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Molecular states of atoms. II

Orbital wave functions

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Orbital energy parameters, previously obtained from atomic valence state energies, are used in calculating approximate wave functions for their orbitals. The radial factors of these wave functions are expressed as linear combinations of three Gaussian type orbitals with selected exponents, the coefficients being determined by normalisation and reproduction of the kinetic energy and interelectron repulsion parameters. Wave functions of universal form are obtained for the non-transition elements up to xenon. Each calculated *s* orbital wave function (except 1*s*) has a radial node, as is appropriate if there is a *p* orbital in the same shell with none.

Key words: Atomic orbital — Valence state — Kinetic energy — Radial node — Gaussian type orbital — Pseudopotential

1. Introduction

Semiempirical molecular orbital methods can be applied effectively in electronic structure calculations if they employ physically realistic interaction parameters and basis functions. To a lesser extent, minimal basis set *ab initio* calculations are not insensitive to the choice of basis functions [1, 2] so that comparison of their predictions with experiment can be required to determine a basis set of optimum general utility. More attention has been given, in semiempirical work, to the selection of the orbital interaction parameters than to the detailed form of the basis orbitals themselves; minimal valence bases of Slater type orbitals (STO's) predominate with exponents obtained from different prescriptions [3, 4, 5], possibly employing an expansion of each STO in Gaussian type orbitals

(GTOs) [6] to facilitate computation. A survey of, e.g., interelectron repulsion parameters would show that typically [7, 8] the values calculated from the STO basis can deviate significantly from those actually used. Since most semiempirical calculations contain parameters adjusted so as to optimise the comparison of their predictions with experiment, such discrepancies may not be of great significance in practice. None the less, we here investigate what form the wave functions of the basis orbitals could take if they are to be consistent with the values of the interaction parameters assigned to the orbitals.

In a previous paper [9] we obtained orbital energy parameters for atoms from an analysis of valence state (VS) energies. These energies were related, using some justified approximations, to the orbital occupation numbers characterising the configurations of atom A by [10]

$$E_A^{VS} = C_A + n_sU_s + n_pU_p + [\tfrac{1}{2}n_s(n_s-1) + \tfrac{2}{5}n_sn_p]g_{ss} + [\tfrac{3}{5}n_sn_p + \tfrac{1}{2}n_p(n_p-1)]g_{pp} \tag{1}$$

This equation contains a configuration-independent core energy parameter C_A. The s orbital has parameters U_s (core-valence interaction energy) and g_{ss} (interelectron repulsion between electrons in the s orbital). U_p and g_{pp} apply similarly to the p subshell. Values for these parameters were obtained by fitting the expression (1) to Hinze's valence state promotion energies [11] for each atom; each valence state has integer subshell occupation numbers n_s and n_p.

In order to employ these parameters in a molecular orbital calculation, it was shown in [9] that, in the theoretical limit of atom A being removed to a very large distance from the other atoms of a molecule, a single determinant description of the molecular electronic structure enables us to identify the energy of A in this "molecular state" (MS) as

$$E_A^{MS} = C_A + \sum_a n_aH_{aa}^A + \tfrac{1}{2}\sum_a \sum_{a'\neq a} n_an_{a'}g_{aa'} + \tfrac{1}{4}\sum_a n_a^2g_{aa} \tag{2}$$

The value of the configuration-independent parameter C_A depends on the zero of the chosen energy scale, in our work the energy of the spectroscopic ground state of the neutral atom A. The Fock operator F^A associated with E_A^{MS} is independent of C_A and its diagonal matrix elements are [9]

$$F_{aa}^A = H_{aa}^A + \sum_{a'\neq a} n_{a'}g_{aa'} + \tfrac{1}{2}n_ag_{aa} \tag{3}$$

with H^A the operator representing the kinetic energy and core potential energy. The approximations in (1) to (3) are [9]

$$g_{xx} = g_{xy} = g_{pp} \tag{4}$$

$$g_{sp} = \tfrac{2}{5}g_{ss} + \tfrac{3}{5}g_{pp} \tag{5}$$

which reflect some limitations in the VS data [9]. Therefore Fock matrix elements can be set up using $H_{aa}^A = U_a$ and values for g_{ss} and g_{pp} from the VS data.

