SLATER SCREENING CONSTANTS IN ATOMIC AND MOLECULAR ORBITALS*

by

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I. INTRODUCTION

Slater screening constants and Slater orbitals (1930) have enabled a whole generation of chemists and physicists to calculate approximate values of many of the physical properties of atoms. The use of screening constants implies that an atomic orbital corresponding to a given set of electronic quantum numbers is the same, except for a uniform scaling of the coordinates, quite irrespective of which atom or ion is under consideration. This concept of interchangeability of orbitals has greatly simplified our mental picture of atomic structure.

An adequate simple model of a molecular orbital certainly must be more complicated than a Slater atomic orbital. The molecular orbitals vary in size and shape as the internuclear separations are changed. Nevertheless, as chemists we feel confident that is must be possible to develop the concept of interchangeability of molecular orbitals on some sort of corresponding states basis. We are impressed with the simple regularities which characterize most molecules: the additivity of bond energies; the accurate reproducibility of bond lengths, bond angles, and bond force constants; etc.

As our theoretical treatments and mathematical experimentation give progressively closer analogues to natural phenomena, it is evident that two types of theories will emerge. First, due to the development of computers capable of remembering and manipulating

very great detail, there will be the highly complex formulations representing numerical models of physical systems which can be assimilated only by the high speed computing machines which generated them. And second, there will be the simplified semi-empirical formulations which the human mind can comprehend and manipulate in a sophisticated conceptual or analytical manner. The computing machines will provide specific answers to specific questions in much the same manner as the results of laboratory experiments. However, there is a great need for the output of the computing machines describing these "numeric systems" to be in an accessible and usable form. These simplified representations will help the scientist to see the important features of the model and make it easier for him to develop a simple concept or understanding of the phenomena. The scientist will then make quantitative definitions of the important features and use the numerical output of the computing machines to interpolate and extrapolate the change of these important features which occur when the "experimental" conditions are changed.

In seeking a simplified formulation of the behaviour of a class of systems, we inevitably try to develop a corresponding states treatment in which all of the systems obey the same equations when each system is characterized by a set of parameters. Thus, the aerodynamical behaviour of geometrically similar objects moving through different media can be characterized by Reynolds, Prandtl, and Schmidt numbers. The volumetric behaviour of a gas or liquid

can be characterized by the critical parameters: P_c, V_c, and T_c. In chemistry, a compound is characterized by its atomic composition and by its chemical bonds. In quantum chemistry, we further characterize a compound by its molecular orbitals. Underlying each of these uses of corresponding states is the inherent notion of the interchangeability of systems of a particular class. This interchangeability is certainly only an approximation, but it may be useful in helping us to comprehend and to predict the behaviour of complex systems. In the present paper, let us consider on a simple basis, first, how Slater screening constants relate to the interchangeability of atomic orbitals and second, their role in molecular orbitals.

II. Atomic Orbitals

The notion of screening constants stems from a well-known theorem of classical electrostatics. Suppose that an atom is composed of a nucleus of charge + Ze surrounded by a spherically symmetric cloud of electrons having a charge density - $e\rho(r)$. Then the electrostatic potential $V(r)$ at a distance r from the nucleus is

$$V(r) = +e(Z - S(r))/ r = +e Z_{eff}(r)/r \qquad (1)$$

Here the screening constant $S(r) = 4\pi \int_0^r \rho\, r'^2\, dr'$ is the number of electrons lying within a sphere of radius r. The effective nuclear charge $Z_{eff}(r) = Z - S(r)$. It is a remarkable fact that $V(r)$ and $Z_{eff}(r)$ are unaffected by that part of the spherically symmetric electronic charge cloud which lies outside of the sphere of radius r. If the electrons were distributed in a set of spherical shells, then for electrons in the n-th shell the electrostatic potential would be $V = e(Z-S_n)/r$ where S_n is the screening constant. If there are N_k electrons in the k-th shell, then

$$S_n = \sum_{k=1}^{n-1} N_k + \frac{1}{2}(N_n - 1) \qquad (2)$$

The reason why each of the other electrons in the n-th shell is only half effective in its shielding of a particular electron is that (if the shell has finite thickness), it is equally probable that an arbitrary other electron has a radius greater than the radius of the particular electron under consideration.

In real atoms, the atomic orbitals are not highly localized in a spherical shell. Thus the concept of a screening constant for each type of orbital represents an approximation. And, indeed, for the expectation value of each different type of property, we should use a different value for the screening constant.

Already in 1921 Schrodinger suggested that the orbits of the semi-classical Bohr quantum mechanics be divided into segments.

