The *ab initio* model potential method. First series transition metal elements

Luis Seijo and Zoila Barandiarán
Departamento de Química, C-14, Universidad Autónoma de Madrid, 28049 Madrid, Spain
Sigeru Huzinaga
Department of Chemistry, The University of Alberta, Edmonton, Alberta T6G 2G2, Canada

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In the *ab initio* core model potential method the Coulomb and exchange core operators are represented accurately and the valence basis set is the only component of the method which is optimized (following the variational principle) in an atomic valence restricted Hartree–Fock (RHF) calculation. In this paper we present the nonrelativistic Ar-like and Mg-like core model potentials and valence Gaussian basis sets for the first series transition metal elements. The pilot RHF molecular calculations on ScO, MnO, CuO, and ScS show that freezing the $3s$ orbital is safe all along the transition series but the same is true for the $3p$ orbital only towards the end of the series. A good agreement exists between the all-electron and model potential results if the same type of valence part of the basis set is used: 0.01 Å in R_e and 25 cm^{-1} in $\bar{\nu}_e$.

I. INTRODUCTION

In a previous paper,[1] we presented the *ab initio* model potential method (AIMP) for valence-electron molecular calculations. As a model potential (MP) method,[2] it makes use of valence orbitals showing the correct nodal structure. This is in contrast with the pseudopotential methods, of which different methods and extensive tabulations of parameters have been published in recent years.[3–8] But the main peculiarity of the present method is that, as a method based on the *ab initio* philosophy, the core potentials are obtained directly from the atomic core orbitals and, as they describe physical interactions, they are not changed anymore in a parametrization procedure; instead, an optimization of the atomic valence basis set is performed according to the variational principle. In this way, the atomic model potential problem bypasses the need of reference all-electron (AE) valence orbitals and becomes entirely parallel to the one of optimization of AE basis sets.

This feature contrasts with other MP methods (and with the pseudopotential methods), in which the core potentials are optimized in order to reproduce the orbital energies and shapes of the reference AE valence atomic orbitals; some of these methods as well as tabulations of parameters have been published recently.[9–11]

We may remark that the fact that the *core* model potentials are obtained without the use of *valence* reference orbitals in the AIMP method, makes it possible to obtain complete-system potentials.[12] This, together with the fact that the model potential equations emerge naturally from the theory of separability of many-electron systems in which strong orthogonality among subsystem wave functions is assumed,[13,14] makes the AIMP method useful not only to represent cores but also functional groups in molecules, as well as crystal lattices in solids.[12]

In Ref. 1 we described the AIMP method and presented core potentials and basis sets for the main group elements up to Xe. In this paper we present core-$3p$ (Ar-like) and core-$3s$ (Mg-like) nonrelativistic potentials and basis sets for the first series transition metal elements (Sec. III). We also show the results of HFR atomic (Sec. III) and molecular calculations on ScO, ScS, MnO, and CuO (Sec. IV) performed in order to assess the quality of the potentials and basis sets and to decide upon the adequate use of them in molecular calculations. In particular, in Sec. IV we address ourselves to the question of what core–valence partition to use and of what characteristics must be fulfilled for the inner part of the molecular valence basis set in order to reach the final goal of reproducing the AE results if the same kind of wave function and valence basis set is used.

II. METHOD

The one-electron contributions to the nonrelativistic MP Hamiltonian for the valence electrons of a molecule may be written in atomic units as[13]

$$h(i) = -\frac{1}{2}\Delta_i - \sum_I (Z^I - Z^I_{\text{core}})/r_{Ii} + \sum_I [V^I_{\text{Coul}}(i) + V^I_{\text{exch}}(i) + P^I(i)], \qquad (1)$$

where I runs over the nuclei. The projection operators $P^I(i)$,

$$P^I(i) = -\sum_c^{\text{core } I} 2\epsilon^I_c |\phi^I_c\rangle\langle\phi^I_c|, \qquad (2)$$

enforce the necessary core–valence orthogonality, preventing the valence orbitals from collapsing onto the core space. $V^I_{\text{Coul}}(i)$ is a radial operator including the Coulomb operators $J^I_c(i)$,

$$V^I_{\text{Coul}}(i) = V^I_{\text{Coul}}(r_{Ii}) = -Z^I_{\text{core}}/r_{Ii} + 2\sum_c^{\text{core } I} J^I_c(i). \qquad (3)$$

Finally, $V^I_{\text{exch}}(i)$ is the nonlocal core exchange operator

$$V^I_{\text{exch}}(i) = -\sum_c^{\text{core } I} K^I_c(i). \qquad (4)$$

In the AIMP method[1]: (i) the projection operators $P^I(i)$ remain as in Eq. (2), (ii) the local Coulomb potential is approximated by[15]

$$V^{I}_{\mathrm{Coul}}(r_{Ii}) \simeq V^{I}_{\mathrm{Coul,MP}}(r_{Ii}) = \sum_{k} A^{I}_{k} \exp(-\alpha^{I}_{k} r^{2}_{Ii})/r_{Ii}, \tag{5}$$