We were also able to provide a prescription for identifying values of the components of

$$H_{aa}^A = T_{aa} - Z_A\Lambda_a \tag{6}$$

where T_{aa} is the kinetic energy of orbital a, Z_A the net positive charge of the core, and $-Z_A\Lambda_a$ the attractive interaction energy between the core and an electron in orbital a. Our prescription was based on the virial theorem [9] and provides physically acceptable values of T_{aa} and Λ_a. The motivation for performing the decomposition in (6) was the requirement, in some semi-empirical molecular orbital methods, of values of T_{aa} to enable generation of off-diagonal kinetic energy matrix elements.

Values of T_{aa}, Λ_a and g_{aa} were tabulated in [9]. For each atom T_{aa} and Λ_a are defined for a reference MS with equal occupation of all the valence shell orbitals. We now investigate what form the wave functions of the orbitals this reference state take, using the constraint that the calculated orbital interaction parameters should agree with those obtained from the VS data.

An a priori derivation of the wave functions of the atomic orbitals requires a solution of the many-electron Schrödinger equation for the atom. This is straightforward at the single determinant level for spin zero atomic ground states. Even if correlation effects are ignored for such states, there is still the problem that the majority of isolated atoms have ground states with non-zero spin. A valence state calculation would use a single Slater determinant atomic wave function for all atoms, spin-averaging the interactions between subshells where necessary, but even so it would be unlikely that the calculated interaction parameters would agree with those obtained from the VS data.

2. Method

We have calculated orbital wave functions of the usual form

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)\, Y_{lm}(\theta, \varphi) \tag{7}$$

where the radial factor is a linear combination

$$R_{nl}(r) = \sum_{i=1}^{3} c_i G_i^{(l)}(r) \tag{8}$$

of normalised GTOs with coefficients to be determined. Y_{lm} denotes a normalised spherical harmonic for subshell l, and $G_i^{(l)}(r)$ denotes the radial factor of a normalised GTO. Following Stewart [6], we use

$$G_i^{(0)}(r) = 2^{7/4}\pi^{-1/4}\alpha_i^{3/4} \exp(-\alpha_i r_i^2) \tag{9}$$

to fit s orbitals, and

$$G_i^{(1)}(r) = 3^{-1/2}2^{11/4}\pi^{-1/4}a_i^{5/4} r \exp(-\alpha_i r^2) \tag{10}$$

to fit p orbitals.

We require that each wave function ψ_{nlm} be normalised and also have expectation values of kinetic energy and interelectron repulsion equal to the VS values T_{aa} and g_{aa} respectively. The VS core-valence interaction parameter Λ_a in (6) is not used because we have no detailed knowledge of the effective core potential for an electron in orbital a and hence cannot calculate a value of Λ_a from ψ_{nlm}. Instead Λ_a will prove useful in selecting the appropriate wave function (see below).

The normalisation condition is expressed as

$$\sum_{ij}^{3} c_i S_{ij} c_j = 1 \tag{11}$$

with S_{ij} the overlap between two normalised GTOs i and j with wave functions of form $G_i(r)\ Y_{lm}(\theta, \varphi)$. Similarly, the kinetic energy constraint takes the form

$$\sum_{ij}^{3} c_i T_{ij} c_j = T_{aa} \tag{12}$$

The matrices S and T are defined unambiguously. Some care, however, is required in deciding on the form of the calculated two-electron repulsion integrals. For the s subshell there is no problem, and we use

$$\gamma_{ss} = \sum_{ijkl}^{3} c_i c_j (s_i s_j \,|\, s_k s_l) c_k c_l = g_{ss} \tag{13}$$

employing the usual notation for the two-electron repulsion integral involving four GTOs. For the p subshell there is only one, average, VS value g_{pp} [9]. It might appear straightforward to identify this as $(xx\,|\,xx)^A$, the two-electron repulsion integral for a single p orbital of A, but that would result in inconsistencies once the diagonal matrix elements for this orbital of the Fock operator are considered. From [9]

$$F_{xx}^A = H_{xx}^A + n_s(xx\,|\,ss)^A + \tfrac{1}{2}n_x(xx\,|\,xx)^A + (n_y + n_z)(xx\,|\,yy)^A \tag{14}$$