In each of these segments, the ellipsoidal trajectories were approximated by assuming a coulomb potential with an effective nuclear charge characteristic of this segment. Schrodinger's concept of atomic structure was a crude beginning of the Hartree atom. In 1927, Pauling (1927,1932) used Schrodinger's procedure to estimate (rather accurately) the molar refractivity, the diamagnetic susceptibility, and the sizes of various atoms.

In 1930, Slater made the use of screening constants simple and practical. It would have seemed logical to use hydrogenic orbitals (Naqvi 1962-4, Naqvi and Victor 1964). However, with hydrogen-like orbitals, many of the integrals required for the estimation of atomic properties are quite difficult to evaluate. Slater was impressed by Zener's (1930) work on analytical Hartree wave functions. Zener found that, as far as energy is concerned, the nodes in the orbitals are quite unimportant. Thus, Slater simplified the Zener wave functions to obtain the familiar Slater orbitals:

$$R(r) = r^{n-1} \exp(- (Z - S) r / n^{*}) . \qquad (3)$$

Here the screening constant S and the effective principal quantum number are embedded parameters which Slater determined so as to give good values for the x-ray energy levels of atoms, atomic and ionic radii, etc. Most of the Slater orbital integrals required for the determination of atomic properties are simple. For example,

the mean value of the k-th power of the radius of an electron is given by the relation

$$\langle r_i^k \rangle = \left[\frac{n_i^*}{2(Z-S_i)}\right]^k \prod_{j=1}^{k} (2n_i^* + j)\, a_o^k \qquad k \geq 1$$

$$\langle r_i^{-1} \rangle = \left[(Z-S_i)/n_i^{*2}\right] a_o^{-1} \tag{4}$$

$$\langle r_i^{-2} \rangle = \left[2(Z-S_i)^2\, n_i^{*-3}\, (2n^*-1)^{-1}\right] a_o^{-2}$$

Much has been written elsewhere on the many different types of applications of Slater screening constants (Hirschfelder, et al 1964). For some properties such as the ionization potentials and the atomic radii they give excellent values. For other properties, they give only fairly good approximations.

For really high accuracy it is necessary to have different screening constants for different properties. For example, consider the expectation value of a property which varies as r^k. If k is large, those portions of configuration space where r is large (and the screening by the other electrons is large) must be given the most weight. Thus, properties which vary as r^k require large screening constants if k is large and small screening constants if k is small. On this account, the energy screening constant

(corresponding to k = -1) should be less than the diamagnetic susceptibility screening constants (corresponding to k = 2). With the use of perturbation theory and hypervirial theorems (Sanders and Hirschfelder 1965, and Robinson 1965) we are now able to calculate good values of the screening constants appropriate to a particular property. In the perturbation theory calculations, the screening constant is adjusted so as to make the first order correction to the expectation value vanish. Table 1 shows a comparison between the Slater screening constant values, the perturbation theory values (calculated with hydrogenic orbitals) and the exact values of the expectation values for a number of one electron operators.

Table 1.

Expectation Values of One Electron Operators for Helium Ground State[a]. All values are given in atomic units

Operator	Slater Orbital with S = 0.30	Perturbation Theory	Exact
r_1	0.882	0.923 (S=0.375)	0.929
r_1^2	1.038	1.170 (S=0.398)	1.192
r_1^4	2.694	3.745 (S=0.434)	3.944
r_1^6	13.05	23.63 (S=0.460)	
r_1^{-2}	5.78	5.977 (S=0.271)	6.017
$(\underline{r}_1)$	4.913	5.616 (S=0.223)	5.688

a. Sanders and Hirschfelder (1965).

III. Molecular Orbitals

Slater type orbitals (STO's) have formed the building blocks for a vast number of calculations on molecules (Karo and Allen 1960). These have ranged from very exact treatments on H_2 to semiempirical π electron calculations. The simpler of these approaches uses at most one Slater Orbital on each atom of the molecule to represent each molecular orbital. The more arduous and sometimes more refined treatments express molecular orbitals as a linear combination of many STO's on all centers of the molecular system. The MO's obtained by the former treatments may be conveniently called minimal basis set MO's and by the latter extended basis set MO's.

Due to their feasibility and often their qualitative success minimal basis set calculations have been and are extensively pursued, particularly for large systems (more than 2 centers). It is thus useful now that extended STO basis set MO's very near the Hartree-Fock solutions are available for many diatomic molecules (Nesbet 1962, Kahalas and Nesbet 1963, McLean 1963, Wahl 1964, Huo 1965 Wahl et al, 1966a,b) to present some comparisons between the minimal STO basis set MO's and the extended STO basis set MO's.

In Table 2 we have compared Total energy, Binding Energy, Ionization potentials, and where relevant dipole moments. Extensive comparisons of this sort which also involve quadrupole moments and field gradients are given in the papers cited.

