in determining the energy [22].

The non-relativistic Hartree-Fock-Slater radial wave equation is given by

$$\{-d^2/dr^2 + l(l+1)/r^2 + V(r)\}P_{nl}(r) = E_{nl}P_{nl}(r)$$

where V(r) includes Slater's X_α statistical approximation to exchange correlation [23]. The functions $P_{nl}(r)$ are normalised, thus they are related to STOs by

$$P_{nl}(r) = rR_{nl}(r)$$

where $R_{nl}(r)$ is given by eqn. (2). Numerical functions $P_{nl}(r)$ were generated using a modified version of the program by Herman and Skillman [24] and outputed at each point over a weighted 441 presentation mesh. The α values were those of Schwarz [25] for He through to Nb with subsequent elements assigned a limiting value of 0.7.

The curve fitting technique was that of an unweighted least squares fit. Thus a minium in the expression

$$S_n(\zeta) = \sum_{i=1}^{441} \{P_{nl}(r_i)^2 - (r_iR_{nl}(r_i))^2\}^2$$

was sought as a function of ζ, the orbital exponent. To find this minimum S_n was unmerically differentiated at two points, ζ guess (ζ_g) and $\zeta_g + h$, then linearly extrapolated to find $dS_n/d\zeta = 0$. The numberical differentiation procedure was by the method of finite differences for equally spaced coordinates. Denoting the derivatives at ζ_g and $\zeta_g + h$ by ΔS_n and $\Delta S_n'$ respectively then Newton's interpolation formula gives

$$\delta\zeta = h\Delta S_n/(\Delta S_n - \Delta S_n')$$

and hence an optimum exponent of

$$\zeta_{opt} = \zeta_g + \delta\zeta.$$

A FORTRAN program was written to implement this procedure. If $\delta\zeta$ was unsatisfactorily large, second and further cycles were repeated using ζ_{opt} from the previous cycle as new input. A threshold value of $|\delta\zeta| < 0.0001$ with $h = 0.05$ worked well. Typically, convergence occurred after 3–4 iterations.

In all cases the electronic configurations of the elements were those given by Cotton and Wilkinson [26]. For the three transition series exponents for both the neutral and singly ionised states were computed. The relevant configurations for the valence orbitals were:

	Orbital	Configuration
I	d	$d^{n-2}s^2$
	s	$d^{n-2}s^2$
	p	$d^{n-2}s^1p^1$
II	d	$d^{n-2}s^1$
	s	$d^{n-2}s^1$
	p	$d^{n-2}p^1$

where I and II denote neutral and singly ionised states respectively. For some elements of the transition series alternative configurations are available, *e.g.* Cr($3d^5 4s^1$). Whenever such a choice occurred exponents for both configurations were computed.

Results and Discussion

The core and valence exponents are given for the first twenty-one elements and for the remainder only the valence ones are given, (Tables I to V). Figures 1 and 2 compare the numerical and fitted analytical radial distribution functions, for two typical examples.

Since the use envisaged for these functions is primarily for semiempirical work it is therefore important that: (a) the tail end of the radial function be reproduced accurately and (b) the position of the outermost maximum of the radial distribution function (RDF) be represented faithfully [27].

From the plots (Figs. 1 and 2) condition (b) is seen to be satisfied. In virtually all cases the maximum for both numerical and analytic RDFs occurs at a common radial distance. The exception occurs for f orbitals where the resulting fit is poor. This is not a fault in the computational procedure but rather is due to the inability of a single STO to represent accurately the behaviour of an f orbital. Undoubtedly a more flexible representation, particularly in the form of a double-zeta fit, would help remedy this situation. A surprising feature of these results concerns the single STO fit for d orbitals. These orbitals in particular are represented frequently by a double-zeta fit to reproduce accurately both the inner and outer behaviour of the function [19]. However the results here produce a reasonable fit within a single STO restriction. This is of interest since a basis set comprising a double-zeta representation for d orbitals without a corresponding representation for the valence s and p functions has an in-built bias towards the former. Consequently a basis set with an equal quality single STO fit is more consistent.

The behaviour of the numerical radial functions at large distances from the nucleus is not produced well by the fitted analytic functions. This is true particularly for valence orbitals with large values of n, the principal quantum number. For the core orbitals of the transition metals an excellent fit was obtained at large radial distances. The plots presented for the valence orbitals tend to over-emphasise this behaviour since the RDF rather than the radial function was plotted. The former decays rapidly at large r values ($\propto e^{-2\zeta 2}$) compared with the radial function ($\propto e^{-\zeta 2}$) which displays a slower decay rate at similar distances.