As discussed in [9], one requirement on any approximate form of Fock matrix elements is that rotational invariance is ensured under any orthogonal transformation of the orbitals of a subshell [7]. The above form will preserve this invariance only for transformations between molecular states with $n_x = n_y = n_z = n_p/3$. In general an averaged quality γ_{pp} should replace the two-electron repulsion integrals in (14) [9]. The choice of γ_{pp} should reproduce F_{xx}^A in (14) over a realistic range of occupation numbers. We have therefore taken

$$\gamma_{pp} = \tfrac{1}{5}(xx\,|\,xx)^A + \tfrac{4}{5}(xx\,|\,yy)^A \tag{15}$$

so that the constraint of the reproduction of g_{pp} from the VS data becomes

$$\gamma_{pp} = \sum_{ijkl}^{3} c_i c_j \{\tfrac{1}{5}(x_i x_j \,|\, x_k x_l) + \tfrac{4}{5}(x_i x_j \,|\, y_k y_l)\} c_k c_l = g_{pp} \tag{16}$$

This choice of γ_{pp} will reproduce F_{xx} in (14) for states with $n_x = n_y = n_z$. Such states include the reference MS defined in [9]. This would not have been the case if

$$\gamma_{pp} = \tfrac{1}{3}(xx\,|\,xx)^A + \tfrac{2}{3}(xx\,|\,yy)^A \tag{17}$$

had been used instead. That form is appropriate for averaging the interelectron repulsion between two electrons in different subshells.

The three simultaneous Eqs. (11), (12), and (13) or (16), can be solved for the coefficients c_1, c_2 and c_3, once the exponents of the GTOs have been fixed. Clearly α_1, α_2, and α_3 should span a range that gives the expansion in (7) the flexibility to reproduce the radial factor $R_{nl}(r)$ over a wide range of radii. Our exponent selection was influenced by the form of the kinetic energy and interelectron repulsion integrals for a single GTO, which indicated that the GTO with largest

Table 1. Calculated *s* orbital radial factors as expansions of three normalised *s* GTOs for all non-transition elements with atomic number ≤54. Exponents are in atomic units, the expectation value $\langle r^{-1} \rangle$ is in eV

	α_1	α_2	α_3	c_1	c_2	c_3	$\langle r^{-1} \rangle$
H	0.11150	0.55749	1.9087	0.86368	0.03539	0.25379	22.277
He	0.60045	3.0023	7.2561	0.77907	0.28177	0.02779	45.732
Li	0.028205	0.28928	0.67869	1.13689	−0.82299	0.27166	6.061
Be	0.052827	0.44191	1.9108	1.15917	−0.92413	0.27420	8.671
B	0.11390	0.98615	3.8460	1.15468	−0.90977	0.26865	12.644
C	0.18680	1.6309	6.2027	1.15363	−0.90586	0.26728	16.169
N	0.19757	1.4794	8.9183	1.17582	−0.95596	0.29000	17.454
O	0.43390	4.0463	12.630	1.14593	−0.86989	0.25796	24.386
F	0.25999	1.7064	15.279	1.20158	−0.97834	0.30563	21.939
Ne	0.34644	2.2278	21.206	1.20630	−0.98100	0.30788	25.787
Na	0.029453	0.31574	0.64871	1.13395	−0.82558	0.30720	6.086
Mg	0.048105	0.40580	1.7111	1.15805	−0.92088	0.27287	8.259
Al	0.071756	0.55078	3.0828	1.17178	−0.95031	0.28675	10.396
Si	0.16059	1.4533	4.9637	1.14932	−0.88732	0.26167	14.908
P	0.25959	2.4891	7.1466	1.14297	−0.85320	0.25655	18.758
S	0.14084	0.94817	7.8651	1.19599	−0.97477	0.30277	15.808
Cl	0.12370	0.69044	10.052	1.24599	−0.99400	0.32270	17.856
Ar	0.21041	1.3098	13.744	1.21429	−0.98487	0.31139	20.722
K	0.011240	0.087585	0.46862	1.16941	−0.94653	0.28471	4.089
Ca	0.044806	0.44318	1.1593	1.13996	−0.83620	0.25923	7.731
Ga	0.033217	0.17982	2.8691	1.25633	−0.99491	0.32574	9.588
Ge	0.27194	3.0342	5.5292	1.13206	−0.85621	0.36735	18.186
As	0.15119	1.1742	6.3451	1.16992	−0.94739	0.28517	15.015
Se	0.24900	2.1563	8.4049	1.15466	−0.90968	0.26862	18.695
Br	0.21843	1.6036	10.258	1.17923	−0.96006	0.29250	18.550
Kr	0.16579	0.95967	12.526	1.23453	−0.99178	0.31901	19.842
Rb	0.023596	0.25268	0.52087	1.13401	−0.82517	0.30598	5.450
Sr	0.038510	0.35966	1.1175	1.14576	−0.86897	0.25782	7.263
In	0.065580	0.47983	3.1008	1.17982	−0.96073	0.29293	10.184
Sn	0.12429	1.0388	4.5037	1.15929	−0.92447	0.27434	13.303
Sb	0.25794	2.5360	6.7543	1.14051	−0.83921	0.25824	18.582
Te	0.29421	2.7881	8.2928	1.14420	−0.86021	0.25681	20.020
I	0.12502	0.75741	8.6223	1.22145	−0.98776	0.31428	16.414
Xe	0.10819	0.54987	10.603	1.26881	−0.77991	0.34717	20.255

