APPROXIMATE FUNCTIONS FOR 4*s*, 4*p* SLATER-ORBITALS FOR TRANSITION METAL IONS HAVING d^n ELECTRON CONFIGURATIONS

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In this paper we give approximate functions for 4*s*, 4*p* Slater-orbitals for transition metal ions having d^n electron configurations.

In molecular orbital calculations, especially on transition metal compounds, it is very often necessary to calculate overlap and Coulomb integrals with 4*s* and 4*p* Slater-orbitals having the radial part

$$\psi(\alpha) = N(\alpha) r^{2.7} e^{-\alpha r},$$

where

$$N(\alpha) = \sqrt{\frac{(2\alpha)^{8.4}}{7.4!}}; \quad \alpha = \frac{Z-\sigma}{3.7a_0},$$

and $Z-\sigma$ is the effective nuclear charge which can be determined from the well known Slater-rules.

The overlap integrals $(nl|n'l')$ with $n=4$; $n'=1, 2, 3$ can be expressed with the aid of integrals

$$I(n|y\pm x) = \frac{(n|y\pm x)!}{(y\pm x)^{n+1}}; \quad G(n|y+x) = \frac{\Gamma(n)}{(y+x)^n},$$

where $\Gamma(n)$ is the complete, $(n|y\pm x)!$ is the incomplete Γ-function [3] and $x=\alpha R$, $y=\alpha' R$ (R is the bond length between two atoms) but these expressions make the calculation of these integrals possible only if $y>x$. If $y<x$, and that is what takes place in transition metals in most cases, these integrals as well as the integrals $(nl|n'l')$ with $n=4$; $n'=4$ ($y \gtrless x$) cannot be expressed in closed forms. This is the reason why we give approximate functions for 4*s*, 4*p* Slater-orbitals for transition metal ions making it possible to calculate these integrals with the aid of the integrals $A_n(a)$ and $B_n(b)$ [4].

Constructions of approximate functions

The simplest approximation for $4s$, $4p$ Slater-orbitals can be obtained if the radial part of these functions are approximated with the function

$$\varphi(\beta) = N(\beta) \cdot r^3 e^{-\beta r},$$

where $N(\beta)$ is the normalization factor determined by

$$\int_0^\infty \varphi^2 r^2 dr = 1; \quad N(\beta) = \sqrt{\frac{(2\beta)^9}{8!}},$$

and β is an appropriate parameter which can be determined in various ways. If we require that the value of $\varphi(\beta)$ at the point of the maximum value of $\psi(\alpha)$ $\left(r_{\max} = \frac{2.7}{\alpha}\right)$ be equal to the maximum value of $\psi(\alpha)$, *i.e*,

$$\varphi(r_{\max}) = \psi_{\max},$$

we get the following equation for β:

$$\beta^9 e^{-\frac{5.4}{\alpha}\beta} = 0.005\,804\,5019\alpha^9,$$

from which β can be determined for various α'*s*. For transition metal ions having d^n electron configurations we get the values for β from this equation which are given in Table I. (In the table the numbers in the first column refer to the ionization states of the ions).

Following that we approximated $\psi(\alpha)$ with the function

$$\varphi(\alpha) = N(\alpha)\{ar^2 + br^3\}e^{-\alpha r},$$

and we determined a and b from two requirements.

a) First, we prescribed that $\varphi(\alpha)$ be normalized and the equation

$$\varphi(r_{\max}) = \psi_{\max}$$

be fulfilled. From this condition we get the following expressions for a and b:

