

# Model Potentials for Molecular Calculations. I. The *sd*-MP Set for Transition Metal Atoms Sc through Hg

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Model potential parameters and valence orbitals were generated for the transition metal atoms Sc through Hg. Only the  $nd$  and  $(n + 1)s$  valence electrons were treated explicitly and the effects of the remaining electrons were replaced by model potentials. For brevity they may be called *sd*-MPs. Major relativistic effects were incorporated on the level of Cowan and Griffin's quasirelativistic Hartree-Fock (QRHF) method for the second and third transition metal atoms. The model potential parameters and valence orbitals were determined so as to reproduce the results of the numerical Hartree-Fock reference calculations. The obtained valence orbitals have inner nodal structure. The model potential method can yield a balanced description of the  $s^2d^{n-1}$ ,  $sd^n$ , and  $d^{n+1}$  configurations of the atoms. The polarization functions were also generated for the use in molecular calculations.

## I. INTRODUCTION

A variety of effective potential methods called pseudopotentials, effective core potentials, or model potentials have been developed by many authors to simplify the treatment of chemically inert core electrons.<sup>1-22</sup> Most of these methods are more or less successful in reproducing results of all-electron calculations for molecules. Also, efforts have been made to include relativistic effects in the core potentials in order to treat the molecules containing heavy atoms.<sup>12-22</sup>

The model potential (MP) method<sup>23</sup> was devised as an economical alternative to the Hartree-Fock-Roothaan method with the frozen-core approximation. The method is unique among various effective core potential methods in that it is capable of producing the valence orbitals with the proper nodal structures. Most of the other methods, based on the Phillips-Kleinman's approach are tied to smoothed-out pseudovalence orbitals without nodal structures.

The MP method has undergone substantial refinements in past years.<sup>7-12</sup> At the first stage of the development,<sup>7,8</sup> model potentials have been prepared for the atoms Li through Ca and some other atoms such as Ni, Cu, Pd, and Br, where the MP parameters and valence orbitals were optimized in reference to the all-electron calculations with MINI-4 basis sets.<sup>24-27</sup> A number of test calculations have shown that the MP method yields molecular orbital energies, dissociation energies, geometries, and spectroscopic constants in very good agreement with the results of the reference calculations.<sup>9</sup> The method also has been modified so as to allow for approximate treatment of relativistic effects<sup>12</sup> on the level of Cowan and Griffin's quasirelativistic Hartree-Fock approach.

In the present work, the MP parameters and valence orbitals were determined systematically for the transition metal atoms Sc through Hg. The  $nd$  and  $(n + 1)s$  valence electrons were treated explicitly and all other

electrons were replaced by the model potentials. These model potentials are called the *sd*-MPs. The nonrelativistic MPs (NRMPs) are generated for the first-row transition metal atom series and the quasirelativistic model potentials (QRMPs) incorporating the mass velocity and Darwin relativistic effects were generated for the second and third series. In order to secure uniform treatment of both NRMP and QRMP parameters, the MP parameters and valence orbitals were determined by using the results of numerical nonrelativistic Hartree-Fock (HF) or quasirelativistic HF (QRHF) calculations as reference data. The model potential determined in this way has been tested in molecular calculations<sup>11</sup> and applied in calculations on clusters such as Pd<sub>4</sub>, Pt<sub>4</sub>,<sup>28</sup> and Pd<sub>4</sub>H.<sup>29</sup> Further representative molecular applications will be given in later work.

## II. DETERMINATION OF MODEL POTENTIALS AND VALENCE ORBITALS

The theoretical background of the MP method has been discussed in detail previously.<sup>8</sup> Here we only outline the method.

In the present article, the (3*d*, 4*s*), (4*d*, 5*s*), and (5*d*, 6*s*) electrons for the first-, second-, and third-row transition metal atoms, respectively, were treated explicitly. The core electrons replaced by the MPs were as follows:

first series (Sc ~ Zn): K(2)L(8)3*s*<sup>2</sup>3*p*<sup>6</sup>,

second series (Y ~ Cd):

K(2)L(8)M(18)4*s*<sup>2</sup>4*p*<sup>6</sup>,

third series (Lu ~ Hg):

K(2)L(8)M(18)N(32)5*s*<sup>2</sup>5*p*<sup>6</sup> (1)

The atomic MP Hamiltonian for valence electrons (in atomic units) was chosen as follows:

$$H = \sum_{i=1}^{N_v} \left[ -\frac{1}{2} \Delta_i + V_{mp}(r_i) + \sum_c B_c |\psi_c\rangle \langle \psi_c| \right] + \sum_{i>j}^{N_v} 1/r_{ij} \quad (2)$$

with

$$V_{mp}(r) = -(Z - N_c)/r \cdot \left[ 1 + \sum_{I=1}^3 A_I \exp(-\alpha_I r^2) + \sum_{I=4}^6 A_I r \exp(-\alpha_I r^2) \right] \quad (3)$$

and the explicit forms of  $\sum B_c |\psi_c\rangle \langle \psi_c|$  are as follows:

$$\begin{aligned} \text{first series:} \quad & \sum_{n=1}^3 B_{ns} |\psi_{ns}\rangle \langle \psi_{ns}| \\ & + \sum_{n=2}^3 B_{np} \sum_{m=-1}^1 |\psi_{np,m}\rangle \langle \psi_{np,m}|. \\ \text{second series:} \quad & \sum_{n=1}^4 B_{ns} |\psi_{ns}\rangle \langle \psi_{ns}| \\ & + \sum_{n=2}^4 B_{np} \sum_{m=-1}^1 |\psi_{np,m}\rangle \langle \psi_{np,m}| \\ & + B_{3d} \sum_{m=-2}^2 |\psi_{3d,m}\rangle \langle \psi_{3d,m}|. \\ \text{third series:} \quad & \sum_{n=1}^5 B_{ns} |\psi_{ns}\rangle \langle \psi_{ns}| \\ & + \sum_{n=2}^5 B_{np} \sum_{m=-1}^1 |\psi_{np,m}\rangle \langle \psi_{np,m}| \\ & + \sum_{n=3}^4 B_{nd} \sum_{m=-2}^2 |\psi_{nd,m}\rangle \langle \psi_{nd,m}| \\ & + B_{4f} \sum_{m=-3}^3 |\psi_{4f,m}\rangle \langle \psi_{4f,m}| \quad (4) \end{aligned}$$

where  $N_v$  and  $N_c$  are the number of valence electrons and core electrons, respectively, and  $Z$  is the atomic number of the atom.  $A_I$ ,  $\alpha_I$ , and  $B_c$  ( $c = 1s, 2s, \dots$ ) are the MP parameters;  $\psi_c$  denotes core orbitals. In the one-electron part of MP Hamiltonian (2), the second and third term represent (i) the local Coulomb interaction, (ii) the nonlocal exchange interaction, and (iii) the Pauli exclusion effect of the core in the form of projection operators. It is to be noted that both the local potential term  $V_{mp}(r_i)$  and the nonlocal projection operators  $\sum B_c |\psi_c\rangle \langle \psi_c|$  share the burden of approximating the nonlocal exchange interaction terms.

Prior to the determination of the model potential parameters we performed the all-electron numerical HF calculations<sup>30</sup> for the first-transition metal atoms and QRHF calculations<sup>12</sup> with Cowan and Griffin's method<sup>31</sup> for the second- and third-row transition metal atoms to prepare the reference functions.

In the QRHF method the mass velocity and Darwin terms of the Pauli Hamiltonian are

added to the Hartree-Fock differential equations, which are subsequently solved in a self-consistent fashion. This technique allows for incorporating the major direct and indirect relativistic effects into the orbital functions while retaining the commonly used non-relativistic formulation of the energy level calculations.

All the calculations were performed for the atoms in the lowest state of the  $s^1d^n$  configuration except for Zn, Cd, and Hg, for which calculations were carried out in the  $1S$  state of the  $s^2d^{10}$  configuration. Although  $s^2d^{n-1}$  is often the ground-state configuration of the transition metal atoms, we have chosen  $s^1d^n$  instead of  $s^2d^{n-1}$  because the valence orbitals derived for the  $s^2d^{n-1}$  state are too contracted to describe the atoms in the  $s^1d^n$  and  $d^{n+1}$  states properly.

The core orbitals,  $\{\psi_C\}$ , are expanded in terms of the Gaussian type functions (GTFs) which were determined by the least-squares fitting to the numerical reference functions. The details of the fitting technique have been given elsewhere.<sup>12</sup> The size of the core orbitals was chosen as  $10s/7p$ ,  $13s/10p/5d$ , and  $14s/10p/7d/4f$  for the first-, second-, and third-row transition metal atoms, respectively. This size is rather large, but the computer time spent for these core orbitals is negligibly small because they are used only for the evaluation of overlap integrals in the molecular calculations. All the core orbitals thus obtained were frozen in the course of determination of the MP parameters.

Valence orbitals were expanded in terms of a small number of GTFs as follows:

$$\begin{aligned} \text{first series (Sc} \sim \text{Zn):} & \quad (5s/5d) \\ \text{second series (Y} \sim \text{Cd):} & \quad (6s/5d) \\ \text{third series (Lu} \sim \text{Hg):} & \quad (7s/5d) \end{aligned} \quad (5)$$

These orbital basis functions were also determined by the least-squares fitting to the numerical radial functions. The orbital exponents were carefully chosen in order to retain the inner nodal structure. The valence orbitals thus obtained yield all of the inner nodes for the  $d$  valence orbital and all the nodes except for the innermost one for the  $s$  valence orbital. The exponents of the valence orbital basis functions were not reoptimized in the atomic model potential calculations.

There are three kinds of model potential parameters to be determined:  $\{A_I\}$ ,  $\{\alpha_I\}$ , and

$\{B_C\}$ . We define  $B_C$  as

$$B_C = -F_C \varepsilon_C \quad (6)$$

where  $\varepsilon_C$ 's are the core orbital energies given by the reference all-electron HF (or QRHF) calculations.

At the initial stage of the parameter optimization  $F_C$ 's are usually taken to be 2.<sup>8</sup> The remaining parameters  $\{A_I\}$  and  $\{\alpha_I\}$  are determined through a series of atomic SCF calculations in which the valence orbital energies and orbital shapes are constrained as described in the following. The pivotal quantity for the process is  $\Delta$ :

$$\Delta = \sum_{i=1}^{N_V} w_i |\varepsilon_i^{\text{ref}} - \varepsilon_i^{\text{MP}}| + \sum_{i=1}^{N_V} \sum_{k=1}^K W_i [r_k R_i^{\text{ref}}(r_k) - r_k R_i^{\text{MP}}(r_k)]^2 \quad (7)$$

where  $\varepsilon_i$  and  $R_i(r)$  are the orbital energy and radial function of the  $i$ th valence orbital, respectively, and  $w_i$  and  $W_i$  are appropriately chosen weight factors. The quantity  $rR(r)$  is computed at  $K$  discrete points  $\{r_k\}$ ; ref and MP stand for "reference" and "model potential", respectively.

The starting values of  $\{A_I\}$  and  $\{\alpha_I\}$  were estimated from the previous work.<sup>8,11</sup> For the set of parameters  $\{A_I\}$  and  $\{\alpha_I\}$  an atomic SCF calculation is performed with the chosen basis set and  $\varepsilon_i^{\text{MP}}$  and  $R_i^{\text{MP}}(r)$  are obtained. They are then put into eq. (7) to compute  $\Delta$ . This process defines the quantity  $\Delta$  as a function of  $\{A_I\}$  and  $\{\alpha_I\}$ , and the minimization of  $\Delta$  with respect to these MP parameters constitutes the optimization procedure of the MP method. In the atomic SCF calculation the valence orbitals are used without contraction.

In the previous papers,  $F_C$ 's were taken to be equal to 2.<sup>7-9,12</sup> The MP calculations using  $F_C = 2$  have successfully mimicked the all-electron calculations for the molecules containing light atoms such as C, O, and Cl.<sup>7-9</sup> However, the MP calculations using the hard-core value of  $F_C (= 2)$  lead to overly repulsive potential curves for AgH and Ag<sub>2</sub>, compared with the all-electron calculations.<sup>12</sup> Performing the test model potential calculations on simple diatomic molecules we have found that the soft-core value of  $F_C (= \sim 1)$  brings about a better agreement of the model potential results with all-electron results.<sup>11</sup> In the light of these past experiences, we decided to use the soft-core value of  $F_C (= 1.0 \sim 1.3)$  for the  $sd$ -MPs in the present article. They

were determined in the following way. First, the MP parameters,  $\{A_I\}$  and  $\{\alpha_I\}$ , were optimized using an extended valence basis set with the hard-core value of  $F_c (= 2)$ . Then, the extended basis set was replaced by a smaller basis set in (5) determined previously by the least-squares fitting. The atomic SCF calculation was repeated with the same  $\{A_I\}$  and  $\{\alpha_I\}$ , but now varying  $F_c$  for the range from 1.0 to 1.5. Dependence of the atomic SCF results on  $F_c$  was always mild and we could choose the  $F_c$  value within the above range that reproduces the all-electron reference calculation almost as satisfactorily as the extended basis set does. After the  $F_c$  value was chosen, the process of optimizing  $\{A_I\}$  and  $\{\alpha_I\}$  was repeated to obtain the finely tuned final model potential. The orbital exponents of the valence orbital basis functions were not subjected to any readjustment.

The total energies and orbital energies given by the MP SCF calculations are shown in Table I along with the reference orbital energies (the HF values for Sc to Zn, and the QRHF values for Y to Hg). The reproduction of the orbital energies is very good. The MP parameters are given in Tables II–IV, and the valence orbitals are given in Tables V–VII. The core orbitals are given in the Appendix.