exponent would dominate the kinetic energy, while the interelectron repulsion would be more sensitive than the kinetic energy to the GTOs with smaller exponents. The equations to be solved are non-linear in the unknown coefficients, so the number of solutions can vary. We decided that it would be desirable for the GTO exponents to be related explicitly to the VS data so that the orbital wave functions might have a universal, numerically similar, form for different elements. The requirement of universality aided the selection of a solution from those obtained and is helpful in identifying physical trends in the form of the wave function for sequences of elements.

Some exploratory work indicated that, within quite narrow limits, such a method of exponent selection could be set up. For each subshell the VS values of kinetic

Table 2. Calculated *p* orbital radial factors as expansions of three normalised GTOs for the non-transition elements with atomic number $3 \leq Z \leq 54$, except for K, Ca, Sr (see text). Units are as in Table 1

	α_1	α_2	α_3	c_1	c_2	c_3	$\langle r^{-1} \rangle$
Li	0.0046578	0.028897	0.15559	0.51054	0.53063	0.29018	5.049
Be	0.015435	0.099418	0.47831	0.50473	0.55187	0.25837	8.983
B	0.031218	0.19350	1.0448	0.51065	0.53020	0.29087	13.078
C	0.043496	0.24686	1.7361	0.51508	0.50419	0.34121	16.187
N	0.070238	0.41412	2.5979	0.51452	0.51228	0.32260	20.168
O	0.066273	0.33248	3.3855	0.50582	0.49869	0.38128	21.192
F	0.11997	0.68002	4.8007	0.51507	0.50398	0.34177	26.900
Ne	0.23005	1.4866	7.0836	0.50409	0.55409	0.25523	34.609
Na	0.0033735	0.019401	0.13114	0.51510	0.50654	0.33520	4.478
Mg	0.0073889	0.035825	0.40412	0.50082	0.50086	0.38878	7.187
Al	0.016440	0.084876	0.79299	0.50928	0.49786	0.37400	10.417
Si	0.017678	0.073195	1.3258	0.46794	0.52174	0.41230	11.927
P	0.031471	0.13974	2.0521	0.48420	0.51085	0.40369	15.425
S	0.034923	0.15056	2.4158	0.47761	0.51521	0.40761	16.464
Cl	0.055051	0.25306	3.3496	0.49132	0.50630	0.39846	20.090
Ar	0.086279	0.42360	4.6020	0.50276	0.49993	0.38615	24.419
K							
Ca							
Ga	0.023317	0.14932	0.73095	0.50581	0.54807	0.26381	11.081
Ge	0.014863	0.054401	1.1464	0.43522	0.54384	0.42301	11.571
As	0.036606	0.17774	1.9965	0.50104	0.50075	0.38849	15.986
Se	0.030276	0.12123	2.4279	0.45946	0.52751	0.41569	15.846
Br	0.043301	0.18257	3.1317	0.47237	0.51874	0.41028	18.516
Kr	0.068850	0.31938	4.1136	0.49308	0.50522	0.39696	22.376
Rb	0.0014235	0.0053155	0.13127	0.44074	0.54016	0.42157	3.548
Sr							
In	0.015039	0.076042	0.75631	0.50683	0.49836	0.37938	10.059
Sn	0.010772	0.037421	1.1477	0.42064	0.55344	0.42637	10.099
Sb	0.024955	0.10313	1.8786	0.46748	0.52206	0.41250	14.183
Te	0.023425	0.085144	2.2797	0.43329	0.54513	0.42349	14.575
I	0.027104	0.10055	2.5319	0.43896	0.54135	0.42205	15.528
Xe	0.052557	0.22831	3.5808	0.47935	0.51405	0.40665	20.129