$$a = 0.759\,826\,1 \cdot \alpha^{-0.7},$$

$$b = 0.460\,902\,4 \cdot \alpha^{+0.3}.$$

b) Then we required the normalization condition and the condition

$$\int_0^\infty (\psi - \varphi)^2 r^2 dr = \min.$$

Table I

Ion		α	β
V, Nb, Ta	1	1.430 077 1	1.539 740 7
	2	1.864 207 6	2.007 161 6
	3	2.298 338 2	2.474 582 9
	4	2.732 468 7	2.942 004 0
	5	3.166 599 3	3.409 425 1
Cr, Mo, W	1	1.506 688 4	1.622 226 5
	2	1.940 818 9	2.089 647 7
	3	2.374 949 5	2.557 069 1
	4	2.809 080 0	3.024 490 3
	5	3.243 210 6	3.491 911 6
	6	3.667 341 1	3.959 332 2
Mn, Tc, Re	1	1.583 299 6	1.704 712 7
	2	2.017 430 2	2.172 133 8
	3	2.451 560 7	2.639 555 1
	4	2.885 691 3	3.106 976 2
	5	3.319 821 8	3.574 397 4
	6	3.753 952 4	4.041 818 8
	7	4.188 082 9	4.509 240 1
Fe, Ru, Os	1	1.659 910 9	1.787 198 8
	2	2.094 041 5	2.254 620 1
	3	2.528 172 0	2.722 041 1
	4	2.962 302 6	3.189 462 6
	5	3.396 433 1	3.656 883 4
	6	3.830 563 6	4.124 304 7
	7	4.264 694 2	4.591 726 3
	8	4.698 824 7	5.059 146 8
Co, Rh, Ir	1	1.736 522 2	1.869 684 9
	2	2.170 652 7	2.337 106 8
	3	2.604 783 3	2.804 527 3
	4	3.038 913 8	3.271 948 4
	5	3.473 044 4	3.739 369 6
	6	3.907 174 9	4.206 791 0
	7	4.341 305 5	4.674 212 3
	8	4.775 436 0	5.141 633 3
	9	5.209 566 6	5.609 055 1
Ni, Pd, Pt	0	1.379 002 9	1.484 749 8
	1	1.813 133 5	1.952 171 0
	2	2.247 264 0	2.419 592 2
	3	2.681 394 6	2.887 013 4
	4	3.115 525 1	3.354 434 7
	5	3.549 655 6	3.821 855 5
	6	3.983 786 2	4.289 276 8
	7	4.417 916 7	4.756 698 4
	8	4.852 047 3	5.224 119 8
	9	5.286 177 8	5.691 540 1
	10	5.720 308 4	6.158 962 4

Table I

Ion		α	β
Cu, Ag, Au	1	1.889 744 7	2.034 657 1
	2	2.323 875 3	2.502 078 2
	3	2.758 005 8	2.969 499 4
	4	3.192 136 4	3.436 920 5
	5	3.626 266 9	3.904 341 7
	6	4.060 397 5	4.371 763 4
	7	4.494 528 0	4.839 184 4
	8	4.928 658 6	5.306 605 7
	9	5.362 789 1	5.774 026 4
	10	5.796 919 7	6.241 447 9
	11	6.231 050 2	6.708 869 4
Zn, Cd, Hg	2	2.400 486 6	2.584 564 4
	3	2.834 617 1	3.051 985 6
	4	3.268 747 6	3.519 406 9
	5	3.702 878 2	3.986 827 8
	6	4.137 088 7	4.454 248 9
	7	4.571 139 3	4.921 670 8
	8	5.005 269 8	5.389 091 4
	9	5.439 400 4	5.856 512 9
	10	5.873 530 9	6.323 933 5
	11	6.307 661 5	6.791 354 6
	12	6.741 792 0	7.258 776 5

These conditions give the following results for a and b:

$$a = 0.710\,569\,7 \cdot \alpha^{-0.7},$$

$$b = 0.473\,713\,1 \cdot \alpha^{0.3}.$$

In the course of testing the approximations, it has turned out (see Table IV) that the first requirements give better approximate functions than the second ones, so we determined a and b for transition metals from the first expressions. These values are given in Table II.