### III. POLARIZATION FUNCTIONS

The need of the polarization functions are well documented for achieving overall reliability in the molecular calculations.<sup>32</sup> The exponents of the polarization functions have been often determined by minimizing the molecular total energy. However, the exponents determined in this way may depend on the particular molecular environments. Our

Table I. Total energies (TE) and orbital energies (in a.u.)<sup>a</sup>

Atom	State	TE	3d	4s
Sc	<sup>4</sup> F ( <i>d</i> <sup>2</sup> <i>s</i> )	−1.5217	−0.206 (−0.215)	−0.192 (−0.196)
Ti	<sup>5</sup> F ( <i>d</i> <sup>3</sup> <i>s</i> )	−3.3972	−0.273 (−0.273)	−0.205 (−0.205)
V	<sup>6</sup> D ( <i>d</i> <sup>4</sup> <i>s</i> )	−6.1515	−0.321 (−0.321)	−0.213 (−0.214)
Cr	<sup>7</sup> S ( <i>d</i> <sup>5</sup> <i>s</i> )	−10.1871	−0.373 (−0.374)	−0.221 (−0.222)
Mn	<sup>6</sup> D ( <i>d</i> <sup>6</sup> <i>s</i> )	−15.3559	−0.383 (−0.383)	−0.222 (−0.227)
Fe	<sup>5</sup> F ( <i>d</i> <sup>7</sup> <i>s</i> )	−21.6583	−0.407 (−0.407)	−0.230 (−0.230)
Co	<sup>4</sup> F ( <i>d</i> <sup>8</sup> <i>s</i> )	−29.6413	−0.432 (−0.432)	−0.233 (−0.233)
Ni	<sup>3</sup> D ( <i>d</i> <sup>9</sup> <i>s</i> )	−39.6549	−0.459 (−0.458)	−0.236 (−0.236)
Cu	<sup>2</sup> S ( <i>d</i> <sup>10</sup> <i>s</i> )	−51.1273	−0.491 (−0.491)	−0.238 (−0.238)
Zn	<sup>1</sup> S ( <i>d</i> <sup>10</sup> <i>s</i> <sup>2</sup> )	−63.7604	−0.783 (−0.783)	−0.297 (−0.293)
			4d	5s
Y	<sup>4</sup> F ( <i>d</i> <sup>2</sup> <i>s</i> )	−1.3215	−0.182 (−0.185)	−0.197 (−0.203)
Zr	<sup>5</sup> F ( <i>d</i> <sup>3</sup> <i>s</i> )	−2.8199	−0.238 (−0.239)	−0.213 (−0.217)
Nb	<sup>6</sup> D ( <i>d</i> <sup>4</sup> <i>s</i> )	−4.9912	−0.287 (−0.287)	−0.226 (−0.229)
Mo	<sup>7</sup> S ( <i>d</i> <sup>5</sup> <i>s</i> )	−8.0101	−0.342 (−0.342)	−0.238 (−0.238)
Tc	<sup>6</sup> D ( <i>d</i> <sup>6</sup> <i>s</i> )	−11.8738	−0.361 (−0.361)	−0.239 (−0.239)
Ru	<sup>5</sup> F ( <i>d</i> <sup>7</sup> <i>s</i> )	−16.6132	−0.393 (−0.394)	−0.235 (−0.239)
Rh	<sup>4</sup> F ( <i>d</i> <sup>8</sup> <i>s</i> )	−22.7636	−0.429 (−0.429)	−0.236 (−0.238)
Pd	<sup>3</sup> D ( <i>d</i> <sup>9</sup> <i>s</i> )	−29.6960	−0.466 (−0.467)	−0.234 (−0.238)
Ag	<sup>2</sup> S ( <i>d</i> <sup>10</sup> <i>s</i> )	−37.5867	−0.512 (−0.512)	−0.237 (−0.237)
Cd	<sup>1</sup> S ( <i>d</i> <sup>10</sup> <i>s</i> <sup>2</sup> )	−47.3834	−0.721 (−0.721)	−0.282 (−0.281)
			5d	6s
Lu	<sup>4</sup> F ( <i>d</i> <sup>2</sup> <i>s</i> )	−1.3245	−0.160 (−0.166)	−0.234 (−0.237)
Hf	<sup>5</sup> F ( <i>d</i> <sup>3</sup> <i>s</i> )	−2.7045	−0.209 (−0.214)	−0.251 (−0.256)
Ta	<sup>6</sup> D ( <i>d</i> <sup>4</sup> <i>s</i> )	−4.7145	−0.252 (−0.258)	−0.268 (−0.274)
W	<sup>7</sup> S ( <i>d</i> <sup>5</sup> <i>s</i> )	−7.6031	−0.305 (−0.307)	−0.287 (−0.289)
Re	<sup>6</sup> D ( <i>d</i> <sup>6</sup> <i>s</i> )	−10.9869	−0.321 (−0.322)	−0.289 (−0.292)
Os	<sup>5</sup> F ( <i>d</i> <sup>7</sup> <i>s</i> )	−15.3317	−0.349 (−0.350)	−0.288 (−0.292)
Ir	<sup>4</sup> F ( <i>d</i> <sup>8</sup> <i>s</i> )	−20.4530	−0.380 (−0.381)	−0.288 (−0.292)
Pt	<sup>3</sup> D ( <i>d</i> <sup>9</sup> <i>s</i> )	−26.5771	−0.413 (−0.414)	−0.287 (−0.292)
Au	<sup>2</sup> S ( <i>d</i> <sup>10</sup> <i>s</i> )	−33.9372	−0.454 (−0.454)	−0.288 (−0.291)
Hg	<sup>1</sup> S ( <i>d</i> <sup>10</sup> <i>s</i> <sup>2</sup> )	−41.9541	−0.604 (−0.604)	−0.328 (−0.327)

<sup>a</sup>The values in parentheses are the reference values: the HF values for Sc to Zn and the QRHF values for Y to Hg. See text for details.

Table II. Model potential parameters of first-series transition metal atoms.<sup>a</sup>

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
A <sub>1</sub>	2.38182	1.79181	1.21349	1.16791	1.09042	0.801137	0.720792	0.629140	0.506690	0.495477
A <sub>2</sub>	1.90005	1.35446	1.06666	0.863778	0.825940	0.692263	0.617513	0.572690	0.474124	0.444466
A <sub>3</sub>	0.863580	0.608610	0.458059	0.367446	0.332400	0.273210	0.228803	0.208870	0.176770	0.142482
A <sub>4</sub>	15.5070	9.11437	6.12818	6.11330	5.00219	4.20480	3.60099	3.30162	2.65546	3.12274
A <sub>5</sub>	26.5536	30.8675	19.1365	13.4884	11.5313	8.04217	5.49869	3.97315	5.01383	3.48936
A <sub>6</sub>	0.313973	0.255772	0.193497	0.144743	0.138520	0.116564	0.098734	0.091356	0.079232	0.069556
α <sub>1</sub>	166.524	138.592	166.840	161.872	154.533	160.313	167.266	168.171	197.608	169.151
α <sub>2</sub>	4.34975	4.53804	4.85727	4.88759	5.79484	6.00990	6.05553	6.54484	6.09610	6.48005
α <sub>3</sub>	0.750411	0.809696	0.850197	0.915365	1.09751	1.12295	1.24865	1.33631	1.38786	1.34701
α <sub>4</sub>	4574.23	4313.16	3830.57	4309.06	3068.48	3186.30	2895.71	2143.03	2673.61	2484.33
α <sub>5</sub>	32.8755	47.1074	44.7076	43.9771	56.9253	57.4313	58.1670	71.2570	75.9692	75.1582
α <sub>6</sub>	0.704069	0.736155	0.793285	0.864164	0.988770	1.02671	0.996671	1.17934	1.28097	1.37744
B <sub>1s</sub>	215.486	238.044	261.720	264.463	288.426	287.291	311.139	305.397	328.792	353.305
B <sub>2s</sub>	24.5925	27.6098	30.7739	31.4515	34.6914	34.8850	38.0975	37.6720	40.8180	44.3617
B <sub>3s</sub>	3.13791	3.51001	3.89082	3.94219	4.34616	4.33555	4.73224	4.65535	5.01126	5.63780
B <sub>4p</sub>	20.1613	22.8936	25.7712	26.5679	29.5397	29.9155	32.8793	32.7004	35.6170	38.9248
B <sub>3p</sub>	1.86669	2.12796	2.39758	2.46108	2.75863	2.80017	3.07944	3.06105	3.32415	3.83940

<sup>a</sup>F<sub>c</sub> values in B<sub>c</sub> = -F<sub>c</sub>ε<sub>c</sub> are taken to be 1.3 for Sc, Ti, and V; 1.2 for Cr and Mn; 1.1 for Fe and Co; and 1.0 for Ni, Cu, and Zn.Table III. Model potential parameters of second-series transition metal atoms.<sup>a</sup>

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
A <sub>1</sub>	6.91373	5.18535	3.97462	3.11385	3.03520	2.32278	2.33668	1.54674	1.49384	1.39173
A <sub>2</sub>	3.66472	2.69200	2.13076	1.73333	1.46761	1.32997	1.14099	1.13859	0.968431	0.896642
A <sub>3</sub>	1.40683	0.970770	0.685515	0.585096	0.502499	0.455107	0.403167	0.314479	0.267545	0.247361
A <sub>4</sub>	75.6758	37.1722	20.1599	14.9973	10.0073	10.3169	7.74945	6.15610	5.31510	3.80137
A <sub>5</sub>	81.5423	57.6453	41.3919	35.3682	27.6726	23.3666	18.8326	16.8382	15.7334	12.3844
A <sub>6</sub>	1.07110	0.762588	0.578342	0.439924	0.350531	0.280249	0.252520	0.231505	0.196306	0.166047
α <sub>1</sub>	166.663	174.977	188.901	164.998	171.537	158.714	196.365	269.700	275.685	237.760
α <sub>2</sub>	5.75456	5.99272	6.32017	6.63674	6.79001	7.32762	7.00244	7.52096	8.03006	7.81593
α <sub>3</sub>	1.42636	1.31697	1.37466	1.52280	1.43464	1.49513	1.58238	1.49882	1.47366	1.59482
α <sub>4</sub>	1103.48	1409.48	1854.06	1984.96	2244.98	1682.37	2248.07	2284.70	2168.06	2155.09
α <sub>5</sub>	65.3689	64.4624	58.3388	61.8470	62.5903	69.5252	65.1922	70.7754	71.3190	65.8827
α <sub>6</sub>	0.663277	0.712903	0.738902	0.745910	0.811830	0.853430	0.932351	1.03016	1.03324	1.10018
B <sub>1s</sub>	882.469	865.556	842.799	887.880	934.266	981.930	987.932	946.004	991.130	1037.62
B <sub>2s</sub>	124.432	123.245	121.115	128.702	136.573	144.688	146.680	141.475	149.248	157.467
B <sub>3s</sub>	21.3307	21.5707	21.5885	23.3106	25.1194	26.9756	27.6845	27.0014	28.7729	30.8102
B <sub>4p</sub>	3.01586	3.12508	3.18358	3.47852	3.80496	4.12908	4.27227	4.19364	4.48879	4.98517
B <sub>3p</sub>	110.529	109.667	107.935	114.847	122.010	129.383	131.268	126.689	133.714	141.147
B <sub>2p</sub>	16.6710	17.0033	17.1431	18.6278	20.1912	21.7933	22.4659	21.9978	23.5219	25.3003
B <sub>4d</sub>	1.72304	1.82636	1.89541	2.10200	2.33820	2.57196	2.69238	2.66998	2.88285	3.27605
B <sub>3d</sub>	8.97224	9.48572	9.85860	10.9933	12.2006	13.4411	14.1089	14.0394	15.2292	16.6650

<sup>a</sup>F<sub>c</sub> values in B<sub>c</sub> = -F<sub>c</sub>ε<sub>c</sub> are taken to be 1.4 for Y; 1.3 for Zr; 1.2 for Nb, Mo, Tc, and Ru; 1.15 for Rh; and 1.05 for Pd, Ag, and Cd.

Table IV. Model potential parameters of third-series transition metal atoms.<sup>a</sup>

	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
A <sub>1</sub>	14.9750	11.3250	9.06402	8.38002	5.84876	5.21949	4.49851	3.51543	3.46270	3.04505
A <sub>2</sub>	4.66963	3.74500	2.99646	2.51505	3.06070	2.63911	2.32539	2.07273	1.78764	1.64340
A <sub>3</sub>	2.86330	1.92808	1.53381	1.18274	0.885107	0.731645	0.603248	0.543471	0.486721	0.468490
A <sub>4</sub>	178.089	100.827	85.8105	60.3178	44.1433	31.6473	24.5184	19.5510	16.8104	22.1671
A <sub>5</sub>	116.090	81.4661	61.8657	52.0007	39.3356	34.9432	29.8842	28.2880	26.2003	24.2154
A <sub>6</sub>	2.11553	1.40409	1.04276	0.849928	0.514972	0.422794	0.352423	0.296594	0.256973	0.224831
$\alpha_1$	315.424	307.644	290.323	310.873	242.962	245.764	234.097	232.592	240.745	236.347
$\alpha_2$	3.54413	3.91243	4.16216	4.46263	6.59363	6.71327	6.45510	7.17190	7.14153	7.59273
$\alpha_3$	2.97657	2.96337	3.15252	3.05937	2.07577	2.02118	2.15965	2.11303	2.15834	2.32165
$\alpha_4$	2074.27	2826.35	3006.75	2085.73	2179.69	2591.31	2752.70	3154.69	3708.92	3367.27
$\alpha_5$	58.3814	54.0920	52.2824	51.1832	75.5540	74.1461	74.4850	72.4156	69.3190	75.1027
$\alpha_6$	0.875390	0.884879	0.909333	0.940253	0.883945	0.921386	0.925495	0.953799	0.977369	1.00886
B <sub>1s</sub>	2932.46	2905.68	2998.07	3092.31	3188.49	3286.61	3386.70	3198.09	3293.52	3391.04
B <sub>2s</sub>	505.403	502.994	521.256	539.970	559.180	578.854	599.010	568.015	587.403	607.414
B <sub>3s</sub>	117.093	117.105	121.950	126.935	132.096	137.396	142.843	136.069	141.333	146.896
B <sub>4s</sub>	24.5910	24.8510	26.1510	27.4968	28.9246	30.3869	31.8985	30.6691	32.1368	33.8048
B <sub>4s</sub>	3.30383	3.44600	3.72775	4.01040	4.32780	4.64424	4.96692	4.85507	5.16071	5.62298
B <sub>2p</sub>	445.530	442.646	457.895	473.446	489.337	505.529	522.030	493.940	509.634	525.776
B <sub>2p</sub>	98.7138	98.6684	102.684	106.802	111.057	115.408	119.862	114.051	118.320	122.839
B <sub>4p</sub>	18.4269	18.6702	19.6940	20.7506	21.8732	23.0222	24.2033	23.2979	24.4345	25.7545
B <sub>4p</sub>	1.73458	1.84686	2.03293	2.21767	2.43248	2.64424	2.85900	2.82084	3.02170	3.35456
B <sub>3d</sub>	76.0959	76.2627	79.5658	82.9502	86.4498	90.0241	93.6789	89.2956	92.7874	96.5065
B <sub>4d</sub>	10.1445	10.4354	11.1663	11.9210	12.7330	13.5629	14.4163	14.0184	14.8388	15.8332
B <sub>4f</sub>	0.951896	1.27320	1.66120	2.06863	2.52980	3.00545	3.50151	3.68290	4.17030	4.82933

<sup>a</sup>F<sub>c</sub> values in B<sub>c</sub> = -F<sub>c</sub>ε<sub>c</sub> are taken to be 1.25 for Lu; 1.2 for Hf, Ta, W, Re, Os, and Ir; and 1.1 for Pt, Au, and Hg.

