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Atomic SCF Valence Orbitals for First Transition Series Metals*

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A consistent set of $4s, 4p$, and $3d$ orbitals are reported that are linear combinations of Slater-type functions for the highest multiplicity term of the configurations $3d^{n-2}4s^14p^1$ for the metals titanium through copper.

In the course of developing an approximate SCF method applicable to first-row transition metal complexes [1], we have obtained $4s, 4p$, and $3d$ atomic orbitals that are solutions to the free-atom one-configuration Roothaan-Hartree-Fock equations [2]. The orbitals obtained were linear combinations of normalized Slater-type orbitals (STO's) for the highest multiplicity term of the configurations $3d^{n-2}4s^14p^1$. The $3d$ orbitals were double-zeta functions and the $4s$ and $4p$ orbitals were represented by single-zeta functions.

The program used was the LCAO atomic SCF program of Clementi [3], designated "ATOM-SCF". The orbital exponents were optimized by a quadratic interpolation technique [4] to a relative minimum energy tolerance of 10^{-5}. The computations were done entirely in double precision on the IBM 360/75 computer at the University of Illinois Digital Computer Laboratory.

Table 1 lists the orbitals, for the metals titanium through copper, as a linear combination of STO's, with a coefficient preceding each STO. Each is given (in parentheses) in terms of its radial (principal) quantum number, n, and its exponent, ζ, so that each STO is in the form $(n; \zeta)$.

It is anticipated that these orbitals will be useful in approximate and semi-empirical molecular SCF calculations as a consistent set of functions which are solutions to the same atomic SCF equations.

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Table 1. *Atomic* SCF *orbitals*

Atom, Configuration, State Function = Σ (Coefficient) $(n;\zeta)$				
Titanium, $4s^1\,4p^1\,3d^2$, ^5S				
$4s=$	-0.03271 $(1;21.4180)$	$+0.12329$ $(2;7.66802)$	-0.31055 $(3;3.69535)$	$+1.03043$ $(4;1.37576)$
$4p=$	0.09380 $(2;9.02208)$	-0.31078 $(3;3.41775)$	$+1.02559$ $(4;1.27018)$	
$3d=$	0.78435 $(3;1.89794)$	$+0.34626$ $(3;4.76954)$		
Vanadium, $4s^1\,4p^1\,3d^3$, ^6S				
$4s=$	-0.03038 $(1;22.4026)$	$+0.11385$ $(2;8.06665)$	-0.28271 $(3;3.91650)$	$+1.02483$ $(4;1.39766)$
$4p=$	0.07368 $(2;9.52540)$	-0.23994 $(3;3.63585)$	$+1.01502$ $(4;1.21428)$	
$3d=$	0.75117 $(3;2.10362)$	$+0.37395$ $(3;5.01660)$		
Chromium, $4s^1\,4p^1\,3d^4$, ^7P				
$4s=$	-0.02982 $(1;23.3834)$	$+0.11148$ $(2;8.45182)$	-0.27290 $(3;4.14196)$	$+1.02214$ $(4;1.44430)$
$4p=$	0.07872 $(2;10.0257)$	-0.25289 $(3;3.86454)$	$+1.01575$ $(4;1.30612)$	
$3d=$	0.77051 $(3;2.42248)$	$+0.34277$ $(3;5.62602)$		
Manganese, $4s^1\,4p^1\,3d^5$, ^8P				
$4s=$	-0.03279 $(1;24.3713)$	$+0.12214$ $(2;8.86222)$	-0.29791 $(3;4.36345)$	$+1.02632$ $(4;1.57472)$
$4p=$	0.08768 $(2;10.5236)$	-0.28170 $(3;4.08114)$	$+1.02027$ $(4;1.44672)$	
$3d=$	0.73343 $(3;2.47294)$	$+0.38892$ $(3;5.75800)$		
Iron, $4s^1\,4p^1\,3d^6$, ^7P				
$4s=$	-0.02618 $(1;25.3536)$	$+0.09794$ $(2;9.25982)$	-0.23136 $(3;4.59002)$	$+1.01527$ $(4;1.48674)$
$4p=$	0.07027 $(2;11.0190)$	-0.22253 $(3;4.29648)$	$+1.01228$ $(4;1.38152)$	
$3d=$	0.72531 $(3;2.60876)$	$+0.39919$ $(3;6.08708)$		
Cobalt, $4s^1\,4p^1\,3d^7$, ^6S				
$4s=$	-0.02708 $(1;26.3326)$	$+0.10008$ $(2;9.66122)$	-0.23671 $(3;4.81351)$	$+1.01578$ $(4;1.56862)$
$4p=$	0.08270 $(2;11.5225)$	-0.25735 $(3;4.55559)$	$+1.01550$ $(4;1.53657)$	
$3d=$	0.71829 $(3;2.71248)$	$+0.41105$ $(3;6.38712)$		
Nickel, $4s^1\,4p^1\,3d^8$, ^5S				
$4s=$	-0.03018 $(1;27.3194)$	$+0.11127$ $(2;10.0605)$	-0.26337 $(3;5.02615)$	$+1.01979$ $(4;1.71101)$
$4p=$	0.06378 $(2;12.0168)$	-0.19728 $(3;4.75134)$	$+1.00907$ $(4;1.44602)$	
$3d=$	0.71086 $(3;2.85094)$	$+0.41869$ $(3;6.71104)$		
Copper, $4s^1\,4p^1\,3d$, ^4P				
$4s=$	-0.03312 $(1;28.3043)$	$+0.12207$ $(2;10.4519)$	-0.28742 $(3;5.25483)$	$+1.02324$ $(4;1.84643)$
$4p=$	0.09329 $(2;12.5159)$	-0.28886 $(3;4.99271)$	$+1.01989$ $(4;1.76637)$	
$3d=$	0.69580 $(3;2.93064)$	$+0.43819$ $(3;6.94841)$		

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