Better approximate functions can be written in the form

$$\Phi(\alpha) = N(\alpha)\{c_1 r + c_2 r^2 + c_3 r^3 + c_4 r^4\} e^{-\alpha r}.$$

a) If we prescribe the normalization condition and the equations

$$\Phi(r_{\max}) = \Phi_{\max} = \psi_{\max}; \quad \Phi(1.5 r_{\max}) = \psi(1.5 r_{\max}),$$

we get the following expressions for the c_k's:

$$c_1 = -0.450\,026\,5 \cdot \alpha^{-1.7},$$

$$c_2 = \quad 0.870\,987\,7 \cdot \alpha^{-0.7},$$

$$c_3 = \quad 0.505\,035\,3 \cdot \alpha^{0.3},$$

$$c_4 = -0.008\,730\,304\,2 \cdot \alpha^{1.3}.$$

Table II

Ion		a	b
V, Nb, Ta	1	0.591 510 7	0.513 117 5
	2	0.491 324 3	0.555 593 7
	3	0.424 350 3	0.591 606 8
	4	0.375 946 1	0.623 125 5
	5	0.339 077 6	0.651 308 8
Cr, Mo, W	1	0.570 292 7	0.521 214 0
	2	0.477 666 4	0.562 347 2
	3	0.414 721 1	0.597 455 2
	4	0.368 739 2	0.628 316 2
	5	0.333 450 7	0.655 996 5
	6	0.305 379 9	0.681 191 4
Mn, Tc, Re	1	0.550 833 1	0.529 027 1
	2	0.464 895 4	0.568 916 5
	3	0.405 606 0	0.603 172 9
	4	0.361 859 0	0.633 408 6
	5	0.328 045 4	0.660 607 4
	6	0.301 003 9	0.685 418 2
	7	0.278 806 9	0.708 294 0
Fe, Ru, Os	1	0.532 911 3	0.536 579 9
	2	0.452 923 2	0.575 313 5
	3	0.396 962 6	0.608 766 8
	4	0.355 282 4	0.638 407 3
	5	0.322 848 0	0.665 144 4
	6	0.296 777 1	0.689 585 0
	7	0.275 291 4	0.712 156 4
	8	0.257 230 1	0.733 171 8
Co, Rh, Ir	1	0.516 342 6	0.543 892 6
	2	0.441 673 2	0.581 548 7
	3	0.388 753 3	0.614 243 4
	4	0.348 988 7	0.643 316 2
	5	0.317 846 2	0.669 610 3
	6	0.292 691 6	0.693 693 9
	7	0.271 881 7	0.715 970 5
	8	0.254 334 4	0.736 737 7
	9	0.239 305 7	0.756 222 3
Ni, Pd, Pt	0	0.606 762 3	0.507 549 7
	1	0.500 971 9	0.550 982 7
	2	0.431 078 5	0.587 631 7
	3	0.380 944 5	0.619 608 3
	4	0.342 959 1	0.648 139 3
	5	0.313 028 5	0.674 007 7
	6	0.288 740 0	0.697 746 7
	7	0.268 572 8	0.719 737 7
	8	0.251 516 6	0.740 263 8
	9	0.236 872 7	0.759 541 5
	10	0.224 140 6	0.777 740 7

Table II

	Ion	*a*	*b*
Cu, Ag, Au	1	0.486 667 2	0.557 866 1
	2	0.421 080 0	0.593 571 2
	3	0.373 506 0	0.624 866 9
	4	0.337 176 4	0.652 880 1
	5	0.308 384 4	0.678 339 2
	6	0.284 915 6	0.701 745 4
	7	0.265 359 9	0.723 459 5
	8	0.248 773 5	0.743 751 1
	9	0.234 498 9	0.762 827 3
	10	0.222 063 0	0.780 851 0
	11	0.211 116 7	0.797 953 1
Zn, Cd, Hg	2	0.411 627 8	0.599 375 2
	3	0.366 410 7	0.630 024 3
	4	0.331 625 0	0.657 541 9
	5	0.303 904 2	0.682 607 1
	6	0.281 211 9	0.705 691 6
	7	0.262 238 9	0.727 137 1
	8	0.246 101 9	0.747 200 7
	9	0.232 182 0	0.766 080 3
	10	0.220 031 4	0.783 932 7
	11	0.209 317 9	0.800 883 8
	12	0.199 789 0	0.817 036 8