Table V. Valence orbitals of first-series transition metal atoms (5s/5d).

Sc		Ti		V		Cr		Mn	
Exponent	4s	Exponent	4s	Exponent	4s	Exponent	4s	Exponent	4s
4.05792	-0.123918	4.50859	-0.142085	4.98293	0.121896	5.48170	0.125583	6.00971	0.119139
0.852923	0.269140	0.984177	0.314752	1.12399	-0.266888	1.27058	-0.272181	1.42468	-0.247653
0.371379	0.163549	0.435766	0.115503	0.503312	-0.143305	0.572299	-0.121814	0.637644	-0.128981
0.062372	-0.624035	0.069355	-0.642395	0.076392	0.629546	0.082771	0.624124	0.087679	0.584790
0.024989	-0.507377	0.027158	-0.477337	0.029325	0.492569	0.031206	0.491085	0.032593	0.526440
Exponent	3d	Exponent	3d	Exponent	3d	Exponent	3d	Exponent	3d
12.9698	0.059272	16.3351	0.052384	19.4681	0.050830	22.7680	0.052942	25.4349	0.054295
3.10607	0.205331	3.99368	0.203284	4.82648	0.202530	5.70909	0.216750	6.42026	0.233767
0.920176	0.411639	1.21301	0.429915	1.48581	0.429135	1.77631	0.432224	2.00032	0.439932
0.269761	0.452683	0.365839	0.458956	0.454106	0.463660	0.548985	0.455524	0.614663	0.442485
0.075763	0.292897	0.103099	0.250019	0.127841	0.239775	0.154990	0.227511	0.170619	0.220397
Fe		Co		Ni		Cu		Zn	
Exponent	4s	Exponent	4s	Exponent	4s	Exponent	4s	Exponent	4s
6.55742	-0.113942	7.13634	-0.103444	7.73397	0.101423	8.36994	0.094256	8.92230	-0.114873
1.58371	0.243259	1.74870	0.221131	1.91940	-0.210635	2.09394	-0.198708	2.32400	0.243836
0.701224	0.114090	0.765530	0.122512	0.830556	-0.104516	0.893787	-0.108993	1.07486	0.118020
0.091656	-0.614878	0.095485	-0.608647	0.099221	0.599636	0.102440	0.591288	0.137640	-0.640208
0.033637	-0.492022	0.034631	-0.496675	0.035596	0.499931	0.036394	0.506664	0.047637	-0.472993
Exponent	3d	Exponent	3d	Exponent	3d	Exponent	3d	Exponent	3d
28.4463	0.048851	31.6025	0.047483	34.8800	0.046396	38.4224	0.044154	46.7857	0.036975
7.22741	0.228455	8.07501	0.235569	8.95700	0.244731	9.91260	0.242367	12.2567	0.217344
2.25860	0.441088	2.53009	0.441782	2.81275	0.447937	3.12112	0.453371	3.96114	0.442189
0.693345	0.447147	0.776164	0.443323	0.862389	0.434719	0.957792	0.431286	1.27340	0.448210
0.190936	0.219729	0.212404	0.217876	0.234758	0.211662	0.260133	0.211195	0.371096	0.207145

Table VI. Valence orbitals of second-series transition metal atoms (6s/5d).

Y		Zr		Nb		Mo		Tc	
Exponent	5s	Exponent	5s	Exponent	5s	Exponent	5s	Exponent	5s
18.4749	-0.079024	19.5163	-0.098433	20.5917	-0.103016	21.7104	0.109004	22.8698	-0.113381
3.90741	0.229757	4.22637	0.272600	4.55825	0.268030	4.90269	-0.279387	5.26243	0.295230
0.652288	-0.363487	0.741718	-0.450999	0.837520	-0.428976	0.940254	0.427654	1.05393	-0.426488
0.318921	-0.236713	0.376579	-0.185247	0.436630	-0.199028	0.498687	0.200247	0.556100	-0.199305
0.060509	0.670665	0.068657	0.685060	0.076267	0.690004	0.083059	-0.706760	0.086725	0.685343
0.025013	0.493975	0.027760	0.466989	0.030250	0.462900	0.032347	-0.443740	0.032230	0.454969
Exponent	4d	Exponent	4d	Exponent	4d	Exponent	4d	Exponent	4d
36.9778	0.054234	40.1874	0.056933	43.6585	0.062717	47.2410	0.071360	51.1651	0.072660
8.81079	0.105853	9.66756	0.115640	10.5915	0.124291	11.5477	0.139047	12.5925	0.151317
0.739120	-0.388752	0.877003	-0.432447	1.01050	-0.437375	1.14614	-0.440766	1.28312	-0.464523
0.215670	-0.519126	0.272654	-0.515009	0.325442	-0.521183	0.379329	-0.523956	0.426185	-0.510448
0.061400	-0.360227	0.080482	-0.298494	0.098049	-0.271245	0.116664	-0.250591	0.129699	-0.239778
Ru		Rh		Pd		Ag		Cd	
Exponent	5s	Exponent	5s	Exponent	5s	Exponent	5s	Exponent	5s
24.0703	0.090455	25.3141	0.102961	26.6233	-0.087890	27.9733	-0.076324	29.2811	-0.095817
5.63554	-0.255456	6.02255	-0.278557	6.42393	0.237660	6.83995	0.220405	7.27142	0.261649
1.17222	0.331386	1.29355	0.364349	1.41679	-0.318684	1.54045	-0.284272	1.71419	-0.318977
0.611131	0.237756	0.664208	0.215657	0.715379	-0.227903	0.763423	-0.228887	0.892837	-0.268838
0.089460	-0.652138	0.091842	-0.643574	0.093967	0.625354	0.095573	0.641494	0.121027	0.669468
0.033766	-0.487331	0.034218	-0.484480	0.034620	0.498915	0.034876	0.481376	0.043424	0.469119
Exponent	4d	Exponent	4d	Exponent	4d	Exponent	4d	Exponent	4d
55.1434	0.071818	59.2365	0.077943	63.4456	-0.069024	67.7607	0.050184	72.0674	-0.074738
13.6546	0.159136	14.7487	0.184169	15.8755	-0.180835	17.0309	0.134845	18.1929	-0.202049
1.42595	-0.470352	1.57348	-0.487617	1.72587	0.489580	1.88338	-0.489766	2.07498	0.497560
0.477247	-0.507907	0.530223	-0.494392	0.585110	0.496993	0.642886	-0.503842	0.738540	0.492392
0.145367	-0.233599	0.161940	-0.223610	0.179333	0.218493	0.198335	-0.216287	0.243100	0.188871



Table VII. Valence orbitals of third-series transition metal atoms (7s/5d).

Lu		Hf		Ta		W		Re	
Exponent	6s	Exponent	6s	Exponent	6s	Exponent	6s	Exponent	6s
58.7495	0.119126	60.9473	0.126589	63.1547	0.131543	65.4900	0.177169	68.0306	0.165622
29.9669	-0.211772	31.1508	-0.222760	32.3877	-0.229915	33.6098	-0.298683	34.8389	-0.276457
4.41706	0.315119	4.61460	0.321925	4.82297	0.328040	5.04754	0.401974	5.26717	0.390985
0.809864	-0.417357	0.873358	-0.403644	0.942500	-0.393136	1.00269	-0.503182	1.11447	-0.403405
0.400708	-0.248087	0.456072	-0.263970	0.513330	-0.279359	0.562501	-0.219788	0.637970	-0.294963
0.073326	0.715931	0.083437	0.713213	0.093206	0.722198	0.102679	0.740948	0.107792	0.734621
0.030017	0.447522	0.033649	0.458620	0.037090	0.456301	0.040257	0.431138	0.041587	0.439549
Exponent	5d	Exponent	5d	Exponent	5d	Exponent	5d	Exponent	5d
83.3004	0.044986	86.6148	0.062021	89.9005	0.072098	93.2255	0.089222	96.5819	0.080140
6.67850	-0.143548	6.94754	-0.172001	7.25076	-0.190017	7.56820	-0.213132	7.91452	-0.224984
0.698346	0.395131	0.791554	0.417262	0.875950	0.428324	0.960280	0.455314	1.04277	0.461735
0.198446	0.506229	0.244885	0.514341	0.284800	0.517688	0.324650	0.509375	0.356530	0.509903
0.055470	0.384241	0.072067	0.323201	0.086498	0.289526	0.101560	0.253589	0.110740	0.244548
Os		Ir		Pt		Au		Hg	
Exponent	6s	Exponent	6s	Exponent	6s	Exponent	6s	Exponent	6s
70.5411	-0.174239	73.1280	-0.144530	75.3806	0.147000	78.5552	-0.159414	81.3603	0.164741
37.1328	0.284680	37.4640	0.250267	39.0268	-0.245276	40.2333	0.261339	41.7021	-0.275356
5.50241	-0.391916	5.74588	-0.369784	5.99843	0.367059	6.25774	-0.392168	6.53351	0.421201
1.21979	0.370692	1.33506	0.313968	1.45580	-0.275496	1.58806	0.274220	1.73625	-0.256139
0.703100	0.320274	0.769143	0.353273	0.834046	-0.369531	0.899751	0.374938	1.01235	-0.446385
0.112299	-0.716940	0.116378	-0.709811	0.120162	0.694462	0.123315	-0.688610	0.144385	0.727643
0.042571	-0.451798	0.043406	-0.456966	0.044145	0.467590	0.044658	-0.466485	0.051785	0.444342
Exponent	5d	Exponent	5d	Exponent	5d	Exponent	5d	Exponent	5d
100.008	0.091363	103.501	0.084802	107.062	0.097890	110.688	0.112471	114.443	0.107327
8.26563	-0.240621	8.62513	-0.251996	8.99278	-0.241889	9.36724	-0.255103	9.74070	-0.268339
1.12928	0.475839	1.21862	0.474221	1.31094	0.481181	1.40605	0.487592	1.52641	0.491357
0.391840	0.502223	0.428574	0.507390	0.466810	0.505039	0.507003	0.501113	0.575541	0.499101
0.122232	0.232849	0.134511	0.224136	0.147520	0.217375	0.161783	0.209156	0.194039	0.192034

group has published Gaussian basis sets for the atoms Li through Rn for use in the all-electron molecular calculations.<sup>33</sup> In this work the exponents of polarization functions have been determined by maximizing the radial overlap integrals between the polarization function and the valence orbital to be polarized.

The polarization functions for the MP calculations were determined in the same way as in the all-electron case: the polarization functions for the first-row transition metal atoms were taken from those determined for all-electron basis sets,<sup>33</sup> and the ones for the second and third series were obtained by maximizing radial overlap integrals with the quasirelativistic Hartree-Fock valence functions. The exponents of the polarization functions are given in Table VIII.

Table VIII. Exponents of *p*-type polarization functions.

Atom	$f_{\text{pol}}^a$	$f_{\text{pol}}^b$	$f_{\text{pol}}^b$
Sc	0.059	0.073	0.024
Ti	0.065	0.083	0.028
V	0.071	0.092	0.030
Cr	0.077	0.103	0.034
Mn	0.080	0.110	0.036
Fe	0.082	0.118	0.038
Co	0.085	0.125	0.040
Ni	0.088	0.133	0.041
Cu	0.090	0.142	0.044
Zn	0.123	0.176	0.055
Y	0.056	0.063	0.020
Zr	0.064	0.072	0.023
Nb	0.070	0.081	0.025
Mo	0.076	0.089	0.028
Tc	0.080	0.095	0.030
Ru	0.083	0.100	0.032
Rh	0.085	0.106	0.033
Pd	0.086	0.111	0.036
Ag	0.087	0.116	0.036
Cd	0.109	0.135	0.042
Lu	0.067	0.075	0.024
Hf	0.075	0.083	0.026
Ta	0.083	0.091	0.026
W	0.090	0.098	0.027
Re	0.095	0.104	0.029
Os	0.098	0.110	0.031
Ir	0.102	0.115	0.033
Pt	0.105	0.121	0.035
Au	0.107	0.126	0.037
Hg	0.125	0.135	0.037

<sup>a</sup>One-member polarization function set.

<sup>b</sup>Two-member polarization function set.