where the parameters $\{A^{I}_{k}, \alpha^{I}_{k}\}$ are determined through least-square fitting to the $V^{I}_{\mathrm{Coul}}(r_{Ii})$ potential calculated with Eq. (3) using AE core orbitals, and (iii) a nonlocal spectral representation is used for the exchange potential in Eq. (4),

$$V^{I}_{\mathrm{exch}}(i) \simeq V^{I}_{\mathrm{exch,\,MP}}(i) = \sum_{l} \sum_{m=-l}^{l} \sum_{a,b} |alm;I\rangle A^{I}_{l;ab} \langle blm;I|, \tag{6}$$

where the $\{|alm;I\rangle\}$ are the spherical primitive Gaussian-type functions in the molecular basis set which are centered on I, and the coefficients $A^{I}_{l;ab}$ are the elements of the matrix

$$A^{I} = (S^{I})^{-1} K^{I} (S^{I})^{-1}, \tag{7}$$

where

$$S^{I}_{ij} = \langle i;I | j;I \rangle, \quad K^{I}_{ij} = \langle i;I | V^{I}_{\mathrm{exch}} | j;I \rangle, \tag{8}$$

$|i;I\rangle$, $|j;I\rangle$ being functions of the set $\{|alm;I\rangle\}$.

Once an atomic AE SCF calculation is done and a core–valence partition is chosen, the atomic core orbitals are used to obtain the operators $P^{I}(i)$, Eq. (2), and $V^{I}_{\mathrm{Coul,MP}}$, Eq. (5), as well as to define the operator V^{I}_{exch}, Eq. (4). If a particular basis set is chosen for the molecular calculation, the operator $V^{I}_{\mathrm{exch,MP}}$, Eq. (6), is obtained using Eqs. (7) and (8),[16] so that, whatever the basis set is, it is always guaranteed that

$$\langle i;I | V^{I}_{\mathrm{exch,MP}} | j;I \rangle = \langle i;I | V^{I}_{\mathrm{exch}} | j;I \rangle. \tag{9}$$

The atomic valence basis set, which is the only component of the AIMP method that has to be optimized in a valence-electron atomic calculation, is obtained by minimization of the valence energy. In this way, the atomic model potential problem becomes entirely parallel to the one of optimization of all-electron basis sets.

III. MODEL POTENTIALS, BASIS SETS, AND ATOMIC RESULTS

Whereas for the main group elements it is usually clear what orbitals constitute the valence, it is not always so for the transition metal elements. In this respect, a trend can be observed lately towards including more orbitals in the valence part in order to achieve higher quality results at a cost of increasing computing time. In particular, core-$2p$ (Ne-like) pseudopotentials[6(c),8] and core-$3s$ (Mg-like) model potentials[10(b)] have been recently published for the first series transition metal elements, in addition to the core-$3p$ (Ar-like) pseudo-[6(a)] and model potentials.[10(a)] Some of them[8] also include relativistic effects. In this section we present the nonrelativistic core-$3p$ (Ar-like) and core-$3s$ (Mg-like) model potential parameters for the first series transition elements Sc to Zn, as well as their corresponding $4s$,$3d$- and $4s$,$3p$,$3d$-valence Gaussian basis sets. The selection among them for actual molecular calculations will depend on the particular precision/economy needs.

We have used the *well-tempered* (WT) core orbital functions and energies[17] that are very close to the HF limit in the core projection, Coulomb, and exchange operators [Eqs. (2)–(4)]. The resulting core-$3s$ local Coulomb model potential parameters [Eq. (5)] after the least-squares fitting are presented in Table I. The core-$3p$ local Coulomb model potential parameters are deposited in PAPS.[24] The nonlocal exchange model potential coefficients $A^{I}_{l;\mathrm{ab}}$ [Eq. (6)] are actually computed along the input processing part of the molecular calculations [Eq. (7)] and a tabulation of them would not be of interest.

The optimization of the valence basis sets by minimizing the valence energy was carried out following the procedure described in Ref. 18. The valence basis sets that we present in Table II (see the PAPS document for the core-$3p$ basis sets) correspond to the pattern ($9_{3222}//5$) and ($9_{3222}/5_{32}/5$) for the core-$3p$ and core-$3s$ calculations, respectively, where, for instance, 9_{3222} means[1] that the three innermost primitives in the s contracted function provide the ability to reach $1s$–$4s$ orthogonality, the two next primitives supply $2s$–$4s$ orthogonality and so on, the two last primitives representing the main region of the $4s$ orbital. This kind of pattern was the optimum for the main group elements[1] and performs with the same degree of quality in transition metal elements.

Some properties of the $4s$ and $3d$ atomic orbitals resulting from core-$3p$ calculations are shown in Table III, where the similarities between them and those of AE calculations using basis sets with a valence part of the same quality can be observed. In this table, E(proj) stands for the expectation value of the core projection operator, Eq. (2), with the MP atomic wave function, and it is a measure of the degree of core–valence orthogonality achieved.