energy and interelectron repulsion were expressed in atomic units as t and g respectively. Then, for hydrogen and helium, we used

$$\alpha_1=\tfrac{1}{2}g^2, \qquad \alpha_2=5\alpha_1, \qquad \alpha_3=5t$$

For s orbitals of the remaining elements, we used

$$\alpha_1=g^2, \qquad \alpha_2 \propto gt^{-1/2} \qquad \alpha_3=5t$$

and for the p orbitals

$$\alpha_1=0.35g^2, \qquad \alpha_2 \propto gt^{-1/2}, \qquad \alpha_3=2t$$

The actual values taken for each element are given in Tables 1 and 2.

3. Results

Solution of the set of non-linear simultaneous equations (11), (12), and (13) or (16) were calculated using the NAG library routine C05NBF [12]. All computation was in double precision arithmetic (18 significant figures) on the UCW Honeywell computer. For hydrogen and helium s orbitals, and most p orbitals, two solutions were found. At least two, and more frequently four, solutions were found for s orbitals.

We found no solutions for the p orbitals of potassium, calcium and strontium, even after searching through many selections of GTO exponents. This suggests that their VS data are incompatible with the GTO expansion (8). The values of g_{pp} for these elements are unexpectedly large. The relative unreliability of the VS data for these elements was noted in [9], and there appeared therefore to be little point in further effort to find solutions consistent with them.

The solutions selected as radial factors for the orbital wave functions are presented in the tables, as coefficients and exponents of normalised GTOs in (8). Also given are the expectation values $\lambda_a=\langle r^{-1}\rangle_a$ calculated from these solutions. The VS core-valence interaction parameter Λ_a should be greater than λ_a for s orbitals, due to significant penetration of the core by these orbitals. For p orbitals we anticipate $\Lambda_a \sim \lambda_a$ because penetration effects should be smaller, although for small Z_A they will be more noticeable because the core is relatively larger with respect to the valence electron distribution. The calculated values of $\langle r^{-1}\rangle_a$ for each computed solution assisted in the identification of the appropriate solution for each subshell. The other solutions either have $\langle r^{-1}\rangle_a > \Lambda_a$ or were not found for many of the elements considered.

The radial factors of these orbital wave functions for some lighter atoms are plotted in the figure. The nodeless radial factors (s for hydrogen, p for the other elements) are not dissimilar to the corresponding STO, although for p orbitals they diminish to zero much more slowly than the STO at larger radii. The calculated hydrogen wave function is similar in magnitude to, but somewhat more diffuse than, the STO. The difference is not as marked as might be expected for an orbital with kinetic energy of 10.4 eV [9] as opposed to the STO value of 13.6 eV, and this may justify to some extent the utility of the hydrogen STO in