#### IV. ATOMIC EXCITATION ENERGIES

In the transition metal compounds the metal atom often has the  $sd^n$  and  $d^{n+1}$  configurations, whereas  $s^2d^{n-1}$  is usually the ground-state configuration for the first- and third-row transition metal atoms. Therefore, the basis sets for the molecular calculation need to be flexible to describe the  $d$  orbitals of various atomic configurations. Hay<sup>34</sup> has observed that if a basis set is determined for  $s^2d^{n-1}$ , an additional diffuse  $d$  function is necessary to describe the  $s^1d^n$  and  $d^{n+1}$  configurations properly.

In the present work, the model potentials were generated for the  $s^1d^n$  configuration. The exponents of valence orbitals determined by the least-squares fitting to the numerical radial functions, contain more diffuse  $d$  functions than the all-electron basis sets determined by minimizing the total energy: the smallest exponent of  $3d$  orbital is 0.2601 for MP (5s/5d) and 0.3755 for all-electron (AE) (5333/53/5)<sup>33</sup> for Cu atom in  $^1S(sd^{10})$  state. These values are far smaller than the value of 0.4649 for AE(5333/53/5)<sup>33</sup> of  $^2D(s^2d^9)$  state.

The excitation energies to the  $s^2d^{n-1}$  and  $d^{n+1}$  configurations from the  $sd^n$  configuration were calculated using the four types of contracted basis sets. The results are shown in Table IX for Cr, Ni, Pd, Mo, Pt, and W as examples. For the first-row transition metal atoms the (311/311) and (41/311) basis sets give nearly the same excitation energies, which agree well with the numerical HF values. The (41/41) basis set also gives a good agreement with the reference values. The minimal basis set, (5/5), gives poor excitation energies. All the split-type basis sets, (411/311), (51/311), and (51/41) for the second series, and (511/311), (61/311), and (61/41) for the third series, give almost the same excitation energies and are able to describe the  $s^2d^{n-1}$ ,  $sd^n$ , and  $d^{n+1}$  configurations properly. The minimal basis sets of the second and third series give better agreement with the reference values than in the case of the first series.

It was found in a previous article<sup>8</sup> that the core potential is hardly affected by an electron excitation such as  $sd^n$  to  $s^2d^{n-1}$ , and that only the flexibility of the valence basis set is required to describe the excited state properly.

**Table IX.** Excitation energies (in eV) for transition metal atoms. The valence orbital set were used in various types of contraction.<sup>a</sup>

Atom	State	Contraction				HF
		(5/5)	(41/41)	(41/311)	(311/311)	
Ni	<sup>3</sup> D 3d <sup>9</sup> 4s	0.0	0.0	0.0	0.0	0.0
	<sup>3</sup> F 3d <sup>8</sup> 4s <sup>2</sup>	2.80	-0.79	-1.01	-1.13	-1.27
	<sup>1</sup> S 3d <sup>10</sup>	8.92	4.75	4.71	4.71	4.20
Cr	<sup>7</sup> S 3d <sup>5</sup> 4s	0.0	0.0	0.0	0.0	0.0
	<sup>5</sup> D 3d <sup>4</sup> 4s <sup>2</sup>	3.54	1.88	1.59	1.57	1.27
	<sup>5</sup> D 3d <sup>6</sup>	10.25	7.34	7.31	7.31	7.03
		(6/5)	(51/41)	(51/311)	(411/311)	RHF
Pd	<sup>3</sup> D 4d <sup>9</sup> 5s	0.0	0.0	0.0	0.0	0.0
	<sup>3</sup> F 4d <sup>8</sup> 5s <sup>2</sup>	3.76	2.26	2.23	2.16	2.09
	<sup>1</sup> S 4d <sup>10</sup>	1.90	0.30	0.29	0.29	-0.10
Mo	<sup>7</sup> S 4d <sup>5</sup> 5s	0.0	0.0	0.0	0.0	0.0
	<sup>5</sup> D 4d <sup>4</sup> 5s <sup>2</sup>	3.05	2.38	2.34	2.34	2.37
	<sup>5</sup> D 4d <sup>6</sup>	5.67	4.69	4.69	4.69	4.36
		(7/5)	(61/41)	(61/311)	(511/311)	RHF
Pt	<sup>3</sup> D 5d <sup>9</sup> 6s	0.0	0.0	0.0	0.0	0.0
	<sup>3</sup> F 5d <sup>8</sup> 6s <sup>2</sup>	1.35	0.51	0.49	0.47	0.40
	<sup>1</sup> S 5d <sup>10</sup>	1.89	1.00	0.99	0.99	0.90
W	<sup>7</sup> S 5d <sup>5</sup> 6s	0.0	0.0	0.0	0.0	0.0
	<sup>5</sup> D 5d <sup>4</sup> 6s <sup>2</sup>	1.57	1.16	1.13	1.11	1.29
	<sup>5</sup> D 5d <sup>6</sup>	6.39	5.77	5.77	5.77	5.45

<sup>a</sup>(41/41) means that five primitive GTF are contracted to two CGTFs, which consist of four and one primitive GTFs, for both *s* and *d* orbitals.

We may conclude that the MP calculation with the basis sets determined in the present work can provide even better balanced description of the  $s^2d^{n-1}$ ,  $sd^n$ , and  $d^{n+1}$  configurations than the all-electron calculations in which the small basis sets such as (4333/43/4) or (5333/53/5) are used for the first-row transition metal atom series.

## V. SUMMARY

The *sd*-MPs were generated systematically for the transition metal atoms Sc through Hg for use in molecular calculations. The use of the model potentials will bring the benefits summarized as follows:

### Saving of Computational Time

In the *sd*MP's only the *s* and *d* valence electrons are treated explicitly and the other electrons are replaced by the model potential. Compared with all-electron calculations, saving of the computational time is substantial especially for the molecules containing heavy atoms. In addition, the core potential in our method is approximated by a simple spherical

local function of  $V_{\text{MP}}$  given by eq. (3), which is independent on the angular momentum of the valence orbitals. The computational time needed for evaluation of the core potential term is negligibly small compared with that used for evaluation of the two-electron integrals of the valence electrons. Most of the other effective core potentials (ECPs) introduce angular momentum dependence of the core potentials and the formulas are more complicated than the ones of the MP method. The use of such ECPs will require significantly more computational time for the calculations of the derivatives with respect to the nuclear coordinates (for the analytic gradient method of geometry optimization).<sup>35</sup>

### Incorporation of Relativistic Effects

The quasirelativistic model potentials were generated for the second- and third-row transition metal atoms. The effects of the mass velocity and Darwin terms were implicitly incorporated in the MP parameters and basis sets. Therefore, the major relativistic effects are easily incorporated into the molecular calculations without solving the Dirac-Hartree-Fock equation. The spin-orbit effects

omitted in this approach could be treated perturbationally, possibly together with the electron correlation effects.

### Balanced Description of the $s^2d^{n-1}$ , $sd^n$ , and $d^{n+1}$ Configurations

The MP method provides good flexibility to describe properly all the  $s^2d^{n-1}$ ,  $sd^n$ , and  $d^{n+1}$  configurations of an atom as discussed in the preceding section. The method provides more flexibility than the all-electron calculation with the limited basis set such as MIDI-i level basis set.

### Elimination of Basis Set Superposition Error (BSSE)

In the all-electron molecular calculations using unsaturated basis sets, BSSE is inevitable, especially in the core region. The use of the MP method provides a good way of eliminating BSSE originating from the core region.

### Good Reproduction of the Numerical HF Values

In Table X the total energies and orbital energies given by the all-electron calculations with various basis sets<sup>33</sup> are shown for Cu in the  $^1S$  ( $sd^{10}$ ) state, along with the numerical HF values. It is seen that the addition of  $d$ -type GTF improves both  $4s$  and  $3d$  orbital energies, and the improvement of the  $3d$  orbital energy is particularly significant.

Table X. Valence orbital energies (in a.u.) for Cu  $^2S$  ( $3d^{10}4s$ ).

Method	Basis	3d	4s
AE	GTF (3333/33/3) <sup>a</sup>	-0.2853	-0.2089
AE	GTF (4322/42/3) <sup>a</sup>	-0.2633	-0.2060
AE	GTF (4333/43/4) <sup>a</sup>	-0.4227	-0.2228
AE	GTF (3333/33/5) <sup>a</sup>	-0.4716	-0.2301
AE	GTF (4333/43/5) <sup>a</sup>	-0.4675	-0.2309
AE	GTF (5333/53/5) <sup>a</sup>	-0.4710	-0.2321
AE	GTF (14s9p7d)	-0.4838	-0.2358
MP	GTF (5s/5p)	-0.4907	-0.2375
AE	STF DZ <sup>b</sup>	-0.4041	-0.2181
AE	STF (11s6p5d) <sup>b</sup>	-0.4907	-0.2379
HF		-0.4912	-0.2385

<sup>a</sup>See ref. 33.

<sup>b</sup>From E. Clementi and C. Roetti, "Roothaan-Hartree-Fock atomic wave functions," *Atomic and Nuclear Data Table 14*, Academic, New York, 1974.

However, the discrepancy in the  $d$  orbital energies between the SCF value and numerical HF value is still 0.02 a.u. even if five primitive  $d$ -type GTFs are used. The orbital energies given by the MP method, also shown in Table X, are nearly the same as those given by the numerical HF calculation. In Figure 1 the  $rR(r)$  functions of the  $3d$  orbital of Cu in  $^1S(sd^{10})$  are plotted for the MP(5s/5d), AE(4333/43/4), and AE(4333/43/5) basis sets. The  $d$ -orbital shape is also described better by the MP basis set than by the AE basis set.

### Nodal Structure of the Valence Orbitals

The  $rR(r)$  functions of the  $6s$  and  $5d$  orbitals of Pt  $^3D(sd^9)$  are plotted for the MP basis sets in Figures 2 and 3, respectively, and they are compared with those of the reference QRHF orbitals. Both  $s$  and  $d$  valence orbitals have proper inner nodal structures and they can reproduce the reference orbitals well.

Hay and Wadt<sup>20,22</sup> have also generated two sets of effective core potentials (ECPs) for the transition metal atoms Sc through Hg. The valence orbitals of the first ECP set are nodeless.<sup>20</sup> They are included in Figures 2 and 3 for comparison. The  $s$  valence orbital of the second set<sup>22</sup> gains a node in the valence region by including the outermost core  $ns$  orbital. The use of the second set is, however, more expensive because the additional eight electrons ( $ns$  and  $np$  electrons) have to be treated explicitly.

An extensive test of MPs prepared in the present work has been successfully conducted in a subsequent article. There are a few exceptions in which the present  $sd$ -MPs fail to reproduce satisfactorily the results of the all-electron calculations. The remedy we have adopted is to treat the outermost core  $np$  electrons explicitly together with the valence  $nd$  and  $(n+1)s$  electrons. These model potentials may be called the  $spd$ -MPs and they will be described in later work.

### APPENDIX

The core orbitals, used for the calculations of the projection operators given by (4), are shown in the Tables as follows:

first series (Sc ~ Zn): Table (XI)

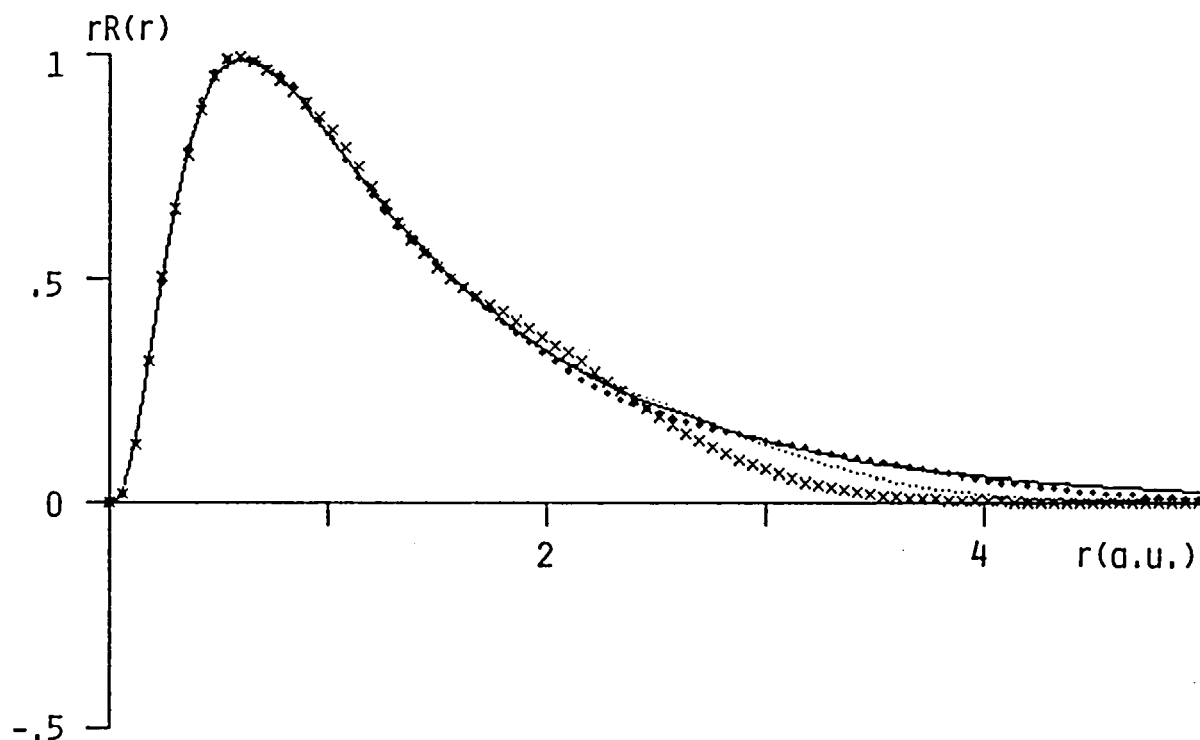


Figure 1.  $rR(r)$  functions of the  $3d$  orbital of Cu in  $^1S(sd^{10})$  corresponding to the numerical HF (—), MP(5s/5d) (\*\*\*\*\*), AE(4333/43/4) (xxxxx), and AE(4333/43/5) (.....).