In order to assess the ability of the MP basis sets to mimic the behavior of AE basis sets with the same quality in the valence part, when an important deformation on the valence orbitals takes place, we have calculated $4s$–$3d$ excitation energies at the HFR level, which are shown in Table IV. In these calculations all the basis sets were augmented with a Hay's d-diffuse function[19] in order to provide a balanced description of the $4s^{2}3d^{n}$, $4s^{1}3d^{n+1}$, and $3d^{n+2}$ configurations. A closeness of MP-$3p$ and AE results is observed if the same splitting pattern is used in the valence contracted function (the only one in MP calculations) either for the one-electron and for the two-electron excitations. If the MP basis set is completely decontracted, the excitation energies are closer to the HF limit but still in the range of AE calculations with a limited basis set.

IV. MOLECULAR CALCULATIONS

In this Section we present the results of RHF molecular calculations carried out in order to test the performance of the method in molecules containing first series transition metal elements. The equilibrium distances R_e and vibrational frequencies $\bar{\nu}_e$ for the ground states of ScO, MnO, and CuO, as well as ScS, have been calculated using the potentials and basis sets in Tables I and II (for O and S those of Ref. 1) and they are compared with the results of AE calculations using basis sets of similar quality in the valence part, whose reproduction is the objective of the method. These oxides are known to be sensitive touch-stones for valence-electron-only methods. The molecular basis sets used are

TABLE I. Core-3*s* local Coulomb model potential parameters [Eq. (5)] for the first series transition metal elements.

Scandium		Titanium		Vanadium		Chromium	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
277 100.00	0.145 465 98	267 000.00	0.157 265 76	266 000.00	0.165 597 16	272 000.00	0.170 838 61
33 560.000	0.211 132 47	31 450.000	0.232 269 49	31 380.000	0.243 765 38	32 730.000	0.247 860 10
6 699.000 0	0.409 241 15	6 222.000 0	0.451 235 95	6 263.000 0	0.470 178 32	6 622.000 0	0.476 048 65
1 671.000 0	0.762 691 95	1 548.000 0	0.840 934 81	1 582.000 0	0.863 915 72	1 689.000 0	0.870 954 50
490.000 00	1.237 622 50	455.100 00	1.307 306 28	473.600 00	1.312 023 97	509.200 00	1.314 890 86
153.200 00	1.377 410 50	140.100 00	1.391 748 11	147.200 00	1.388 729 71	158.800 00	1.393 341 09
42.710 000	2.532 823 83	41.200 000	2.782 963 56	44.360 000	2.825 488 89	48.170 000	2.867 085 69
16.214 000	3.423 857 26	16.588 000	3.038 841 21	18.164 000	2.950 586 21	19.835 000	2.895 413 62
3.486 000	1.051 195 47	3.398 000	1.099 222 92	3.706 000	1.116 114 31	3.991 000	1.137 391 13
1.339 300 0	0.848 558 89	1.424 400 0	0.698 211 91	1.574 200 0	0.663 600 34	1.677 900 0	0.626 175 75

Manganese		Iron		Cobalt		Nickel	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
282 000.00	0.174 297 17	290 000.00	0.178 487 98	298 000.00	0.182 515 51	305 000.00	0.186 829 87
34 960.00	0.247 466 85	36 740.000	0.249 609 25	38 600.000	0.251 189 87	40 270.000	0.253 639 11
7 206.000 0	0.472 745 98	7 670.000 0	0.475 351 16	8 167.000 0	0.476 844 84	8 617.000 0	0.480 279 92
1 858.000 0	0.862 746 22	1 995.000 0	0.863 906 65	2 142.000 0	0.864 205 37	2 278.000 0	0.867 173 44
563.600 00	1.307 361 30	609.300 00	1.305 441 93	657 700 00	1.304 325 93	703.400 00	1.305 261 63
177.400 00	1.386 486 80	192.800 00	1.386 667 71	209.000 00	1.386 904 29	224.000 00	1.390 755 29
53.850 000	2.827 523 30	58.760 000	2.833 390 20	63.940 000	2.834 920 33	68.830 000	2.852 159 92
22.191 999	2.947 380 00	24.311 000	2.936 791 96	26.554 000	2.930 419 38	28.748 000	2.900 427 70
4.509 000	1.129 914 80	4.933 000	1.136 613 35	5.388 000	1.140 487 03	5.832 000	1.145 651 18
1.919 000	0.644 077 54	2.105 400	0.633 739 81	2.300 200 0	0.628 187 44	2.495 300 0	0.617 821 94

Copper		Zinc	
α_k	$-A_k$	α_k	$-A_k$
311 000.00	0.191 396 75	318 000.00	0.195 497 96
41 720.000	0.257 196 89	43 530.000	0.258 291 74
8 996.000 0	0.486 053 89	9 547.000 0	0.484 938 80
2 399.000 0	0.872 347 40	2 571.000 0	0.869 074 42
745.400 00	1.307 422 20	803.300 00	1.303 411 42
237.700 00	1.395 586 60	257.700 00	1.390 287 92
73.490 000	2.880 371 10	79.970 000	2.855 194 12
30.851 000	2.855 910 00	33.640 000	2.883 303 55
6.210 000 0	1.158 650 10	6.817 000 0	1.152 487 02
2.624 600 0	0.595 065 07	2.912 800 0	0.607 513 04

described in Table V. The AE basis sets, as well as all the polarization functions, were taken from Ref. 18. The MP basis sets *P* 5 and *P* 32 correspond to Table II for Sc, Mn, and Cu, and to Ref. 1 for O and S.