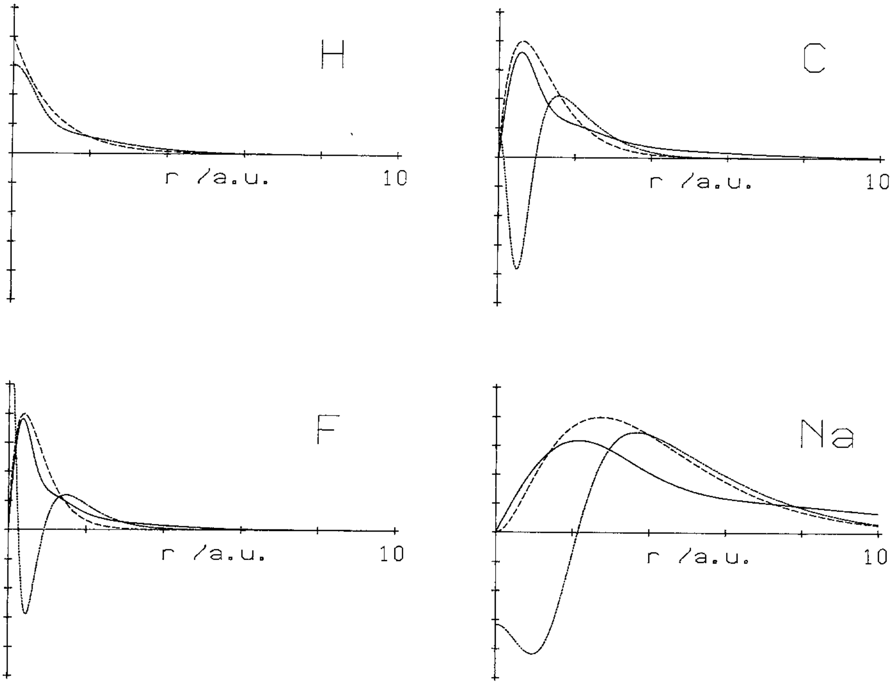

Fig. 1. Radial factors of the orbital wave functions calculated for hydrogen, carbon, fluorine and sodium. *Dotted lines* indicate *s* orbitals, *solid lines p* orbitals, and the *dashed lines* STOs with Slater's exponents for comparison. The plot for each element has, for clarity, been scaled to give the same STO peak height. The fluorine 2*s* orbital wave function at the origin has about twice the amplitude of the STO peak

semi-empirical work. The other *s* orbitals are markedly different from STO form, having a radial node roughly where the STO peaks. This is quite consistent, for a first row atom, with the node required in a 2*s* wave function to make it orthogonal to the 1*s* core wave function. Because we consider only the outer shell electrons explicitly we expect to find their *p* orbitals lacking radial nodes in all rows of the Periodic Table and therefore, by analogy with first row elements, to find this radial node in the *s* orbital wave function.

For $r \rightarrow 0$ the *p* orbital vanishes by construction, while the calculated wave functions for the *s* orbital can not be expected to be very realistic close to the nucleus because the weighting in (8) of the most compact GTO, which dominates the wave function's variation there, is determined mainly by the need to reproduce the kinetic energy of the orbital correctly rather than mimic the detailed structure of a Hartree-Fock *s* orbital near the nucleus.

4. Conclusion

Atomic orbital wave functions have been obtained which are consistent with orbital energy parameters derived from experimental data. We envisage two areas of useful application for them. The first is in the development of semi-empirical and pseudopotential methods (these wave functions can be regarded as approximate eigenfunctions of an experimentally derived pseudopotential, for which the detailed form of the eigenfunctions near the nucleus is not expected to be realistic), where the above consistency permits the universal form of the wave functions to be considered explicitly in systematic investigation of suitable approximations to multi-centre matrix elements. Relatively little work of this type has been done, in contrast to the effort expanded in optimising the parameters of semiempirical methods which use standard bases. The second area is improvement in the prediction of valence electron densities in molecular orbital calculations, for the *s* wave functions in particular are more realistic than nodeless STO's and diminish more rapidly with increasing radius than their partner *p* wave functions, correctly reflecting the difference between the *s* and *p* orbital energies. We intend to investigate the utility of these basis functions in approximate molecular orbital calculations.

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