It is of interest to compare the valence s and p exponents calculated here for the transition metals with those of other authors. For the second and third transition series exponents for the +1 metal ions are available. Although the procedure used in obtaining these exponents differs from that employed here a comparison of single zeta exponents is still valid. For both the transition series the present exponents are consistently smaller than those of Basch and Gray. Consequently our functions decay more slowly at large radial distances. Since these functions also coincide with the outermost maximum of the

TABLE I. Orbital Exponents He to Sc.

	1s	2s	2p	3s	3p	3d	4s
He	1.5596						
Li	2.6613	0.6309					
Be	3.6494	0.8789					
B	4.6362	1.2338	1.0696				
C	5.6218	1.5533	1.4500				
N	6.6063	1.8596	1.8166				
O	7.5904	2.1632	2.1739				
F	8.5748	2.4652	2.5173				
Ne	9.5599	2.7645	2.8485				
Na	10.5485	3.1238	3.3802	0.8404			
Mg	11.5378	3.4881	3.8855	1.0393			
Al	12.5293	3.8532	4.3909	1.3448	0.9273		
Si	13.5218	4.2171	4.8957	1.5893	1.2064		
P	14.5152	4.5799	5.3965	1.8086	1.4535		
S	15.5094	4.9430	5.8919	2.0199	1.6886		
Cl	16.5038	5.3077	6.3821	2.2269	1.9160		
Ar	17.4987	5.6752	6.8682	2.4295	2.1347		
K	18.4942	6.0466	7.3528	2.6644	2.4431		0.8648
Ca	19.4896	6.4226	7.8380	2.8992	2.7188		1.0282
Sc	20.4861	6.8035	8.3270	3.1046	2.9417	2.3105	1.1186

TABLE II. (n – 1)d ns np Exponents for Transition Series[a].

	Neutral			+1 Ions		
	3d	4s	4p	3d	4s	4p
Sc	2.3105	1.1186	0.8401	2.3219	1.2578	1.0401
Ti	2.6165	1.1896	0.8627	2.6230	1.3112	1.0878
V	2.8760	1.2545	0.8957	2.8836	1.3763	1.1338
Cr	3.1190	1.3153	0.9239	3.1272	1.4385	1.1768
Mn	3.3588	1.3738	0.9493	3.3673	1.4986	1.2178
Fe	3.5997	1.4296	0.9717	3.6084	1.5563	1.2567
Co	3.8446	1.4831	0.9920	3.8572	1.6121	1.2939
Ni	4.0930	1.5347	1.0103	4.1013	1.6661	1.3294
Cu	4.1332	1.4443	1.0266	4.3495	1.7182	1.3632
Zn	4.5897	1.6330	1.0423	4.5970	1.7696	1.3963
	4d	5s	5p	4d	5s	5p
Y	1.9363	1.2897	0.9269	1.9633	1.3946	1.1513
Zr	2.2055	1.3657	0.9869	2.2217	1.4683	1.2108
Nb	2.4226	1.4277	1.0347	2.4364	1.5336	1.2633
Mo	2.6204	1.4803	1.0724	2.6325	1.5921	1.3095
Tc	2.8137	1.5293	1.1058	2.8246	1.6472	1.3521
Ru	3.0037	1.5746	1.1345	3.0134	1.6991	1.3911
Rh	3.1907	1.6172	1.1596	3.1993	1.7486	1.4271
Pd	3.3739	1.6578	1.1816	3.3814	1.7962	1.4606
Ag	3.5522	1.6968	1.2011	3.5588	1.8421	1.4919
Cd	3.7253	1.7343	1.2186	3.7311	1.8869	1.5214
	5d	6s	6p	5d	6s	6p
Lu	2.3106	1.5900	1.0927	2.3789	1.7056	1.3850
Hf	2.6669	1.6725	1.1408	2.6920	1.7776	1.4413
Ta	2.8851	1.7384	1.1812	2.9031	1.8425	1.4943
W	3.0642	1.7950	1.2172	3.0791	1.9012	1.5431
Re	3.2252	1.8453	1.2498	3.2382	1.9551	1.5881
Os	3.3758	1.8910	1.2798	3.3873	2.0050	1.6300
Ir	3.5197	1.9329	1.3075	3.5301	2.0515	1.6679
Pt	3.6588	1.9719	1.3332	3.6682	2.0954	1.7035
Au	3.7944	2.0082	1.3569	3.8030	2.1369	1.7367
Hg	3.9276	2.0424	1.3788	3.9355	2.1764	1.7677