Several points have become clear. One is that the minimal basis set provides a poor and unreliable quantitative representation

TABLE 2

COMPARISON OF SLATER LCAO-MO SCF WAVEFUNCTIONS WITH RECENT EXTENDED BASIS SET SCF WAVEFUNCTIONS FOR Li_2, N_2, F_2, CO, BF, LiF, HF, AND LiH

	Total Energy (hartrees)			Dissociation Energy (ev)			Ionization Potential (Koopman's) (ev)**		
Molecule	Minimal[a] STO Set	Extended STO Set	Expt.	Minimal[a] STO Set	Extended STO Set	Expt.	Minimal[a] STO Set	Extended STO Set	Expt.
LiH	-7.9667	-7.9860[b]	-8.0703	1.39	1.44[b]	2.52	8.24		
Li_2	-14.84075	-14.8715[c]	-14.9944	.15	.17[c]	1.05	4.86	4.93[c]	4.96
N_2	-108.57362	-108.9928[d]	-109.586	1.19	5.31[d]	9.90	14.82	17.36[d]	15.77
F_2	-197.85686	-198.7683[e]	-199.670	-.30	-1.37[e]	1.68	11.75	18.04[e]	15.7
HF	-99.4785	-99.9911[f]	-100.527	1.21	4.11[f]	6.08	12.65	18.16[f]	15.77
LiF	-106.3652	-106.9885[g]	-107.502	.37	4.03[g]	5.99	9.26	13.02[g]	
CO	-112.34357	-112.7860[h]	-113.377	5.38	7.84[h]	11.24	13.08	14.978[h]	14.01
BF	-123.61550	-124.1659[h]	-124.777	5.24	6.18[h]	8.58	9.61	10.999[h]	10.969

	Dipole Moments		
	Minimal[a] STO Set	Extended STO Set	Expt.
CO	.730	.274[h]	.118*
	C^-O^+	C^+O^-	C^-O^+
BF	2.16	.945[h]	--
	B^-F^+	B^-F^+	--
LiF	2.94	6.297[g]	6.284
	Li^+F^-	Li^+F^-	Li^+F^-
HF	.878	1.827[f]	1.818
	H^+F^-	H^+F^-	H^+F^-
LiH	6.41	5.888[b]	5.882
	Li^+H^-	Li^+H^-	Li^+H^-

a. Ransil (1960)

b. Kahalas and Nesbet (1963)

c. Wahl et al (1966_a)

d. Wahl et al (1966_b)

e. Wahl (1964)

f. Nesbet (1963)

g. Mclean (1963)

h. Huo (1965)

* There is some indication that the experimental assignment of sign as C^-O^+ is doubtable. (Nesbet(1965)).

** Ionization Potentials calculated directly as the difference between the SCF energy of the ion and the neutral system show better agreement (see d.)

of the molecular orbital: (see, for example, dipole moment behavior), second the Hartree-Fock values of one electron properties are quite good and definite while small basis set properties can oscillate widely with charge in basis set composition. Third we obviously must go beyond the Hartree-Fock model to describe chemical binding in a non-empirical manner/ (Nesbet 1965). Perhaps the most compelling reason for pursuing the exhaustive and expensive calculations necessary to obtain HF solutions is that they provide us with good one electron properties and a solid and consistent platform from which we can build the improvements necessary to adequately describe molecules/ (Das and Wahl 1966, Gilbert 1965). Last it is encouraging that the molecular Hartree-Fock wave-function seems to be attainable with an extended but manageable basis set of STO's, derived from atomic SCF calculations.

Although not sufficient as an accurate description of charge distributions and not suitable when crudely used for predicting molecular properties, the Slater screening constants and the single Slater atomic orbitals seem to provide a rough measure for the size of many molecular orbitals. Although, of course, there are other molecular orbitals which are so distorted that they bare little relation to the atomic orbitals.

(Wahl, 1966)

The preceding paper/has presented the electron density of very nearly the Hartree-Fock molecular orbitals of the homonuclear diatomic molecules in the first row of the periodic table. As a step in parameterization of these orbitals, (since we now have them we should try to put them in a simpler form) it is interesting to see how accurately we can estimate some general features of these molecular Hartree-Fock orbitals with a very unsophisticated used of Slater screening constants. First of all, we can consider the distance from the nucleus

at which a 2s or 2p atomic orbital has a maximum charge density. According to Slater orbitals this should occur at $r_{max} = (Z-S)^{-1} a_o$. If the molecular orbitals were the same as the atomic orbitals in the separated atoms, and if neglect of overlap is justifiable, then the values of r_{max} measured towards the outside of the molecule for the $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, and $1\pi_g$ Hartree-Fock orbitals should all be comparable to the $(Z-S)^{-1} a_0$ for the separated atoms. Table 3 shows this comparison, whereas our simple Slater screening constant prediction of the r_{max} is excellent for the $1\pi_u$, $3\sigma_g$, and $1\pi_g$. It is very poor for the $2\sigma_g$ and the $2\sigma_u$.