We carried out model potential calculations either for the Ar-like core, MP-3*p*, and for the Mg-like core, MP-3*s*, so that the results orient us about the precision that should be expected when a particular core–valence partition is chosen for a specific molecule. The results are presented in Table VI.

First of all, the results of the MP calculations when the AE basis set is used reveal that the 3*p* orbital is a true core orbital at the end part of the row, whereas for the lighter transition metal elements large errors may occur if its valence character is disregarded. The degree of noncore character of the 3*p* orbital is, however, molecule dependent; in ScO freezing the 3*p* affects R_e by 0.07 Å, but in ScS the error is lower: 0.02 Å. In the middle of the row its valence character is not crucial, the error associated with freezing it being of the order of 0.01 Å in R_e. On the other hand, the core character of the 3*s* orbital is apparent all along the first transition series and the MP-3*s* results using the AE basis sets virtually coincide with the AE results.

It should be noticed that in the MP-3*p* calculation with the AE basis set the role of the five- and three-primitive contracted *p* functions is not to represent the 3*p* orbital, but to provide the ability to reach a high degree of orthogonality between the 3*p* core orbital and the valence molecular orbitals. If these functions are dropped from the AE basis set, the atoms are artificially kept apart in order to reduce the overlap between those orbitals, and the equilibrium distance for ScO rises to 1.654 Å, only 0.02 Å lower than the AE one, 1.668 Å. But the only reason for this seeming success is a fortuitous cancellation of errors. − 0.07 Å is the error associated to freezing the Sc 3*p* orbital, whereas an extra error of + 0.05 Å is due to improperly dropping the Sc *p* functions from the basis set, often done on the basis that there are no Sc *p* orbitals to represent. This is, in our opinion, the reason for the rather small deviation of R_e (0.04 Å) in the MP-3*p* cal-

TABLE II. 4*s*,3*p*,3*d*-valence Gaussian basis sets for the first series transition metal elements.