(Here the distance $r=1.5r_{\max}$ is the coordinate of the point where the value of $\psi(\alpha)$ is about the half of the maximum value).

b) The conditions

$$\int_0^\infty \Phi^2 r^2 dr = 1; \quad \int_0^\infty (\psi-\Phi)^2 r^2 dr = \min.$$

give the following results:

$$c_1 = -0.241\,228\,4 \cdot \alpha^{-1.7},$$

$$c_2 = \quad 0.703\,008\,5 \cdot \alpha^{-0.7},$$

$$c_3 = \quad 0.546\,784\,4 \cdot \alpha^{0.3},$$

$$c_4 = -0.012\,017\,239 \cdot \alpha^{1.3},$$

Table IV shows that with the latter parameters we get somewhat (if only a little) better approximate functions, so we give the values of c_k-s in Table III according to these expressions.

Table III

Ion		$c_1 \cdot 10^2$	c_2	c_3	$c_4 \cdot 10^2$
V, Nb, Ta	1	−13.131 59	0.547 279 1	0.608 728 8	−1.913 250 8
	2	− 8.367 353 7	0.454 584 4	0.659 119 8	−2.700 519
	3	− 5.861 714 8	0.392 618 5	0.701 843 4	−3.545 216 5
	4	− 4.368 019 5	0.347 833 9	0.739 235 2	−4.439 422 1
	5	− 3.399 539 5	0.313 722 3	0.772 669 9	−5.377 441 7
Cr, Mo, W	1	−12.016 79	0.527 647 7	0.618 333 9	−2.047 552 8
	2	− 7.813 648 2	0.441 947 8	0.667 131 7	−2.845 674 3
	3	− 5.543 907 2	0.383 709 4	0.708 781 5	−3.699 605
	4	− 4.167 440 6	0.341 165 9	0.745 392 9	−4.601 908 3
	5	− 3.264 154	0.308 516 2	0.778 231 3	−5.547 182 4
	6	− 2.636 457 2	0.282 544 4	0.808 120 6	−6.531 285 9
Mn, Tc, Re	1	−11.045 14	0.509 643 5	0.627 603 2	−2.183 920 7
	2	− 7.315 953 1	0.430 131 8	0.674 925 2	−2.992 559 3
	3	− 5.252 618 9	0.375 275 9	0.715 654 6	−3.855 494 6
	4	− 3.981 104 8	0.334 800 1	0.751 434 3	−4.765 730 6
	5	− 3.137 135 5	0.303 515	0.783 701 1	−5.718 127 5
	6	− 2.545 643	0.278 495 6	0.813 135	−6.708 725 5
	7	− 2.113 500 9	0.257 958 5	0.840 273 5	−7.734 362 8
Fe, Ru, Os	1	−10.192 58	0.493 661 4	0.636 562 9	−2.322 280 7
	2	− 6.866 784 6	0.419 054 8	0.682 514 1	−3.141 126 1
	3	− 4.984 908	0.367 278 8	0.722 200 9	−4.012 853
	4	− 3.807 662	0.328 715 3	0.757 364 4	−4.930 862 7
	5	− 3.017 791 2	0.298 706 3	0.789 083 6	−5.890 263
	6	− 2.459 698 3	0.274 584 9	0.818 078 3	−6.887 254 9
	7	− 2.049 363 4	0.254 705 9	0.844 855 5	−7.918 792
	8	− 1.737 987 6	0.237 995 1	0.869 786 8	−8.982 3642
Co, Rh, Ir	1	−10.524 01	0.532 590 9	0.719 332 4	− 2.745 355 3
	2	− 7.201 687 5	0.455 571 7	0.769 135 1	− 3.669 286 1
	3	− 5.282 337 2	0.400 986 6	0.812 375 8	− 4.650 687 7
	4	− 4.064 588 5	0.359 970 7	0.850 826 6	− 5.682 612 5
	5	− 3.239 144 1	0.327 848 1	0.885 601 9	− 6.759 856 5
	6	− 2.651 374 0	0.301 902 0	0.917 454 2	− 7.878 360 5
	7	− 2.216 579 2	0.280 437 3	0.946 916 5	− 9.034 843 5
	8	− 1.885 018 8	0.262 337 8	0.974 382 4	−10.226 60
	9	− 0.016 258 3	0.246 836 2	1.000 152 0	−11.451 34
Ni, Pd, Pt	0	−15.573 17	0.625 855 9	0.671 266 7	− 2.034 458 7
	1	− 9.779 287 3	0.516 736 5	0.728 709 6	− 2.903 841 3
	2	− 6.789 313 6	0.444 643 6	0.777 180 1	− 3.838 525 0
	3	− 5.028 339 6	0.392 932 1	0.819 471 4	− 4.829 288 3
	4	− 3.896 141 4	0.353 751 3	0.857 205 3	− 5.869 548 6
	5	− 3.121 197 6	0.322 878 9	0.891 418 1	− 6.954 345 6
	6	− 2.565 278 9	0.297 826 1	0.922 814 3	− 8.079 769 0
	7	− 2.151 632 3	0.277 024 3	0.951 898 8	− 9.242 658 5
	8	− 1.834 701 0	0.259 431 4	0.979 046 0	−10.440 39
	9	− 1.585 976 8	0.244 326 4	1.004 541 9	−11.670 74
	10	− 1.386 835 0	0.231 193 9	1.028 611 5	−12.931 81