(n – 1)d ns Exponents for Transition Series[b]
Neutral atoms

	d	s
Cr	2.8960	1.2175
Cu	4.3416	1.5841
Nb	2.2943	1.3509
Mo	2.4975	1.3914
Tc	2.6950	1.4287
Ru	2.8898	1.4629
Rh	3.0834	1.4946
Pd	3.2740	1.5244
Ag	3.4598	1.5525
Pt	3.5753	1.8374
Au	3.7133	1.8655

[a] Ground state $d^{n-2}\ s^2$. [b] Ground state $d^{n-1}\ s^1$.

TABLE III. Valence Exponents Ga to Sr; In to Ba; Tl to Ac.

	4s	4p	5s	
Ga	1.9148	1.1942		
Ge	2.1227	1.5352		
As	2.2999	1.7902		
Se	2.4637	1.9915		
Br	2.6196	2.1708		
Kr	2.7702	2.3390		
Rb	2.9484	2.6004	0.9944	
Sr	3.1267	2.8219	1.1727	
	5s	5p	6s	
In	2.0234	1.3670		
Sn	2.2244	1.6197		
Sb	2.3861	1.8467		
Te	2.5329	2.0496		
I	2.6723	2.2273		
Xe	2.8070	2.3858		
Cs	2.9674	2.6133	1.0360	
Ba	3.1279	2.8043	1.2061	
	6s	6p	6d	7s
Tl	2.3034	1.5966		
Pb	2.4953	1.8863		
Bi	2.6531	2.0923		
Po	2.7949	2.2649		
At	2.9266	1.4210		2.4210
Rn	3.0512	2.5678		
Fr	3.1983	2.8033		1.1579
Ra	3.3417	2.9881		1.3178
Ac	3.4716	3.1335	2.1662	1.4184

TABLE IV. Valence Exponents for the Lanthanides[a].

	Configuration	4f	5d	6s
Ce	$4f^2 6s^2$	1.0881		1.2559
Pr	$4f^3 6s^2$	1.1928		1.2757
Nd	$4f^4 6s^2$	1.2915		1.2944
Pm	$4f^5 6s^2$	1.3692		1.3121
Sm	$4f^6 6s^2$	1.4318		1.3292
Eu	$4f^7 6s^2$	1.4851		1.3458
Gd	$4f^7 5d^1 6s^2$	1.5954	2.2477	1.4606
Tb	$4f^9 6s^2$	1.5754		1.3778
Dy	$4f^{10} 6s^2$	1.6155		1.3933
Ho	$4f^{11} 6s^2$	1.6533		1.4085
Er	$4f^{12} 6s^2$	1.6894		1.4235
Tm	$4f^{13} 6s^2$	1.7243		1.4384
Yb	$4f^{14} 6s^2$	1.7581		1.4530
Lu	$4f^{14} 5d^1 6s^2$	1.8366	2.3106	1.5900

[a] Neutral atoms.

TABLE V. Valence Exponents for the Actinides[a].

	Configuration	5f	6d	7s
Th	$5f^{0}6d^{2}7s^{2}$		2.3516	1.4994
Pa	$5f^{2}6d^{1}7s^{2}$	1.2706	2.2679	1.4601
U	$5f^{3}6d^{1}7s^{2}$	1.3161	2.3083	1.4782
Np	$5f^{5}7s^{2}$	1.3166		1.4162
Pu	$5f^{6}7s^{2}$	1.3608		1.4295
Am	$5f^{7}7s^{2}$	1.4064		1.4421
Cm	$5f^{7}6d^{1}7s^{2}$	1.5146	2.4309	1.5426
Bk	$5f^{8}6d^{1}7s^{2}$	1.5791	2.4543	1.5577
Cf	$5f^{10}7s^{2}$	1.5715		1.4771
Es	$5f^{11}7s^{2}$	1.6462		1.4880
Fm	$5f^{12}7s^{2}$	1.7339		1.4985
Md	$5f^{13}7s^{2}$	1.8246		1.5088
No	$5f^{14}7s^{2}$	1.9063		1.5189
Lr	$5f^{14}6d^{1}7s^{2}$	2.0335	2.5488	1.6439

[a]Neutral atoms.