Sc ($3p^64s^23d^1$–^2D)		Ti ($3p^64s^23d^2$–^3F)		V ($3p^64s^23d^3$–^4F)		Cr ($3p^64s^13d^5$–^7S)	
exp. 4*s*	coeff. 4*s*	exp. 4*s*	coeff. 4*s*	exp. 4*s*	coeff. 4*s*	exp. 4*s*	coeff. 4*s*
2402.931 45	−0.001 341 33	2609.464 81	−0.001 358 98	2812.476 61	−0.001 377 16	2988.679 05	−0.001 306 67
361.569 173	−0.009 160 02	395.029 348	−0.009 208 37	427.568 660	−0.009 259 80	457.240 722	−0.008 696 04
81.218 071 8	−0.027 714 92	89.279 755 3	−0.027 765 39	97.365 661 7	−0.027 672 34	104.903 914	−0.025 608 67
7.749 152 61	0.114 844 96	8.654 831 41	0.114 939 04	9.631 617 41	0.114 188 93	11.018 052 1	0.095 776 52
3.092 323 54	0.092 839 10	3.498 992 05	0.089 912 65	3.896 286 04	0.090 200 34	4.974 185 45	0.078 061 57
1.318 361 38	−0.190 671 94	1.481 841 65	−0.190 894 26	1.702 639 11	−0.184 462 09	1.736 799 67	−0.174 697 55
0.493 380 481	−0.378 384 80	0.556 695 323	−0.364 562 38	0.633 958 058	−0.357 256 73	0.662 375 244	−0.302 851 87
0.692 259 552*E*−01	0.711 086 32	0.771 966 475*E*−01	0.688 883 99	0.832 269 418*E*−01	0.687 224 54	0.790 869 116*E*−01	0.668 695 19
0.272 329 463*E*−01	0.437 612 65	0.299 225 999*E*−01	0.456 362 44	0.317 816 679*E*−01	0.451 917 01	0.299 568 970*E*−01	0.453 945 02
exp. 3*p*	coeff. 3*p*	exp. 3*p*	coeff. 3*p*	exp. 3*p*	coeff. 3*p*	exp. 3*p*	coeff. 3*p*
165.634 365	−0.017 377 95	186.361 867	−0.017 429 46	208.165 560	−0.017 448 75	231.920 038	−0.017 157 84
38.205 454 5	−0.101 123 16	43.059 535 6	−0.102 396 89	48.185 931 17	−0.103 323 36	53.766 190 1	−0.102 483 32
11.237 327 3	−0.230 086 21	12.736 533 2	−0.234 987 10	14.326 191 3	−0.238 887 46	16.050 025 7	−0.239 272 61
1.294 616 65	0.610 783 25	1.487 224 05	0.613 866 84	1.689 329 43	0.616 216 42	1.883 859 65	0.616 962 35
0.433 831 374	0.480 951 58	0.497 845 05	0.478 183 69	0.564 340 844	0.476 204 95	0.610 856 541	0.479 230 25
exp. 3*d*	coeff. 3*d*	exp. 3*d*	coeff. 3*d*	exp. 3*d*	coeff. 3*d*	exp. 3*d*	coeff. 3*d*
19.217 381 5	0.027 113 46	23.297 756 1	0.026 859 68	27.104 781 1	0.027 062 95	27.372 449 3	0.030 948 87
5.123 372 45	0.137 930 45	6.297 654 73	0.138 830 83	7.392 077 48	0.141 289 48	7.424 158 65	0.156 883 40
1.662 062 96	0.347 528 40	2.070 792 07	0.353 135 70	2.448 344 93	0.358 208 39	2.424 122 42	0.370 026 25
0.544 175 628	0.486 133 83	0.690 052 155	0.486 416 37	0.821 297 980	0.484 743 69	0.780 242 117	0.470 503 31
0.163 201 082	0.344 128 13	0.210 853 107	0.328 922 76	0.251 705 762	0.320 953 91	0.219 319 749	0.338 244 73
Mn ($3p^64s^23d^5$–^6S)		Fe ($3p^64s^23d^6$–^5D)		Co ($3p^64s^23d^7$–^4F)		Ni ($3p^64s^23d^8$–^3F)	
exp. 4*s*	coeff. 4*s*	exp. 4*s*	coeff. 4*s*	exp. 4*s*	coeff. 4*s*	exp. 4*s*	coeff. 4*s*
3370.012 98	−0.001 330 78	3672.192 28	−0.001 317 23	3942.949 76	−0.001 317 26	4285.323 29	−0.001 291 43
512.789 752	−0.008 993 18	558.126 035	−0.008 933 84	600.441 842	−0.008 901 90	651 911 666	−0.008 765 64
116.561 802	−0.027 267 66	126.774 647	−0.027 237 93	137.004 675	−0.027 067 34	148.431 042	−0.026 885 87
11.545 006 3	0.115 996 77	12.491 165 4	0.119 139 59	13.557 469 7	0.119 819 65	14.615 658 1	0.120 663 57
4.362 818 17	0.094 578 93	4.479 527 22	0.098 668 75	4.783 482 66	0.094 441 42	5.084 914 95	0.088 548 49
2.169 642 25	−0.191 167 38	2.386 379 70	−0.203 402 15	2.537 418 89	−0.209 739 24	2.695 829 83	−0.211 511 41
0.772 578 961	−0.337 719 05	0.842 901 582	−0.326 834 09	0.897 646 931	−0.313 476 02	0.963 777 478	−0.300 423 48
0.967 690 119*E*−01	0.667 064 40	0.105 544 905	0.653 929 93	0.116 642 530	0.623 088 08	0.124 706 722	0.616 312 81
0.359 339 475*E*−01	0.465 711 28	0.386 189 088*E*−01	0.477 808 83	0.421 197 946*E*−01	0.509 604 79	0.444 012 721*E*−01	0.514 892 86
exp. 3*p*	coeff. 3*p*	exp. 3*p*	coeff. 3*p*	exp. 3*p*	coeff. 3*p*	exp. 3*p*	coeff. 3*p*
255.680 584	−0.017 374 89	280.871 375	−0.017 386 51	307.286 422	−0.017 373 60	335.211 140	−0.017 329 09
59.336 118 0	−0.104 439 83	65.282 026 4	−0.105 071 54	71.502 129 5	−0.105 556 46	78.052 116 1	−0.105 886 11
17.781 298 1	−0.244 780 36	19.636 896 6	−0.247 511 78	21.576 811 1	−0.249 758 95	23.616 187 0	−0.251 733 49
2.123 474 75	0.619 129 00	2.359 278 49	0.621 218 47	2.606 004 73	0.622 370 40	2.862 374 01	0.623 521 32
0.705 479 701	0.474 088 40	0.782 863 443	0.472 185 57	0.863 194 192	0.471 312 64	0.946 249 872	0.470 407 51

TABLE II. (*continued.*)

Mn ($3p^64s^23d^5$–^6S)		Fe ($3p^64s^23d^6$–^5D)		Co ($3p^64s^23d^7$–^4F)		Ni ($3p^64s^23d^8$–^3F)	
exp. $3d$	coeff. $3d$	exp. $3d$	coeff. $3d$	exp. $3d$	coeff. $3d$	exp. $3d$	coeff. $3d$
35.111 989 5	0.027 390 73	38.664 428 0	0.028 251 23	42.858 615 3	0.028 504 49	47.296 629 4	0.028 692 88
9.704 003 53	0.145 116 07	10.724 071 1	0.149 786 43	11.936 672 6	0.151 786 10	13.207 975 8	0.153 696 37
3.246 697 34	0.365 224 63	3.590 978 76	0.370 286 46	4.005 020 19	0.372 547 01	4.435 978 69	0.374 874 00
1.096 286 11	0.481 261 77	1.205 600 71	0.477 119 44	1.340 956 26	0.475 004 28	1.482 292 03	0.473 227 54
0.335 827 616	0.312 222 85	0.363 417 737	0.311 812 51	0.400 044 778	0.312 462 42	0.438 585 592	0.312 182 26