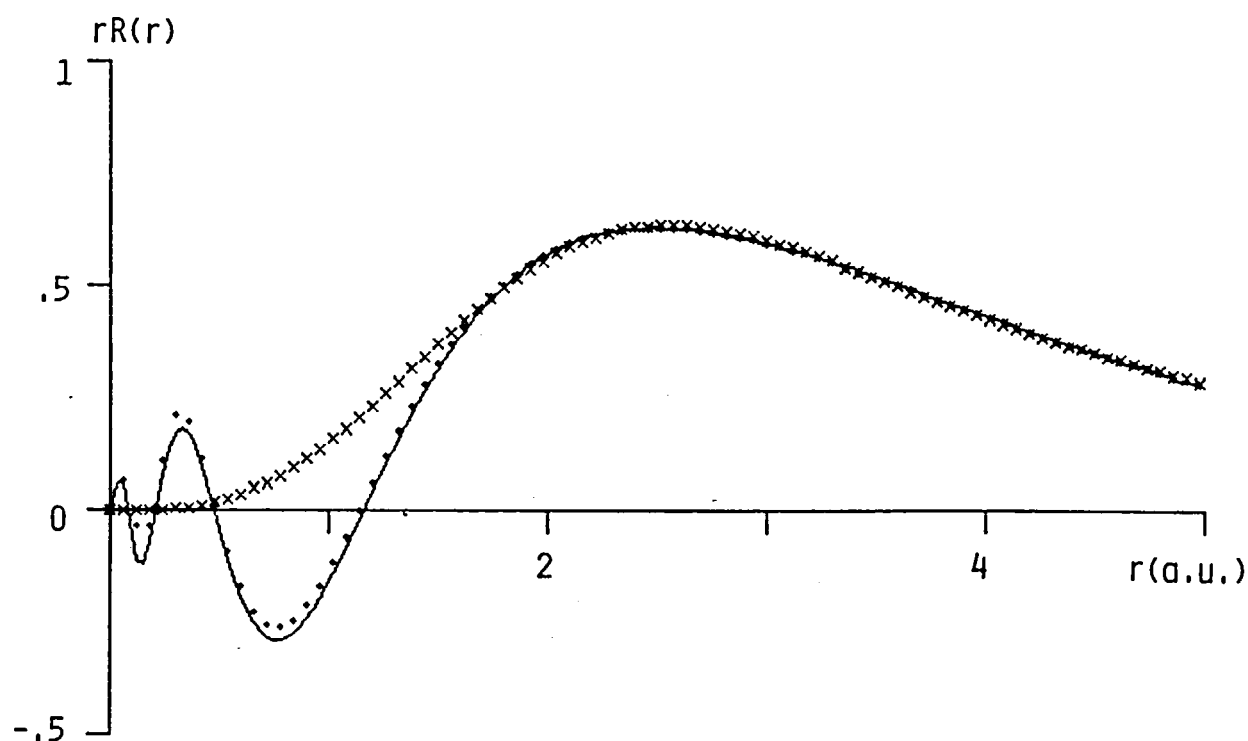


Figure 2.  $rR(r)$  functions of the  $6s$  orbital of Pt in  $^3P(sd^9)$  corresponding to the RHF (—), MP(7s/5d) (\*\*\*\*\*), and the pseudo-orbital given by Hay and Wadt ref. 20 (xxxxx).

second series (Y ~ Cd): Table (XII)  
third series (Lu ~ Hg): Table (XIII)

The normalized  $1s$ ,  $2p$ ,  $3d$ , and  $4f$  primitive GTFs are used for  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals, respectively.

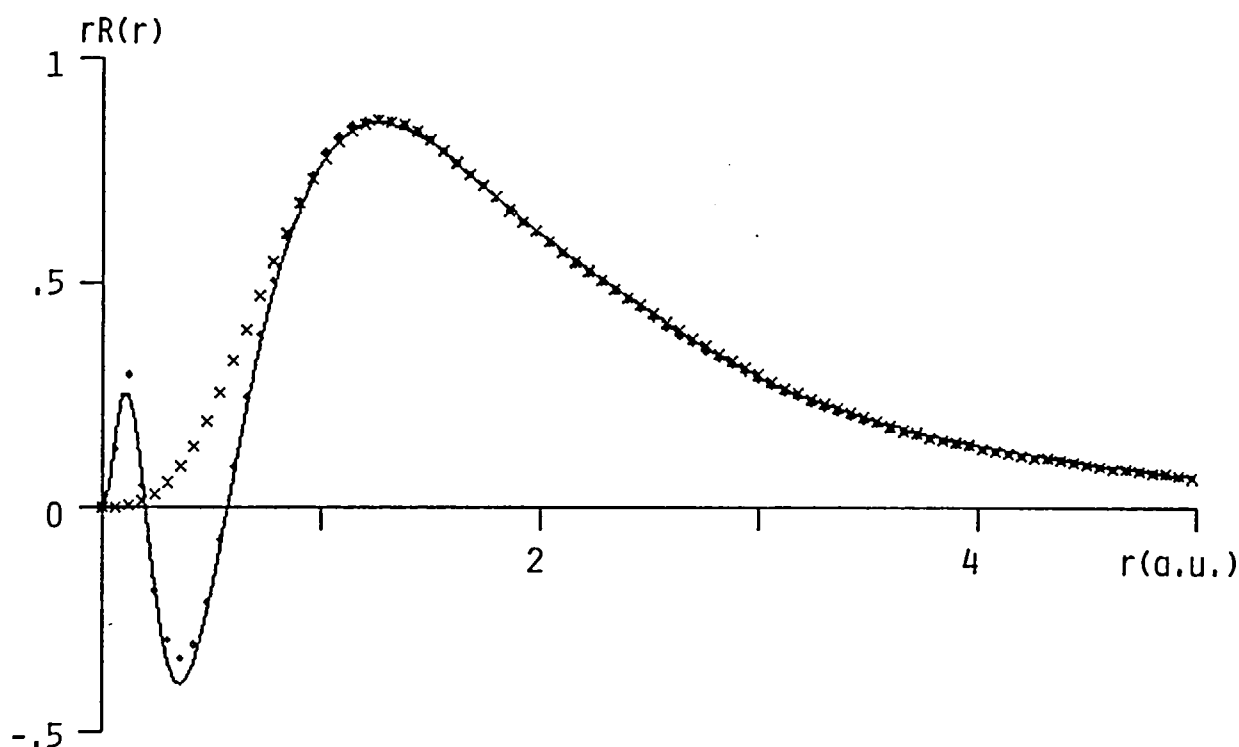


Figure 3.  $rR(r)$  functions of the  $5d$  orbital of Pt in  $^3P(sd^9)$  corresponding to the RHF(—), MP(7s/5d) (\*\*\*\*\*), and the pseudo-orbital given by Hay and Wadt ref. 20 (xxxxx).

Table XI. Core orbitals of first-series transition metal atoms.

Core orbitals of Sc			
Exponent	1s	2s	3s
5833.14	0.021081	0.006767	0.002379
802.772	0.147954	0.047491	0.016698
182.975	0.473775	0.152073	0.053470
51.8286	0.485204	0.155742	0.054760
84.1777	-0.003250	0.108486	0.043708
8.91890	0.019914	-0.664339	-0.267657
3.55842	0.013478	-0.449624	-0.181150
6.13288	0.004089	0.002384	-0.237714
0.929673	-0.013879	-0.008092	0.806879
0.363904	-0.006945	-0.004049	0.403812
Exponent	2p	3p	
223.599	0.034946	0.012688	
48.6631	0.217888	0.079108	
14.5608	0.528264	0.191795	
4.86936	0.396631	0.144003	
1.98890	0.007423	-0.376610	
0.734035	0.011743	-0.595810	
0.269306	0.004181	-0.212143	
Core orbitals of Ti			
Exponent	1s	2s	3s
6457.64	0.020873	0.006753	0.002708
888.772	0.146681	0.047457	0.019030
202.614	0.471634	0.152593	0.061188
57.4368	0.487825	0.157832	0.063289
92.9207	-0.003425	0.109373	0.044816
9.89517	0.020980	-0.669583	-0.274365
3.96534	0.013941	-0.444950	-0.182321
6.94432	0.004667	0.002393	-0.240496
1.06144	-0.015737	-0.008068	0.810998
0.413040	-0.007844	-0.004021	0.404283

Table XI (Continued)

Exponent	2p	3p	
250.339	0.034491	0.012821	
54.5710	0.216466	0.080465	
16.3829	0.528394	0.196415	
5.50525	0.396475	0.147378	
2.28868	0.007636	-0.381886	
0.845089	0.011905	-0.595371	
0.308909	0.004211	-0.210609	
Core orbitals of V			
Exponent	1s	2s	3s
7092.41	0.020766	0.006772	0.002737
976.252	0.146019	0.047620	0.019245
222.631	0.470452	0.153423	0.062004
63.1619	0.489274	0.159562	0.064485
102.095	-0.003498	0.110226	0.045821
10.9313	0.021381	-0.673710	-0.280061
4.39697	0.014011	-0.441489	-0.183527
7.80343	0.004647	0.002412	-0.242318
1.19854	-0.015619	-0.008107	0.814541
0.463350	-0.007757	-0.004026	0.404515
Exponent	2p	3p	
278.404	0.034117	0.012925	
60.7755	0.215350	0.081585	
18.2992	0.528637	0.200273	
6.17425	0.396108	0.150064	
2.60694	0.007806	-0.385728	
0.962299	0.012043	-0.595091	
0.350626	0.004250	-0.209984	
Core orbitals of Cr			
Exponent	1s	2s	3s
7746.47	0.020702	0.006802	0.002486
1066.33	0.145648	0.047852	0.017487
243.222	0.469908	0.154386	0.056419
69.0482	0.489968	0.160976	0.058828
111.668	-0.003531	0.111036	0.046723
12.0250	0.021537	-0.677217	-0.284968
4.85020	0.013953	-0.438750	-0.184622
8.71019	0.004563	0.002420	-0.243353
1.34065	-0.015325	-0.008125	0.817319
0.514280	-0.007590	-0.004024	0.404881
Exponent	2p	3p	
307.755	0.033814	0.012945	
67.2679	0.214507	0.082118	
20.3069	0.528996	0.202510	
6.87513	0.395535	0.151419	
2.94333	0.007933	-0.388316	
1.08522	0.012151	-0.594748	
0.394134	0.004301	-0.210512	
Core orbitals of Mn			
Exponent	1s	2s	3s
8429.59	0.020644	0.006825	0.002519
1160.41	0.145305	0.048041	0.017728
264.731	0.469403	0.155196	0.057270
75.1997	0.490610	0.162208	0.059857
121.679	-0.003560	0.111774	0.047573
13.1710	0.021682	-0.680406	-0.289591
5.32472	0.013903	-0.436290	-0.185692
9.66231	0.004493	0.002424	-0.244650
1.49112	-0.015086	-0.008139	0.821465
0.569325	-0.007413	-0.003998	0.403656

Table XI (Continued)

Exponent	2p	3p
338.682	0.033519	0.013030
74.1131	0.213637	0.083050
22.4267	0.529184	0.205717
7.61656	0.395224	0.153641
3.30003	0.008082	-0.391367
1.21708	0.012290	-0.595150
0.441364	0.004319	-0.209134

Core orbitals of Fe

Exponent	1s	2s	3s
9140.63	0.020592	0.006848	0.002546
1258.38	0.144999	0.048216	0.017931
287.139	0.468949	0.155938	0.057990
81.6128	0.491181	0.163330	0.060739
132.131	-0.003587	0.112448	0.048307
14.3695	0.021808	-0.683311	-0.293547
5.81981	0.013854	-0.434084	-0.186480
10.6608	0.004427	0.002423	-0.245430
1.64815	-0.014855	-0.008128	0.823554
0.626556	-0.007284	-0.003987	0.403908

Exponent	2p	3p
370.601	0.033320	0.013115
81.1776	0.213205	0.083917
24.6147	0.529767	0.208514
8.38003	0.394311	0.155199
3.67389	0.008138	-0.393758
1.35439	0.012301	-0.595206
0.490277	0.004314	-0.208758

Core orbitals of Co

Exponent	1s	2s	3s
9882.72	0.020540	0.006866	0.002570
1360.55	0.144696	0.048368	0.018105
310.494	0.468512	0.156610	0.058624
88.2957	0.491745	0.164376	0.061531
143.023	-0.003614	0.113064	0.048966
15.6208	0.021926	-0.685937	-0.297064
6.33608	0.013813	-0.432118	-0.187140
11.7053	0.004368	0.002420	-0.245991
1.81239	-0.014642	-0.008110	0.824616
0.686628	-0.007188	-0.003982	0.404841

Exponent	2p	3p
404.504	0.033064	0.013154
88.6912	0.212404	0.084499
26.9480	0.529754	0.210748
9.19818	0.394266	0.156848
4.06844	0.008294	-0.395234
1.49890	0.012495	-0.595428
0.541492	0.004383	-0.208866

Core orbitals of Ni

Exponent	1s	2s	3s
10652.8	0.020494	0.006883	0.002591
1466.61	0.144425	0.048509	0.018261
334.748	0.468116	0.157230	0.059189
95.2405	0.492250	0.165336	0.062240
154.353	-0.003635	0.113632	0.049560
16.9250	0.022030	-0.688312	-0.300204
6.87365	0.013774	-0.430366	-0.187702
12.7961	0.004313	0.002416	-0.246387
1.98378	-0.014443	-0.008087	0.825027
0.749424	-0.007110	-0.003982	0.406149



Table XI (Continued)

Exponent	2p	3p	
439.470	0.032878	0.013256	
96.4397	0.211931	0.085445	
29.3545	0.530055	0.213704	
10.0404	0.393754	0.158751	
4.48055	0.008379	-0.396642	
1.64953	0.012580	-0.595540	
0.594721	0.004416	-0.209032	
Core orbitals of Cu			
Exponent	1s	2s	3s
11451.7	0.020451	0.006899	0.002609
1576.65	0.144173	0.048638	0.018395
359.915	0.467749	0.157801	0.059682
102.449	0.492717	0.166224	0.062867
166.122	-0.003657	0.114154	0.050086
18.2819	0.022123	-0.690481	-0.302955
7.43217	0.013738	-0.428790	-0.188135
13.9333	0.004263	0.002410	-0.246563
2.16179	-0.014256	-0.008060	0.824715
0.814466	-0.007051	-0.003986	0.407880
Exponent	2p	3p	
475.764	0.032719	0.013295	
104.486	0.211556	0.085961	
31.8553	0.530384	0.215509	
10.9157	0.393195	0.159765	
4.91100	0.008447	-0.397665	
1.80623	0.012651	-0.595585	
0.649865	0.004452	-0.209600	
Core orbitals of Zn			
Exponent	1s	2s	3s
12280.0	0.020410	0.006914	0.002640
1690.74	0.143932	0.048755	0.018617
386.009	0.467394	0.158323	0.060456
109.925	0.493169	0.167054	0.063790
178.304	-0.003677	0.114643	0.050869
19.6951	0.022207	-0.692031	-0.307065
8.01870	0.013725	-0.427720	-0.189786
15.0907	0.004238	0.002439	-0.249138
2.36159	-0.014042	-0.008079	0.825484
0.908548	-0.006960	-0.004004	0.409205
Exponent	2p	3p	
514.266	0.032487	0.013338	
113.026	0.210753	0.086530	
34.5130	0.530176	0.217678	
11.8491	0.393487	0.161557	
5.37664	0.008578	-0.398835	
1.99317	0.012841	-0.597059	
0.731286	0.004423	-0.205677	

Table XII. Core orbitals of second-series transition metal atoms.