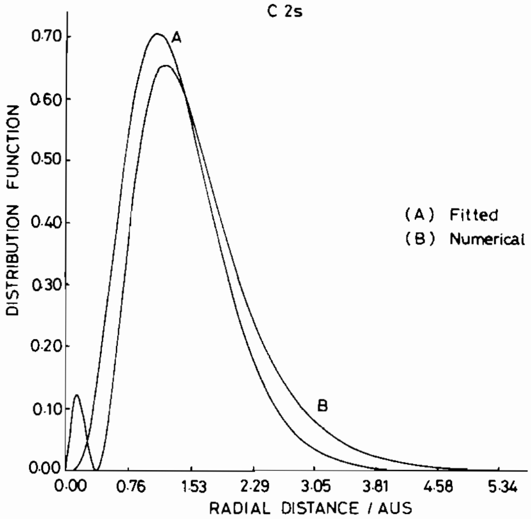

Fig. 1. Distribution function for C 2s orbital.

numerical RDFs it would appear that for a single STO fit they are of superior quality to those of Basch and Gray.

For the first transition series comparison of the valence s functions with those of Richardson and coworkers shows little difference, despite the different methods of computation. These exponents suffer from the restriction of being tabulated for the neutral metal atoms only. It is assumed that the same s exponent may be used for higher states of ionisation. An examination of Table II shows that this assumption may be unsatisfactory since the s exponents for the neutral and +1 states differ. Indeed for very high states of ionization the use of a neutral s exponent may introduce considerable error. The comparison of p functions for the neutral state is more difficult since no $d^{n-2}s^{1}p^{1}$ configuration is listed by Richardson and coworkers [15, 16]. However a comparison of their results for the configuration $d^{n-1}p^{1}$ with the present ones for the $d^{n-2}s^{1}p^{1}$ configuration shows that the latter are slightly larger. For the +1 ions the $d^{n-2}p^{1}$ configuration was considered by Richardson and coworkers and these are similar to the ones calculated in the present study.

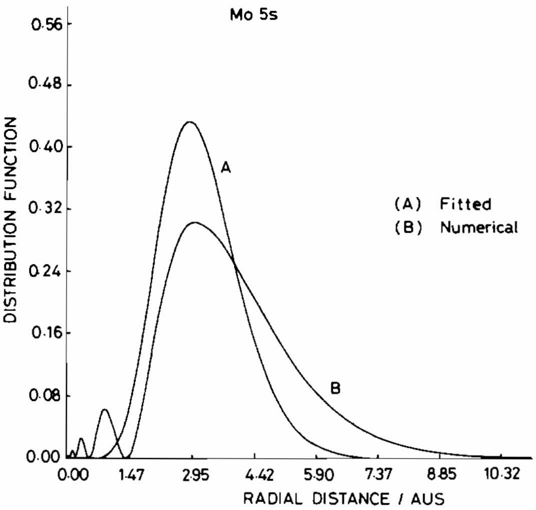

Fig. 2. Distribution function for a Mo 5s orbital.

These new exponents are particularly useful for semiempirical molecular orbital calculations, as to date no complete set is readily available. To compare their use with existing exponents comparative self-consistent charge and configuration calculations (extended Hückel) are reported for $M(CO)_6$, M = Cr, Mo, W. In one set of calculations the radial functions of Richardson and coworkers [15, 16] for Cr, those of Basch and Gray for Mo and W [18] and those of Clementi and Raimondi [8] for C and O were considered. In the second set of calculations the new exponents were used.

The results are shown in Table VI, from which it is noted that there is little variation between the sets of exponents. In both cases the absolute charges increase as the atomic number increases, while the new exponents give slightly larger absolute charges. Both series of calculations give the HOMO as $2t_{2g}$, as expected.

The ionization potentials (Koopmans' theorem) of all the hexacarbonyls are similar in agreement with experiment. Thus it is seen that the new set of exponents is suitable for semiempirical molecular orbital calculations.

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TABLE VI. Comparison of Electronic Properties of $M(CO)_6$.

	Literature exponents[a]			New exponents		
	Cr	Mo	W	Cr	Mo	W
q_M	0.234	0.310	0.316	0.301	0.392	0.426
q_c	−0.039	−0.052	−0.053	−0.050	−0.065	−0.071
$E_{2t_{2g}}$(eV)	−11.816	−11.590	−11.731	−10.776	−11.257	−11.307

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