Cu ($3p^64s^23d^9$–^2D)		Cu ($3p^64s^13d^{10}$–^2S)		Zn ($3p^64s^23d^{10}$–^1S)	
exp. $4s$	coeff. $4s$	exp. $4s$	coeff. $4s$	exp. $4s$	coeff. $4s$
4662.709 79	−0.001 327 60	4725.667 38	−0.001 038 24	4956.874 93	−0.001 257 11
708.534 980	−0.009 052 13	711.257 019	−0.007 181 49	753.247 438	−0.008 571 76
160.947 377	−0.028 080 11	160.293 952	−0.022 365 45	171.328 469	−0.026 454 68
15.556 964 7	0.129 881 14	16.322 017 2	0.089 744 24	17.136 691 6	0.117 542 44
5.330 504 78	0.076 352 20	7.566 962 01	0.048 860 03	5.974 941 20	0.082 446 38
2.747 332 13	−0.221 259 51	2.487 110 75	−0.163 843 86	3.115 234 64	−0.205 922 05
1.019 555 38	−0.287 660 55	0.929 908 965	−0.222 671 35	1.118 799 44	−0.283 735 67
0.133 440 271	0.607 897 81	0.101 633 938	0.573 667 85	0.140 166 708	0.604 208 02
0.468 427 305$E-01$	0.522 235 25	0.362 849 633$E-01$	0.532 611 44	0.487 445 380$E-01$	0.523 055 21
exp. $3p$	coeff. $3p$	exp. $3p$	coeff. $3p$	exp. $3p$	coeff. $3p$
364.165 348	−0.017 276 29	364.668 523	−0.017 122 67	394.070 259	−0.017 261 76
84.862 643 6	−0.106 086 37	85.013 560 1	−0.105 131 79	91.914 712 5	−0.106 415 05
25.738 604 6	−0.253 246 64	25.788 883 5	−0.251 439 62	27.949 363 4	−0.254 882 55
3.128 249 65	0.623 864 77	3.108 978 55	0.624 507 02	3.407 980 59	0.624 979 94
1.031 436 33	0.470 406 91	1.004 846 31	0.472 210 42	1.121 932 45	0.469 492 70
exp. $3d$	coeff. $3d$	exp. $3d$	coeff. $3d$	exp. $3d$	coeff. $3d$
51.497 210 8	0.029 389 32	47.715 679 3	0.031 937 87	56.386 935 3	0.029 313 01
14.430 778 6	0.157 235 29	13.269 974 4 .	0.166 517 63	15.841 731 8	0.157 688 01
4.859 723 87	0.378 759 98	4.403 233 17	0.383 924 53	5.338 013 74	0.379 305 17
1.624 918 66	0.470 463 37	1.422 487 75	0.462 673 35	1.780 914 31	0.469 754 33
0.479 348 422	0.308 257 76	0.390 636 169	0.325 302 44	0.521 473 016	0.309 857 30

TABLE III. Valence energy, projection energy, orbital energies, and radial spectation values for the first series transition metal elements. The all-electron results correspond to the basis set (5333/53/5) of Ref. 18. All numbers in atomic units.

						4*s*			3*d*		
	Calc.	*E*(val)	*E*(proj)	$\epsilon(4s)$	$\epsilon(3d)$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
Sc $s^2d^1{-}^2D$	MP-3*p*	− 1.551 616	0.000 013	− 0.209 09	− 0.343 82	0.318	3.974	18.188	0.802	1.656	3.497
	AE			− 0.209 43	− 0.342 74	0.319	3.969	18.166	0.801	1.658	3.506
Ti $s^2d^2{-}^3F$	MP-3*p*	− 3.337 415	0.000 015	− 0.219 49	− 0.439 47	0.334	3.793	16.614	0.909	1.447	2.656
	AE			− 0.219 82	− 0.438 89	0.335	3.789	16.603	0.909	1.447	2.653
V $s^2d^3{-}^4F$	MP-3*p*	− 6.089 909	0.000 016	− 0.229 04	− 0.507 51	0.348	3.641	15.346	1.000	1.313	2.186
	AE			− 0.229 25	− 0.506 60	0.349	3.641	15.377	1.000	1.312	2.179
Cr $s^1d^5{-}^7S$	MP-3*p*	− 10.127 823	0.000 047	− 0.217 63	− 0.365 42	0.342	3.706	15.990	1.006	1.351	2.389
	AE			− 0.217 67	− 0.364 47	0.343	3.709	16.070	1.006	1.350	2.384
Mn $s^2d^5{-}^6S$	MP-3*p*	− 15.126 910	0.000 018	− 0.245 80	− 0.634 07	0.374	3.398	13.426	1.168	1.122	1.598
	AE			− 0.246 32	− 0.633 94	0.375	3.398	13.469	1.168	1.123	1.603
Fe $s^2d^6{-}^5D$	MP-3*p*	− 21.464 753	0.000 019	− 0.255 55	− 0.640 13	0.388	3.276	12.509	1.238	1.065	1.447
	AE			− 0.255 97	− 0.639 59	0.389	3.277	12.544	1.238	1.065	1.448
Co $s^2d^7{-}^4F$	MP-3*p*	− 29.376 671	0.000 021	− 0.264 29	− 0.666 38	0.401	3.172	11.748	1.312	1.008	1.302
	AE			− 0.264 57	− 0.665 74	0.402	3.173	11.776	1.312	1.008	1.301
Ni $s^2d^8{-}^3F$	MP-3*p*	− 38.957 166	0.000 022	− 0.272 53	− 0.695 89	0.413	3.080	11.096	1.385	0.957	1.176
	AE			− 0.272 81	− 0.694 76	0.415	3.079	11.105	1.385	0.956	1.175
Cu $s^1d^{10}{-}^2S$	MP-3*p*	− 50.598 548	0.000 012	− 0.231 02	− 0.468 29	0.374	3.391	13.561	1.394	0.977	1.262
	AE			− 0.232 09	− 0.470 99	0.376	3.380	13.469	1.393	0.979	1.270
$s^2d^9{-}^2D$	MP-3*p*	− 50.596 885	0.000 202	− 0.280 72	− 0.737 48	0.431	2.990	10.492	1.463	0.907	1.056
	AE			− 0.281 06	− 0.727 11	0.427	2.990	10.485	1.458	0.911	1.071
Zn $s^2d^{10}{-}^1S$	MP-3*p*	− 63.724 790	0.000 025	− 0.287 75	− 0.766 40	0.437	2.921	10.021	1.532	0.867	0.970
	AE			− 0.287 94	− 0.765 49	0.438	2.916	9.981	1.533	0.867	0.970