Core orbitals of Y					
Exponent	1s	2s	3s	4s	
33058.6	0.018414	0.006599	0.002758	0.001015	
3775.31	0.128784	0.046152	0.019290	0.007101	
780.464	0.448332	0.160668	0.067154	0.024721	
209.108	0.530139	0.189984	0.079408	0.029232	
342.408	-0.004303	0.103164	0.050483	0.018602	
37.6433	0.027682	-0.663412	-0.324640	-0.119625	
15.8086	0.018932	-0.453716	-0.222025	-0.081813	
29.4695	0.005771	0.004169	-0.273530	-0.130992	
4.83950	-0.018782	-0.013567	0.890256	0.426340	
2.11670	-0.007698	-0.005561	0.364971	0.174783	
3.61369	0.0	-0.001034	-0.001191	0.296790	
0.684853	0.0	0.003131	0.003612	-0.898499	
0.282092	0.0	0.001347	0.001554	-0.386525	
Exponent	2p	3p	4p	Exponent	3d
1061.76	0.028395	0.013230	0.004493	138.997	0.025855
227.800	0.190003	0.088526	0.030062	38.2426	0.158071
69.2314	0.512040	0.238570	0.081013	13.3840	0.405670
23.9781	0.423663	0.197393	0.067030	4.98309	0.482855
11.0515	0.014196	-0.412465	-0.186373	1.80507	0.194110
4.42399	0.020972	-0.609366	-0.275343		
1.88048	0.005829	-0.169371	-0.076529		
1.07213	-0.004906	-0.001409	0.489692		
0.441815	-0.005722	-0.001642	0.571155		
0.173043	-0.001402	-0.000403	-0.140062		
Core orbitals of Zr					
Exponent	1s	2s	3s	4s	
35924.4	0.018177	0.006538	0.002754	0.001040	
4064.15	0.126977	0.045674	0.019240	0.007266	
835.723	0.444763	0.159981	0.067393	0.025450	
223.208	0.534501	0.192259	0.080991	0.030584	
363.806	-0.004559	0.102377	0.050540	0.019257	
39.7769	0.029628	-0.665055	-0.328318	-0.125097	
16.7284	0.020117	-0.451563	-0.222923	-0.084939	
31.3369	0.006821	0.004155	-0.276145	-0.135669	
5.16415	-0.022269	-0.013562	0.901539	0.442922	
2.26740	-0.008812	-0.005368	0.356811	0.175300	
3.95655	0.0	-0.001017	-0.001200	0.311191	
0.765567	0.0	0.002994	0.003537	-0.915898	
0.314880	0.0	0.001252	0.001479	-0.382978	
Exponent	2p	3p	4p	Exponent	3d
1134.78	0.028023	0.013197	0.004641	151.610	0.025018
243.172	0.188055	0.088560	0.031145	41.8159	0.154818
73.9084	0.509975	0.240161	0.084460	14.6934	0.403176
25.6289	0.426557	0.200877	0.070644	5.51108	0.485099
11.7917	0.014919	-0.415652	-0.196164	2.01906	0.193771
4.74040	0.021949	-0.611508	-0.288597		
2.02414	0.005882	-0.163880	-0.077340		
1.19949	-0.005450	-0.001388	0.503152		
0.497679	-0.006164	-0.001572	0.569223		
0.194764	-0.001475	-0.000375	0.136349		

Table XII (Continued)

Core orbitals of Nb					
Exponent	1s	2s	3s	4s	
38664.9	0.018116	0.006541	0.002776	0.001071	
4333.87	0.126328	0.045611	0.019357	0.007467	
886.532	0.443781	0.160229	0.068001	0.026229	
236.025	0.536225	0.193606	0.082166	0.031693	
385.325	-0.004585	0.101815	0.050674	0.019849	
42.1227	0.029900	-0.663931	-0.330440	-0.129436	
17.7433	0.020389	-0.452748	-0.225334	-0.088265	
33.2643	0.006870	0.004205	-0.278695	-0.139998	
5.50323	-0.022474	-0.013755	0.911746	0.458000	
2.42404	-0.008616	-0.005272	0.349550	0.175591	
4.31242	0.0	-0.001020	-0.001206	0.323193	
0.849419	0.0	0.002935	0.003470	-0.928408	
0.348751	0.0	0.001210	0.001430	-0.382660	
Exponent	2p	3p	4p	Exponent	3d
1211.69	0.027641	0.013148	0.004758	164.614	0.024301
259.322	0.186031	0.088490	0.032026	45.4988	0.152022
78.8173	0.507753	0.241526	0.087411	16.0437	0.401063
27.3627	0.429617	0.204358	0.073960	6.05676	0.487092
12.5601	0.015707	-0.418544	-0.204855	2.24056	0.193285
5.06874	0.023028	-0.613621	-0.300336		
2.17125	0.005958	-0.158750	-0.077700		
1.33369	-0.006067	-0.001373	0.512787		
0.556039	-0.006729	-0.001521	0.568592		
0.217710	-0.001595	-0.000359	0.134787		
Core orbitals of Mo					
Exponent	1s	2s	3s	4s	
41581.3	0.018059	0.006545	0.002797	0.001098	
4617.21	0.125684	0.045548	0.019466	0.007644	
939.450	0.442790	0.160467	0.068580	0.026929	
249.295	0.537956	0.194955	0.083320	0.032716	
407.577	-0.004608	0.101244	0.050779	0.020353	
44.5972	0.030101	-0.661102	-0.331578	-0.132898	
18.8538	0.020729	-0.455265	-0.228340	-0.091518	
35.2673	0.006911	0.004419	-0.280943	-0.143920	
5.85387	-0.022661	-0.014489	0.921211	0.471914	
2.58522	-0.008427	-0.005387	0.342585	0.175498	
4.68192	0.0	-0.001176	-0.001208	-0.333056	
0.936271	0.0	0.003309	0.003405	-0.937244	
0.383570	0.0	0.001358	-0.001397	-0.384536	
Exponent	2p	3p	4p	Exponent	3d
1286.92	0.027444	0.013177	0.004884	177.989	0.023687
275.049	0.185021	0.088838	0.032923	49.2861	0.149623
83.5788	0.506871	0.243374	0.090194	17.4335	0.399284
29.0340	0.430979	0.206934	0.076689	6.61963	0.488850
13.3430	0.016036	-0.422421	-0.213180	2.46936	0.192669
5.40379	0.023355	-0.615215	-0.310476		
2.31986	0.005831	-0.153595	-0.077512		
1.47418	-0.006003	-0.001356	0.519647		
0.616690	-0.006570	-0.001486	0.568728		
0.241818	-0.001557	-0.000352	0.134801		

Table XII (Continued)

Core orbitals of Tc					
Exponent	1s	2s	3s	4s	
44686.3	0.018005	0.006549	0.002817	0.001124	
4914.97	0.125043	0.045480	0.019567	0.007808	
994.570	0.441787	0.160686	0.069131	0.027587	
263.032	0.539701	0.196300	0.084452	0.033701	
430.817	-0.004631	0.100618	0.050832	0.020790	
47.1156	0.030378	-0.659796	-0.333329	-0.136327	
19.9477	0.021023	-0.456609	-0.230679	-0.094343	
37.3360	0.006964	0.004467	-0.283246	-0.147803	
6.21902	-0.022878	-0.014677	0.930542	0.485575	
2.75083	-0.008260	-0.005298	0.336019	0.175342	
5.06458	0.0	-0.001173	-0.001203	0.341742	
1.02610	0.0	0.003249	0.003336	-0.946452	
0.419857	0.0	0.001323	0.001358	-0.385249	
Exponent	2p	3p	4p	Exponent	3s
1371.31	0.027061	0.013109	0.004965	191.780	0.023148
292.670	0.182944	0.088624	0.033567	53.1902	0.147511
88.9220	0.504485	0.244388	0.092565	18.8673	0.397737
30.9215	0.434194	0.210337	0.079667	7.20153	0.490415
14.1682	0.016894	-0.424800	-0.220560	2.70627	0.192037
5.75671	0.024542	-0.617094	-0.320400		
2.47486	0.005936	-0.149268	-0.077499		
1.62189	-0.006704	-0.001355	0.525739		
0.680734	-0.007272	-0.001470	0.570291		
0.266917	-0.001704	-0.000345	0.133717		
Core orbitals of Ru					
Exponent†	1s	2s	3s	4s	
47987.5	0.017955	0.006554	0.002837	0.001148	
5227.56	0.124409	0.045413	0.019660	0.007955	
1051.93	0.440777	0.160895	0.069654	0.028185	
277.243	0.541448	0.197642	0.085563	0.034623	
454.964	-0.004653	0.099962	0.050847	0.021156	
49.7231	0.030657	-0.658379	-0.334891	-0.139338	
21.0817	0.021329	-0.458051	-0.232992	-0.096941	
39.4774	0.007019	0.004516	-0.285420	-0.151423	
6.59739	-0.023100	-0.014864	0.939386	0.498369	
2.92103	-0.008111	-0.005217	0.329831	0.174984	
5.46155	0.0	-0.001170	-0.001194	0.348977	
1.11908	0.0	0.003196	0.003267	-0.953318	
0.457162	0.0	0.001298	0.001327	-0.387229	
Exponent	2p	3p	4p	Exponent	3d
1460.75	0.026652	0.013019	0.005023	206.025	0.022664
311.300	0.180700	0.088271	0.034059	57.2192	0.145613
94.5659	0.501804	0.245129	0.094581	20.3470	0.396366
32.9168	0.437723	0.213825	0.082503	7.80280	0.491857
15.0257	0.017869	-0.426670	-0.227064	2.95115	0.191411
6.12355	0.025921	-0.618951	-0.329391		
2.63447	0.006090	-0.145413	-0.077385		
1.77659	-0.007566	-0.001361	0.529839		
0.747596	-0.008169	-0.001468	0.572148		
0.293382	-0.001914	-0.000344	0.134037		

Table XII (Continued)

Core orbitals of Rh					
Exponent	1s	2s	3s	4s	
51498.6	0.017909	0.006561	0.002857	0.001170	
5555.77	0.123782	0.045344	0.019746	0.008089	
1111.63	0.439758	0.161091	0.070153	0.028739	
291.940	0.543201	0.198985	0.086655	0.035499	
480.049	-0.004674	0.099277	0.050825	0.021465	
52.4219	0.030938	-0.656854	-0.336275	-0.142019	
22.2568	0.021647	-0.459588	-0.235285	-0.099368	
41.6931	0.007076	0.004566	-0.287472	-0.154841	
6.98930	-0.023325	-0.015053	0.947728	0.510475	
3.09605	-0.007974	-0.005145	0.324038	0.174537	
5.87311	0.0	-0.001167	-0.001185	0.355151	
1.21532	0.0	0.003151	0.003200	-0.958922	
0.495703	0.0	0.001280	0.001300	-0.389655	
Exponent	2p	3p	4p	Exponent	3d
1545.32	0.026496	0.013044	0.005115	220.712	0.022231
328.812	0.179866	0.088552	0.034726	61.3708	0.143910
99.8425	0.501072	0.246687	0.096741	21.8721	0.395153
34.7661	0.438872	0.216065	0.084732	8.42341	0.493172
15.8901	0.018149	-0.430132	-0.233926	3.20408	0.190792
6.49410	0.026163	-0.620047	-0.337210		
2.79466	0.005963	-0.141331	-0.076862		
1.93715	-0.007438	-0.001363	0.533245		
0.816791	-0.008005	-0.001467	0.574012		
0.320823	-0.001878	-0.000344	0.134660		
Core orbitals of Pd					
Exponent	1s	2s	3s	4s	
55231.8	0.017867	0.006568	0.002876	0.001191	
5900.35	0.123161	0.045276	0.019827	0.008212	
1173.73	0.438729	0.161282	0.070630	0.029255	
307.134	0.544960	0.200333	0.087731	0.036338	
505.950	-0.004696	0.098588	0.050783	0.021731	
55.2769	0.031133	-0.653392	-0.336564	-0.144024	
23.5556	0.022043	-0.462623	-0.238298	-0.101974	
43.9928	0.007122	0.004814	-0.289201	-0.157971	
7.39327	-0.023523	-0.015899	0.955159	0.521738	
3.27651	-0.007845	-0.005304	0.318622	0.174041	
6.30001	0.0	-0.001339	-0.001177	0.360460	
1.31491	0.0	0.003584	0.003147	-0.963547	
0.535525	0.0	0.001460	0.001282	-0.392351	
Exponent	2p	3p	4p	Exponent	3d
1644.09	0.026067	0.012929	0.005144	235.843	0.021842
349.268	0.177466	0.088021	0.035020	65.6452	0.142374
106.024	0.498069	0.247037	0.098286	23.4428	0.394074
36.9518	0.442720	0.219585	0.087364	9.06345	0.494373
16.8108	0.019257	-0.431242	-0.239219	3.46512	0.190183
6.88848	0.027765	-0.621776	-0.344912		
2.96394	0.006176	-0.138301	-0.076717		
2.10573	-0.008475	-0.001377	0.535317		
0.889486	-0.009126	-0.001481	0.576348		
0.349693	-0.002151	-0.000348	0.135947		