The next question which we can ask is how well do the Slater screening constants with Slater orbitals predict the position of the outermost electron density contour as shown in the preceding paper. This contour corresponds to an electron density in the orbital of 6.1×10^{-5} ea_0^{-3}. Table 3 shows this comparison. The agreement is excellent for the $1\sigma_g$ and $1\sigma_u$ orbitals which, except for H_2 really "look like" atomic cores.

Table 3

Comparison of r_{max} for Hartree-Fock Molecular Orbitals with r_{max} for Slater Atomic Orbitals. Here r_{max} is the distance from the nucleus to the maximum electron density in the outer loop of the orbital. The Hartree-Fock Molecular orbitals are given in the preceding paper.

	Minimal STO Atom	r_{max} (a_o)				
		Extended Basis MO's				
	$(Z-S)^{-1}$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$
Li_2	1.54	2.3				
B_2	0.77	1.7	0.90	0.80		
C_2	.65	1.0	.75	.65		
N_2	.51	.80	.65	.50	.50	
O_2	.44	.75	.60	.45	.45	.40
F_2	.38	.70	.57	.35	.35	.35

Table 4

$r_c(a_o)$ OUTER PERIMETER

	Minimal STO Atom	Extended Basis MO's		Minimal STO Atom	Extended Basis MO's				
	1s	$1\sigma_g$	$1\sigma_u$	2s,2p	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$
H_2	4.5	(3.8)							
		4.5							
Li_2	2.30	(2.3)	(2.3)	7.1	(6.2)				
		2.3	2.3		7.7				
B_2	1.50	(1.5)	(1.5)	4.55	(3.9)	(5.5)	5.3		
		1.5	1.5		4.5	4.5			
C_2	1.25	(1.25)	(1.25)	3.87	(3.25)	(4.7)	5.0		
		1.35	1.25		3.9	4.0			
N_2	1.10	(1.15)	(1.22)	3.39	(2.8)	(4.1)	4.5	(4.3)	
		1.2	1.12		3.5	3.5			
O_2	.99	(1.0)	(1.0)	3.02	(2.8)	(3.5)	4.1	(3.9)	3.8
		1.0	1.0		3.2	3.1			
F_2	.90	(.9)	(.9)	2.75	(2.7)	3.1	3.8	(3.5)	3.7
		.9	.9		3.0	3.0			

Comparison of the outer perimeter of the Molecular Hartree-Fock Molecular Orbitals with the outer perimeter of the Slater Atomic Orbitals. The outer perimeter of the orbitals is taken to be the radius at which the electron density is $6.1 \times 10^{-5} e\, a_o^{-3}$. This corresponds to the outermost contour shown in the pictures of molecular orbitals in the preceding paper. Two sets of numbers are given for the molecular orbitals: the values in parentheses are measured from the nucleus outward along the internuclear axis, the other values are measured from the nucleus perpendicular to the internuclear axis.

For the other orbitals the outer perimeter predicted by non overlapping single STO's with atomic screening constants is quite poor. The $2\sigma_g$ Hartree Fock MO perimeter shows a "pulling in" along the molecular axis relative to the simple Slater atomic orbital while the $2\sigma_u$ Hartree Fock perimeter has moved out relative to the Slater atomic orbital. The $1\pi_u$ $3\sigma_g$ and $1\pi_g$ orbitals all have a much larger perimeter than the corresponding Slater atomic orbital. However, the charge along this perimeter is extremely small and it is only as they reflect more significant shifts in charge that these observations are important. The differences displayed in Tables 3 and 4 arise from 1) neglect of overlap, 2) the HF MO's form an orthonormal set while the Slater AO's are only normalized, 3) The inadequacies of a single STO in representing any orbital, atomic or molecular, 4) The Slater AO has been "frozen" in the molecule and not allowed to distort through the variational procedure. Since these are just the 4 consequences of the usual assumptions made in the most simple use of single STO's in molecules, these comparisons may be instructive.

IV. Conclusion

Certainly these are crude observations and a detailed analysis of these MO's is needed, but we feel that some "Slater-type" parameterization of these accurate "MO's" can provide us with molecular building blocks and "Molecular" Screening Parameters useful for proceeding to larger systems and estimating molecular properties just as Slater Screening constants have enabled us to think about and represent atoms adequately for many purposes.

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