culation on ScO in Ref. 20. In ScS, however, freezing the Sc 3*p* orbital may be acceptable (2.11 vs 2.13 Å): therefore, the positive deviations on R_e due to dropping the Sc *p* functions from the basis set are not compensated, the result being 2.317 Å, too far away from the AE one, 2.133 Å. These results, which essentially coincide with those of similar calculations on main group element molecules,[1] point out the *need* of providing the molecular basis set with enough flexibility to reach a high core–valence orthogonality.

In columns *P* 5 of Table VI we can observe the evolution of the MP-3*p* and MP-3*s* results upon reduction of the valence basis sets. This reduction, whose main effect is lowering the degree of core–valence orthogonality, brings about errors ranging from 0.01 to 0.03 Å in R_e and from 20 to 50 cm^{-1} in $\bar{\nu}_e$, both for the MP-3*p* and MP-3*s* calculations. The analysis of the contributions to the projection energy in the MP-3*s* calculation on MnO, where the errors associated to the basis set reduction are larger, reveals that the main contribution comes from the overlap between the Mn 2*p* core orbital and the valence molecular orbitals with a main character of oxygen. In order to reduce this overlap, we split the five-primitive *p* contracted function of the *P* 5 basis set representing the 3*p* orbital in two contracted functions of 2*p* and 3*p* character, respectively (*P* 32 basis set). This splitting is, of

TABLE IV. Excitation energies from the lowest states of the $4s^2 3d^n$ configurations to the lowest states of the $4s^1 3d^{n+1}$ and $3d^{n+2}$ configurations. The basis sets include one *d*-diffuse function (Ref. 19). All numbers in eV.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu[a]
$4s^1 3d^{n+1}$ configuration									
Numerical HF	1.01	0.54	0.12	− 1.27	3.32	1.80	1.53	1.28	− 0.37
MP-3*p* uncontracted	1.13	0.65	0.22	− 1.41	3.37	1.85	1.57	1.31	− 0.54
MP-3*p* (81/411)	1.17	0.69	0.26	− 1.52	3.41	1.91	1.65	1.41	− 0.40
AE (53321/53/411)	1.16	0.68	0.25	− 1.46	3.40	1.88	1.61	1.35	− 0.26
$3d^{n+2}$ configuration									
Numerical HF	4.47	4.25	3.27	5.75	9.15	7.46	7.05	5.47	
MP-3*p* uncontracted	4.75	4.55	3.57	5.69	9.35	7.66	7.23	5.65	
MP-3*p* (81/411)	4.79	4.59	3.62	5.60	9.38	7.70	7.27	5.69	
AE (53321/53/411)	4.79	4.57	3.60	5.68	9.38	7.70	7.27	5.70	

[a] The basis set of the $4s^2 3d^9{-}^2D$ state was used.

TABLE V. Basis sets used in the molecular calculations on ScO, MnO, CuO, and ScS.

Basis set label	Sc, Mn, Cu	O	S
AE	(53321/531*1*/311)	(521/41)	(5321/521/1*)
*P*5	(81/51*1*/311)	(41/41)	(61/51/1*)
*P*32	(81/321*1*/311)	(41/41)	(61/51/1*)

course, undesirable in terms of computer economy, but after it is done the size of the molecular basis set is still in the range of the ones used in other pseudopotential[21] and model potential methods[22,23] and the results evolve, as expected, towards reducing the discrepancies with the AE ones. All the results of the MP-3*s* calculations with the *P*32 basis set keep the discrepancy with the AE results under the margin of 0.01 Å for R_e and 25 cm^{-1} for $\bar{\nu}_e$.