Table XII (Continued)

Core orbitals of Ag					
Exponent	1s	2s	3s	4s	
59200.7	0.017829	0.006577	0.002895	0.001211	
6262.08	0.122548	0.045206	0.019902	0.008324	
1238.34	0.437692	0.161458	0.071081	0.029731	
322.838	0.546722	0.201677	0.088788	0.037137	
533.012	-0.004717	0.097846	0.050691	0.021944	
58.1689	0.031416	-0.651664	-0.337608	-0.146147	
24.8194	0.022385	-0.464339	-0.240560	-0.104136	
46.3622	0.007182	0.004866	-0.291016	-0.160996	
7.81270	-0.023752	-0.016091	0.962512	0.532481	
3.46159	-0.007739	-0.005243	0.313594	0.173487	
6.74199	0.0	-0.001335	-0.001165	0.364984	
1.41773	0.0	0.003539	0.003087	-0.967177	
0.576501	0.0	0.001447	0.001262	-0.395339	
Exponent	2p	3p	4p	Exponent	3d
1735.30	0.025932	0.012951	0.005219	251.407	0.021490
368.031	0.176727	0.088264	0.035566	70.0398	0.140991
111.658	0.497419	0.248429	0.100104	25.0583	0.393122
38.9233	0.443757	0.221628	0.089304	9.72259	0.495472
17.7318	0.019508	-0.434385	-0.245188	3.73412	0.189571
7.28359	0.027961	-0.622612	-0.351432		
3.13247	0.006056	-0.134862	-0.076122		
2.27975	-0.008319	-0.001385	0.537098		
0.964240	-0.008961	-0.001490	0.578435		
0.379514	-0.002128	-0.000354	0.137378		
Core orbitals of Cd					
Exponent	1s	2s	3s	4s	
63419.7	0.017795	0.006585	0.002914	0.001237	
6641.81	0.121941	0.045124	0.019969	0.008475	
1305.53	0.436645	0.161580	0.071503	0.030348	
339.065	0.548492	0.202969	0.089819	0.038122	
562.816	-0.004724	0.096846	0.050430	0.022127	
60.5340	0.032503	-0.666291	-0.346955	-0.152232	
25.3230	0.022121	-0.453464	-0.236130	-0.103606	
48.7912	0.007331	0.003174	-0.294031	-0.165808	
8.20903	-0.024626	-0.010660	0.987768	0.557015	
3.52093	-0.007389	-0.003198	0.296450	0.167172	
7.17940	0.0	0.0	0.0	0.372200	
1.53027	0.0	0.0	0.0	-0.979788	
0.634271	0.0	0.0	0.0	-0.394233	
Exponent	2p	3p	4p	Exponent	3d
1830.10	0.025795	0.012968	0.005323	267.613	0.021145
387.470	0.175966	0.088468	0.036313	74.6157	0.139563
117.484	0.496726	0.249731	0.102505	26.7427	0.391971
40.9617	0.444846	0.223648	0.091799	10.4118	0.496438
18.6811	0.019782	-0.437482	-0.252805	4.01667	0.189509
7.69051	0.028184	-0.623293	-0.360178		
3.30337	0.005960	-0.131806	-0.076164		
2.46276	-0.008213	-0.001296	0.542849		
1.05029	-0.008814	-0.001391	0.582680		
0.417437	-0.001989	-0.000313	0.131577		

Table XIII. Core orbitals of third-series transition metal atoms.

Core orbitals of Lu					
Exponent	1s	2s	3s	4s	5s
279598.	0.018203	0.007267	0.003460	0.001814	0.000726
23294.2	0.110006	0.043914	0.020910	0.010962	0.004385
3881.27	0.407866	0.162819	0.077528	0.040642	0.016258
902.211	0.590395	0.235684	0.112224	0.058831	0.023534
1639.48	-0.005111	0.073404	0.041423	0.012163	0.003265
167.268	0.039855	-0.572184	-0.322895	-0.094808	-0.025448
73.1682	0.037506	-0.538473	-0.303871	-0.089221	-0.023949
133.644	0.010078	0.008128	-0.307483	-0.321553	-0.150476
22.8241	-0.034416	-0.027755	1.05003	1.09808	0.513866
9.63087	-0.008651	-0.006975	0.263948	0.276026	0.129171
5.24098	0.0	0.006468	-0.007403	-1.22845	-0.941622
2.20470	0.0	0.001678	-0.001921	-0.318744	-0.244321
0.786642	0.0	0.0	0.001574	0.000726	1.03797
0.306680	0.0	0.0	0.000457	0.000211	0.301425
Exponent	2p	3p	4p	5p	
5323.86	0.022732	0.012549	0.006148	0.002114	
1069.05	0.156424	0.086352	0.042304	0.014548	
315.963	0.473321	0.261289	0.128005	0.044021	
109.574	0.477420	0.263552	0.129114	0.044403	
48.2911	0.031693	-0.521415	-0.383746	-0.142360	
19.0424	0.038783	-0.638070	-0.469601	-0.174210	
8.23676	-0.011614	-0.028060	0.690373	0.353046	
3.27385	-0.009945	-0.024032	0.591278	0.302371	
1.06978	0.0	0.005160	0.012367	-0.661908	
0.357016	0.0	0.004279	0.010255	-0.548882	
Exponent	3d	4d			
513.058	0.039710	0.019637			
141.105	0.240446	0.118906			
49.8796	0.541472	0.267770			
19.0477	0.365206	0.180602			
15.5887	0.008556	-0.311252			
6.00256	0.017969	-0.653705			
2.20318	0.008640	-0.314319			
Exponent	4f				
43.5253	0.127172				
12.2135	0.427885				
3.72448	0.534551				
0.993422	0.308482				
Core orbitals of Hf					
Exponent	1s	2s	3s	4s	5s
297070.	0.018296	0.007327	0.003495	0.001836	0.000747
24526.9	0.109704	0.043935	0.020957	0.011007	0.004476
4053.49	0.406680	0.162869	0.077688	0.040803	0.016595
936.752	0.591989	0.237083	0.113088	0.059396	0.024156
1714.10	-0.005102	0.072201	0.040829	0.012014	0.003259
174.234	0.040050	-0.566720	-0.320478	-0.094304	-0.025578
76.1971	0.038420	-0.543650	-0.307432	-0.090465	-0.024537
138.886	0.010150	0.008288	-0.307136	-0.322628	-0.153829
23.6864	-0.034724	-0.028355	1.05079	1.10379	0.526287
9.98559	-0.008714	-0.007114	0.263685	0.276985	0.132066
5.46938	0.0	0.006615	-0.007723	-1.23161	-0.965456
2.31034	0.0	0.001719	-0.002005	-0.320021	-0.250864
0.839482	0.0	0.0	0.001595	0.000839	1.06216
0.326289	0.0	0.0	0.000435	0.000229	0.289887

Table XIII (Continued)

Core orbitals of Hf					
Exponent	2p	3p	4p	5p	
5537.87	0.022690	0.012555	0.006175	0.002176	
1108.92	0.156019	0.086333	0.042459	0.014961	
327.222	0.472872	0.261662	0.128687	0.045345	
113.387	0.478189	0.264604	0.130134	0.045855	
50.1233	0.031741	-0.520174	-0.384896	-0.146541	
19.7916	0.038993	-0.639030	-0.472841	-0.180025	
8.59481	-0.011472	-0.028625	0.688247	0.362997	
3.43211	-0.009905	-0.024714	0.594252	0.313422	
1.13995	0.0	0.005624	0.012734	-0.677002	
0.385126	0.0	0.004480	0.010145	-0.539355	
Exponent	3d	4d			
532.591	0.039482	0.019677			
146.458	0.239644	0.119433			
51.8033	0.541217	0.269730			
19.8020	0.365771	0.182292			
16.3295	0.008553	-0.308482			
6.31850	0.018130	-0.653922			
2.33794	0.008780	-0.316694			
Exponent	4f				
47.7940	0.119968				
13.5564	0.418314				
4.22520	0.538221				
1.17395	0.306343				
Core orbitals of Ta					
Exponent	1s	2s	3s	4s	5s
315569.	0.018395	0.007390	0.003531	0.001858	0.000768
25823.0	0.109419	0.043962	0.021006	0.011055	0.004567
4232.78	0.405492	0.162916	0.077844	0.040967	0.016925
972.392	0.593567	0.238479	0.113950	0.059968	0.024775
1792.15	-0.005089	0.070989	0.040223	0.011862	0.003248
181.488	0.040234	-0.561035	-0.317885	-0.093745	-0.025667
79.3384	0.039374	-0.549039	-0.311088	-0.091739	-0.025118
144.311	0.010213	0.008455	-0.306699	-0.323661	-0.157108
24.5528	-0.035074	-0.029038	1.05337	1.11163	0.539595
10.2697	-0.008767	-0.007258	0.263294	0.277855	0.134874
5.70176	0.0	0.006826	-0.009798	-1.23877	-0.991837
2.41548	0.0	0.001760	-0.002525	-0.319388	-0.255721
0.897028	0.0	0.0	0.002023	0.000993	1.08229
0.347875	0.0	0.0	0.000529	0.000260	0.282812
Exponent	2p	3p	4p	5p	
5758.76	0.022649	0.012561	0.006203	0.002235	
1149.90	0.155617	0.086304	0.042618	0.015357	
338.756	0.472420	0.262002	0.129378	0.046622	
117.285	0.478963	0.265631	0.131170	0.047268	
51.9684	0.031843	-0.519707	-0.386696	-0.150813	
20.5330	0.039193	-0.639673	-0.475958	-0.185625	
8.95997	-0.011374	-0.028798	0.687297	0.373141	
3.59524	-0.009873	-0.024994	0.596520	0.323857	
1.21450	0.0	0.005661	0.013038	-0.690899	
0.414183	0.0	0.004354	0.010028	-0.531431	
Exponent	3d	4d			
552.633	0.039250	0.019718			
151.945	0.238808	0.119971			
53.7751	0.540917	0.271742			
20.5761	0.366410	0.184075			
17.0929	0.008555	-0.305838			
6.64617	0.018305	-0.654396			
2.47876	0.008915	-0.318695			



Table XIII (Continued)

Core orbitals of Ta					
Exponent	4f				
51.9573	0.114401				
14.8681	0.410698				
4.71620	0.541221				
1.35274	0.304141				
Core orbitals of W					
Exponent	1s	2s	3s	4s	5s
335154.	0.018500	0.007457	0.003569	0.001882	0.000789
27186.0	0.109149	0.043994	0.021054	0.011103	0.004654
4419.44	0.404300	0.162960	0.077988	0.041126	0.017240
1009.17	0.595129	0.239876	0.114797	0.060538	0.025378
1873.86	-0.005078	0.069769	0.039614	0.011715	0.003236
189.052	0.040403	-0.555110	-0.315190	-0.093209	-0.025743
82.5986	0.040370	-0.554657	-0.314932	-0.093133	-0.025722
149.886	0.010282	0.008628	-0.306149	-0.324632	-0.160247
25.4601	-0.035392	-0.029698	1.05385	1.11747	0.551614
10.6419	-0.008840	-0.007416	0.263216	0.279107	0.137775
5.94409	0.0	0.007001	-0.010145	-1.24332	-1.01620
2.52815	0.0	0.001800	-0.002608	-0.319572	-0.261196
0.959141	0.0	0.0	0.002024	0.001092	1.09825
0.371598	0.0	0.0	0.000516	0.000279	0.280125
Exponent	2p	3p	4p	5p	
5986.76	0.022609	0.012567	0.006231	0.002291	
1192.01	0.155217	0.086273	0.042781	0.015731	
350.573	0.471963	0.262327	0.130082	0.047833	
121.270	0.479740	0.266650	0.132225	0.048621	
53.9038	0.031881	-0.518113	-0.387702	-0.154543	
21.3276	0.039431	-0.640824	-0.479525	-0.191145	
9.33804	-0.011246	-0.029480	0.685551	0.382316	
3.76613	-0.009830	-0.025764	0.599142	0.334127	
1.29309	0.0	0.006193	0.013324	-0.703249	
0.443942	0.0	0.004626	0.009953	-0.525290	
Exponent	3d	4d			
573.176	0.039041	0.019761			
157.564	0.238095	0.120510			
55.7938	0.540907	0.273777			
21.3694	0.367320	0.185917			
17.8770	0.007480	-0.303362			
6.98434	0.018867	-0.655089			
2.62480	0.009704	-0.320350			
Exponent	4f				
56.0194	0.110073				
16.1515	0.404670				
5.19867	0.543708				
1.53003	0.301702				
Core orbitals of Re					
Exponent	1s	2s	3s	4s	5s
355754.	0.018600	0.007529	0.003608	0.001907	0.000811
28612.0	0.108815	0.044050	0.021109	0.011155	0.004742
4613.08	0.402755	0.163040	0.078129	0.041288	0.017551
1047.03	0.596073	0.241297	0.115630	0.061106	0.025975
1959.32	-0.005450	0.068561	0.038995	0.011564	0.003220
196.943	0.044213	-0.549112	-0.312314	-0.092618	-0.025787
85.9809	0.038611	-0.560647	-0.318875	-0.094565	-0.026327
155.643	0.011002	0.009227	-0.305532	-0.325574	-0.163331
26.3896	-0.036185	-0.030348	1.05423	1.12338	0.563570
11.0221	-0.008935	-0.007494	0.263128	0.280389	0.140663
6.19367	0.0	0.006600	-0.010303	-1.24839	-1.04089
2.64403	0.0	0.001878	-0.002930	-0.319357	-0.266275
1.02456	0.0	0.0	0.002037	0.001188	1.11366
0.396896	0.0	0.0	0.000520	0.000303	0.278060