Table III

Ion		$c_1 \cdot 10^2$	c_2	c_3	$c_4 \cdot 10^2$
Cu, Ag, Au	1	− 9.114 912 5	0.501 981 6	0.737 813 3	− 3.064 349 0
	2	− 6.413 218 5	0.434 331 2	0.785 035 7	− 4.009 505 7
	3	− 4.793 205 3	0.385 259 5	0.826 426 2	− 5.009 424 7
	4	− 3.738 517 2	0.347 786 7	0.863 475 4	− 6.057 870 9
	5	− 3.009 928 9	0.318 088 6	0.897 146 6	− 7.150 094 6
	6	− 2.483 540 8	0.293 881 3	0.928 102 7	− 8.282 342 6
	7	− 2.089 656 4	0.273 710 3	0.956 821 2	− 9.451 559 7
	8	− 1.785 483 4	0.256 601 9	0.983 658 0	− 10.655 20
	9	− 1.547 653 1	0.241 878 1	1.008 887 7	− 11.891 10
	10	− 1.355 821 3	0.229 050 8	1.032 724 9	− 13.157 41
	11	− 1.199 178 2	0.217 759 5	1.055 343 7	− 14.452 53
Zn, Cd, Hg	2	− 6.069 166 4	0.424 580 9	0.792 711 7	− 4.182 184 2
	3	− 4.575 065 8	0.377 940 9	0.833 247 2	− 5.191 069 8
	4	− 3.590 785 6	0.342 060 6	0.869 641 0	− 6.247 553 7
	5	− 2.904 830 6	0.313 467 4	0.902 791 3	− 7.347 090 6
	6	− 2.405 863 0	0.290 061 1	0.933 321 9	− 8.486 067 7
	7	− 2.030 468 5	0.270 491 0	0.961 685 0	− 9.661 529 9
	8	− 1.560 995 5	0.227 699 1	0.886 429 8	− 9.751 253 4
	9	− 1.355 163 3	0.214 820 0	0.908 827 1	− 10.864 78
	10	− 1.189 322 5	0.203 578 1	0.930 006 2	− 12.005 32
	11	− 1.053 542 7	0.193 665 7	0.950 116 0	− 13.171 45
	12	− 0.940 828 1	0.184 849 3	0.969 278 8	− 14.361 93