V. CONCLUSIONS

In this paper we present the Ar-like core (MP-3*p*) and Mg-like core (MP-3*s*) nonrelativistic *ab initio* model potentials and basis sets for the first series transition metal elements Sc to Zn. The results of the test molecular calculations show that, whereas the 3*p* orbital is a true core orbital only at the end part of the series, the 3*s* orbital may be safely frozen wherever in the series. The quality of the MP-3*s* model potentials is such that the molecular results virtually coincide with the AE ones if the AE basis set is used. Upon substantial reduction of the molecular basis sets the MP-3*s* results agree with those of AE calculations with similar quality in the valence part of the basis set in 0.01 to 0.03 Å in R_e and 25 to 50 cm^{-1} in $\bar{\nu}_e$. As in the main group elements,[1] the lack of a high degree of orthogonality between the core orbitals and the molecular valence orbitals may be detrimental in some cases (agreement in R_e of only 0.03 Å); improvement of the core–valence orthogonality in these cases by providing the valence molecular basis set with enough flexibility keeps the agreement within the limits of 0.01 Å in R_e and 25 cm^{-1} in $\bar{\nu}_e$.

TABLE VI. AE, MP-3*s*, and MP-3*p* calculated values of R_e and $\bar{\nu}_e$ for the ground states of ScO, ScS, MnO, and CuO.

		R_e/Å Basis set			$\bar{\nu}_e$/cm^{-1} Basis set		
Molecule	Calcn.	AE	*P*32	*P*5	AE	*P*32	*P*5
ScO	AE	1.668			1070		
σ^1–$^2\Sigma$	MP-3*s*	1.663	1.658	1.665	1064	1088	1086
	MP-3*p*	1.585		1.588	946		1013
ScS	AE	2.133			639		
σ^1–$^2\Sigma$	MP-3*s*	2.129	2.136	2.144	642	622	620
	MP-3*p*	2.112		2.118	627		607
MnO	AE	1.776			670		
$\delta^2\pi^2\sigma^1 - {}^6\Sigma$	MP-3*s*	1.777	1.789	1.806	665	649	616
	MP-3*p*	1.788	1.796	1.815	623	607	582
CuO	AE	1.872			581		
$\sigma^2\delta^4\pi^3 - {}^2\Pi$	MP-3*s*	1.871	1.873	1.881	581	589	557
	MP-3*p*	1.873		1.880	586		558

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[1] S. Huzinaga, L. Seijo, Z. Barandiarán, and M. Klobukowski, J. Chem. Phys. **86**, 2132 (1987).

[2] V. Bonifacic and S. Huzinaga, J. Chem. Phys. **60**, 2779 (1974).

[3] R. N. Dixon and I. L. Robertson, *Theoretical Chemistry*, Specialist Periodical Reports (The Chemical Society, London, 1978), Vol. 3, p. 100, and references therein.

[4] M. Krauss and W. J. Stevens, Annu. Rev. Phys. Chem. **35**, 357 (1984), and references therein.

[5] G. B. Bachelet, D. R. Hamann, and M. Schluter, Phys. Rev. B **26**, 4199 (1982).

[6] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985); W. R. Wadt and P. J. Hay, *ibid.* **82**, 284 (1985); P. J. Hay and W. R. Wadt, *ibid.* **82**, 299 (1985).

[7] L. F. Pacios and P. A. Christiansen, J. Chem. Phys. **82**, 2665 (1985); M. M. Hurley, L. F. Pacios, P. A. Christiansen, R. B. Rass, and W. C. Ermler, *ibid.* **84**, 6840 (1986).

[8] M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 886 (1987).

[9] S. Huzinaga, M. Klobukowski, and Y. Sakai, J. Phys. Chem. **88**, 4880 (1984), and references therein.

[10] Y. Sakai, E. Miyoshi, M. Klobukowski, and S. Huzinaga, J. Comput. Chem. **8**, 226 (1987); **8**, 256 (1987).

[11] L. G. M. Petterson, U. Wahlgren, and O. Gropen, J. Chem. Phys. **86**, 2176 (1987).

[12] Z. Barandiarán and L. Seijo, J. Chem. Phys. **89**, 5739 (1988).

[13] S. Huzinaga, D. McWillians, and A. A. Cantu, Adv. Quantum Chem. **7**, 187 (1973).

[14] G. Höjer and J. Chung, Int. J. Quantum Chem. **14**, 623 (1978).

[15] Y. Sakai, J. Chem. Phys. **75**, 1303 (1981); Y. Sakai and S. Huzinaga, *ibid.* **76**, 2537, 2552 (1982).

[16] The calculation of the coefficients $A^{l}_{i,ab}$ [Eqs. (7) and (8)] is not time consuming and can be performed during the input processing part of the molecular calculation.

[17] S. Huzinaga and M. Klobukowski, J. Mol. Struct. (Theochem) **167**, 1 (1988).

[18] J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, edited by S. Huzinaga (Elsevier, Amsterdam, 1984).

[19] P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[20] J. Andzelm, E. Radzio, Z. Barandiarán, and L. Seijo, J. Chem. Phys. **83**, 4565 (1985).

[21] M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 2123 (1987).

[22] Y. Sakai and E. Miyoshi, J. Chem. Phys. **87**, 2885 (1987).

[23] E. Miyoshi, Y. Sakai, A. Murakami, H. Iwaki, H. Terashima, T. Shoda, and T. Kawaguchi, J. Chem. Phys. **89**, 4193 (1988).

[24] See AIP document no. PAPS JCPSA-91-7011-3 for 3 pages of core-3*p* local Coulomb model potential parameters and basis sets. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.