Table XIII (Continued)

Core orbitals of Re					
Exponent	2p	3p	4p	5p	
6222.08	0.022571	0.012572	0.006261	0.002348	
1235.27	0.154820	0.086237	0.042945	0.016106	
362.677	0.471501	0.262633	0.130787	0.049050	
125.343	0.480521	0.267657	0.133289	0.049988	
55.9016	0.031903	-0.516180	-0.388474	-0.158191	
22.1526	0.039688	-0.642131	-0.483265	-0.196790	
9.72767	-0.011116	-0.030303	0.683633	0.391461	
3.94401	-0.009784	-0.026674	0.601797	0.344600	
1.37649	0.0	0.006850	0.013621	-0.714701	
0.476413	0.0	0.004984	0.009912	-0.520079	
Exponent	3d	4d			
594.156	0.038818	0.019806			
163.299	0.237257	0.121055			
57.8548	0.540569	0.275814			
22.1805	0.368025	0.187777			
18.6824	0.007449	-0.300994			
7.33319	0.019080	-0.655935			
2.77587	0.009840	-0.321806			
Exponent	4f				
60.2216	0.106024				
17.4772	0.398790				
5.69726	0.546035				
1.71425	0.300256				
Core orbitals of Os					
Exponent	1s	2s	3s	4s	5s
377690.	0.018718	0.007602	0.003648	0.001932	0.000832
30119.8	0.108573	0.044096	0.021162	0.011206	0.004825
4815.52	0.401534	0.163080	0.078262	0.041444	0.017843
1086.20	0.597557	0.242694	0.116468	0.061676	0.026554
2048.93	-0.005443	0.067329	0.038371	0.011413	0.003200
205.182	0.044607	-0.542715	-0.309294	-0.091997	-0.025794
89.4939	0.039462	-0.566736	-0.322983	-0.096069	-0.026937
161.586	0.011098	0.009435	-0.304835	-0.326437	-0.166234
27.3432	-0.036542	-0.031064	1.05454	1.12927	0.575066
11.4128	-0.009016	-0.007666	0.263109	0.281753	0.143479
6.45090	0.0	0.006767	-0.010669	-1.25380	-1.06502
2.76355	0.0	0.001924	-0.003034	-0.318875	-0.270864
1.09364	0.0	0.0	0.002037	0.001272	1.12617
0.423951	0.0	0.0	0.000515	0.000322	0.278669
Exponent	2p	3p	4p	5p	
6464.96	0.022535	0.012578	0.006290	0.002401	
1279.73	0.154426	0.086192	0.043105	0.016454	
375.075	0.471037	0.262905	0.131481	0.050188	
129.505	0.481306	0.268637	0.134347	0.051282	
57.8899	0.032011	-0.515553	-0.390236	-0.161990	
22.9503	0.039918	-0.642904	-0.486631	-0.202004	
10.1213	-0.011046	-0.030485	0.683508	0.400850	
4.12412	-0.009751	-0.026913	0.603390	0.353864	
1.46244	0.0	0.006828	0.013846	-0.725321	
0.509163	0.0	0.004855	0.009845	-0.515698	
Exponent	3d	4d			
615.688	0.038591	0.019848			
169.176	0.236393	0.121579			
59.9652	0.540209	0.277835			
23.0112	0.368784	0.189670			
19.5062	0.007426	-0.298829			
7.69103	0.019299	-0.656926			
2.93120	0.009969	-0.322972			

Table XIII (Continued)

Core orbitals of Os					
Exponent	4f				
64.3538	0.102788				
18.7848	0.394043				
6.19100	0.548015				
1.89806	0.298472				
Core orbitals of Ir					
Exponent	1s	2s	3s	4s	5s
400907.	0.018842	0.007678	0.003690	0.001958	0.000853
31706.4	0.108347	0.044151	0.021217	0.011259	0.004905
5026.45	0.400306	0.163124	0.078388	0.041596	0.018122
1126.64	0.599009	0.244095	0.117298	0.062244	0.027117
2142.85	-0.005434	0.066093	0.037739	0.011261	0.003178
213.792	0.045013	-0.536095	-0.306112	-0.091342	-0.025778
93.1417	0.040332	-0.573073	-0.327227	-0.097642	-0.027556
167.740	0.011194	0.009649	-0.303993	-0.327144	-0.168936
28.2967	-0.036910	-0.031814	1.05714	1.13764	0.587476
11.6924	-0.009101	-0.007845	0.263375	0.283432	0.146363
6.71161	0.0	0.006945	-0.013563	-1.26412	-1.09170
2.88022	0.0	0.001973	-0.003853	-0.316460	-0.273294
1.16571	0.0	0.0	0.002625	0.001407	1.13704
0.452496	0.0	0.0	0.000663	0.000355	0.280483
Exponent	2p	3p	4p	5p	
6715.64	0.022500	0.012583	0.006320	0.002452	
1325.41	0.154036	0.086146	0.043267	0.016784	
387.773	0.470568	0.263171	0.132177	0.051273	
133.759	0.482093	0.269617	0.135414	0.052529	
60.0037	0.032017	-0.513234	-0.390708	-0.165072	
23.8278	0.040200	-0.644398	-0.490559	-0.207259	
10.5312	-0.010923	-0.031462	0.681772	0.408918	
4.31324	-0.009704	-0.027956	0.605800	0.363351	
1.55209	0.0	0.007615	0.014101	-0.734840	
0.542914	0.0	0.005310	0.009833	-0.512437	
Exponent	3d	4d			
637.716	0.038367	0.019888			
175.181	0.235530	0.122091			
62.1208	0.539836	0.279834			
23.8603	0.369559	0.191567			
20.3490	0.007413	-0.296813			
8.05817	0.019521	-0.658027			
3.09080	0.010086	-0.323945			
Exponent	4f				
68.5102	0.100023				
20.1015	0.390024				
6.68914	0.550024				
2.08440	0.296919				
Core orbitals of Pt					
Exponent	1s	2s	3s	4s	5s
425651.	0.018990	0.007753	0.003732	0.001984	0.000874
33386.4	0.108247	0.044193	0.021271	0.011309	0.004981
5247.26	0.399521	0.163110	0.078509	0.041741	0.018384
1168.51	0.601198	0.245447	0.118139	0.062811	0.027665
2241.38	-0.005012	0.064833	0.037110	0.011110	0.003154
222.791	0.040910	-0.529023	-0.302809	-0.090650	-0.025734
96.9315	0.044808	-0.579435	-0.331664	-0.099290	-0.028188
174.079	0.010536	0.009382	-0.303140	-0.327824	-0.171523
29.3000	-0.036744	-0.032721	1.05726	1.14335	0.598218
12.1032	-0.009157	-0.008154	0.263511	0.284968	0.149100
6.98484	0.0	0.007922	-0.014280	-1.26988	-1.11486
3.00697	0.0	0.001969	-0.003550	-0.315697	-0.277159
1.24155	0.0	0.0	0.002584	0.001474	1.14622
0.482958	0.0	0.0	0.000640	0.000365	0.283922

Table XIII (Continued)

Core orbitals of Pt					
Exponent	2p	3p	4p	5p	
6974.37	0.022466	0.012588	0.006349	0.002500	
1372.34	0.153648	0.086092	0.043422	0.017095	
400.777	0.470095	0.263403	0.132852	0.052302	
138.105	0.482885	0.270569	0.136466	0.053725	
62.0925	0.032129	-0.512527	-0.392386	-0.168495	
24.6643	0.040448	-0.645244	-0.493993	-0.212126	
10.9434	-0.010872	-0.031651	0.682145	0.417650	
4.50339	-0.009674	-0.028163	0.606975	0.371627	
1.64414	0.0	0.007566	0.014288	-0.743890	
0.577351	0.0	0.005182	0.009786	-0.509515	
Exponent	3d	4d			
660.314	0.038115	0.019923			
181.331	0.234495	0.122576			
64.3263	0.539093	0.281796			
24.7291	0.370135	0.193478			
21.2094	0.008624	-0.294974			
8.43384	0.019273	-0.659208			
3.25433	0.009494	-0.324720			
Exponent	4f				
72.6335	0.097672				
21.4118	0.386413				
7.18690	0.551350				
2.27195	0.294935				
Core orbitals of Au					
Exponent	1s	2s	3s	4s	5s
451565.	0.019108	0.007839	0.003777	0.002012	0.000895
35139.4	0.107929	0.044280	0.021334	0.011365	0.005056
5475.94	0.397792	0.163202	0.078629	0.041888	0.018636
1211.58	0.601814	0.246906	0.118956	0.063372	0.028194
2342.28	-0.005412	0.063661	0.036502	0.010969	0.003131
233.041	0.045810	-0.517471	-0.296710	-0.089157	-0.025447
101.536	0.042188	-0.590217	-0.338422	-0.101693	-0.029023
180.700	0.011386	0.010712	-0.301548	-0.328065	-0.173814
30.3109	-0.037662	-0.035433	1.05618	1.14905	0.608787
12.5332	-0.009287	-0.008738	0.263346	0.286504	0.151794
7.27591	0.0	0.008423	-0.014086	-1.27388	-1.13562
3.14729	0.0	0.002380	-0.003979	-0.317072	-0.282660
1.32035	0.0	0.0	0.002555	0.001405	1.15407
0.514732	0.0	0.0	0.000653	0.000359	0.288135
Exponent	2p	3p	4p	5p	
7241.40	0.022434	0.012594	0.006379	0.002545	
1420.55	0.153263	0.086038	0.043577	0.017388	
414.094	0.469619	0.263634	0.133527	0.053279	
142.546	0.483678	0.271526	0.137524	0.054875	
64.3316	0.032117	-0.509793	-0.392485	-0.171060	
25.5994	0.040756	-0.646926	-0.498063	-0.217075	
11.3745	-0.010749	-0.032808	0.680382	0.424739	
4.70372	-0.009624	-0.029379	0.609275	0.380349	
1.73996	0.0	0.008522	0.014519	-0.751781	
0.612793	0.0	0.005755	0.009805	-0.507703	
Exponent	3d	4d			
683.273	0.037931	0.019965			
187.579	0.233821	0.123069			
66.5684	0.539066	0.283731			
25.6136	0.371145	0.195347			
22.0910	0.007389	-0.293189			
8.81953	0.019967	-0.660466			
3.42219	0.010307	-0.325429			

Table XIII (Continued)

Core orbitals of Au					
Exponent	4f				
76.8547	0.095529				
22.7518	0.383239				
7.69560	0.553030				
2.46375	0.293527				
Core orbitals of Hg					
Exponent	1s	2s	3s	4s	5s
479105.	0.019253	0.007925	0.003823	0.002041	0.000920
36992.2	0.107756	0.044356	0.021396	0.011421	0.005150
5715.06	0.396555	0.163235	0.078740	0.042029	0.018954
1256.15	0.603199	0.248296	0.119771	0.063930	0.028832
2450.48	-0.005401	0.062417	0.035865	0.010820	0.003115
242.993	0.046222	-0.510010	-0.293056	-0.088408	-0.025452
105.660	0.043157	-0.597335	-0.343234	-0.103546	-0.029810
187.466	0.011481	0.010956	-0.300456	-0.328538	-0.176881
31.3687	-0.038051	-0.036307	1.05596	1.15465	0.621650
12.9696	-0.009386	-0.008958	0.263629	0.288269	0.155201
7.56813	0.0	0.008650	-0.014448	-1.28001	-1.16392
3.28026	0.0	0.002440	-0.004074	-0.316275	-0.287590
1.40437	0.0	0.0	0.002553	0.001588	1.17159
0.555726	0.0	0.0	0.000637	0.000396	0.285152
Exponent	2p	3p	4p	5p	
7517.22	0.022403	0.012599	0.006407	0.002603	
1470.12	0.152877	0.085974	0.043723	0.017763	
427.737	0.469137	0.263831	0.134173	0.054510	
147.085	0.484480	0.272460	0.138561	0.056293	
66.5281	0.032231	-0.508992	-0.394033	-0.175137	
26.4781	0.041023	-0.647840	-0.501521	-0.222912	
11.8083	-0.010708	-0.033014	0.680851	0.435543	
4.90483	-0.009599	-0.029592	0.610280	0.390399	
1.84497	0.0	0.008444	0.014748	-0.761527	
0.659196	0.0	0.005593	0.009767	-0.504349	
Exponent	3d	4d			
706.779	0.037722	0.020000			
193.964	0.232991	0.123527			
68.8575	0.538682	0.285599			
26.5162	0.371932	0.197191			
23.0008	0.007370	-0.291163			
9.22074	0.020173	-0.661399			
3.59723	0.010424	-0.326750			
Exponent	4f				
81.3372	0.093119				
24.1795	0.379054				
8.24190	0.553968				
2.67438	0.293372				

These orbitals also will be used for the *spd*-MPs, which will be presented in a later paper. In the MP calculation with *spd*-MPs the 3*p*, 4*p*, and 5*p* orbitals for the first, second, and third series, respectively, have to be omitted from the core orbitals, because they are treated as the valence orbitals in the *spd*-MPs.

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