Table IV

Overlaps	R_1	R_2	R_3	R_4	R_5
$(4s, 2s)$	0.691 572	0.569 532	0.448 946	0.339 375	0.246 842
$(\varphi(\beta), 2s)$	0.685 608	0.563 225	0.442 371	0.332 783	0.240 599
$(\varphi_a(\alpha), 2s)$	0.694 817	0.572 630	0.453 004	0.342 389	0.249 691
$(\varphi_b(\alpha), 2s)$	0.695 779	0.573 928	0.453 452	0.343 804	0.250 945
$(\Phi_a, 2s)$	0.691 380	0.569 521	0.449 029	0.339 490	0.246 947
$(\Phi_b, 2s)$	0.691 470	0.569 398	0.448 767	0.339 155	0.246 589
$(4s, 2p_z)$	0.509 303	0.519 700	0.475 883	0.400 290	0.314 700
$(\varphi(\beta), 2p_z)$	0.511 590	0.522 873	0.477 863	0.400 082	0.302 224
$(\varphi_a(\alpha), 2p_z)$	0.509 955	0.519 396	0.475 123	0.400 364	0.315 692
$(\varphi_b(\alpha), 2p_z)$	0.507 514	0.518 183	0.474 989	0.400 956	0.316 630
$(\Phi_a, 2p_z)$	0.508 230	0.519 651	0.475 691	0.400 340	0.314 856
$(\Phi_b, 2p_z)$	0.509 306	0.520 401	0.476 109	0.400 519	0.314 848
$(4s, 3d_{z^2})$	0.243 243	0.334 104	0.389 547	0.401 638	0.376 484
$(\varphi(\beta), 3d_{z^2})$	0.242 788	0.334 573	0.393 877	0.406 061	0.379 546
$(\varphi_a(\alpha), 3d_{z^2})$	0.246 518	0.334 970	0.388 692	0.400 130	0.375 268
$(\varphi_b(\alpha), 3d_{z^2})$	0.243 412	0.332 070	0.386 544	0.398 922	0.374 900
$(\Phi_a, 3d_{z^2})$	0.242 005	0.332 916	0.388 716	0.401 155	0.376 290
$(\Phi_b, 3d_{z^2})$	0.243 292	0.334 039	0.389 626	0.401 850	0.376 770

Test of approximations

In order to test the various approximations we have calculated the overlap integrals [1, 2]

$$(4s, 2s); \quad (4s, 2p_z); \quad (4s, 3d_{z^2})$$

exactly and with the approximate functions with SLATER-exponents $\alpha=2.5$; $\alpha'=1.5$ and with the bond lengths:

$$R_1 = 1.734\,358\,6 \text{ Å},$$

$$R_2 = 2.167\,948\,3 \text{ Å},$$

$$R_3 = 2.601\,538\,0 \text{ Å},$$

$$R_4 = 3.035\,127\,6 \text{ Å},$$

$$R_5 = 3.468\,717\,3 \text{ Å}.$$

These bond lengths have been so chosen that in the integrals [3] ($p=3.7$):

$$I(u_1, p) = \frac{(y-x)^{p+1}}{\Gamma(p+1)} \cdot I(p|y-x),$$

$$I(u_2, p) = \frac{(y+x)^{p+1}}{\Gamma(p+1)} \cdot I(p|y+x),$$

the parameter u_1 should have the following values:

$$u_1 = 0.8; 1; 1.2; 1.4; 1.6$$

and u_2 should be: $u_2=4u_1$. With these parameters we get the values for the overlaps summarized in Table IV.

This table shows that the function $\varphi(\beta)$ in itself is already a good enough appoximation for $4s$ and $4p$ Slater-orbitals. Considering that these orbitals are also approximate-functions for the atomic orbitals we can use $\varphi(\beta)$ instead of Slater-orbitals in molecular orbital calculations.

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ПРИБЛИЖЕНИЕ ФУНКЦИЙ 4s, 4p ОРБИТАЛЕЙ СЛЕТЕРА ДЛЯ ИОНОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ ИМЕЮЩИХ ЭЛЕКТРОННУЮ КОНФИГУРАЦИЮ d^n

В. Мараз

В работе мы задаем приближение функции $4s, 4p$ орбиталей Слетера для ионов переходных металлов имеющих электронную конфигурацию d^n.