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Energy-adjusted *ab initio* pseudopotentials for the second and third row transition elements

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Summary. Nonrelativistic and quasirelativistic *ab initio* pseudopotentials substituting the $M^{(Z-28)+}$-core orbitals of the second row transition elements and the $M^{(Z-60)+}$-core orbitals of the third row transition elements, respectively, and optimized $(8s7p6d)/[6s5p3d]$-GTO valence basis sets for use in molecular calculations have been generated. Additionally, corresponding spin-orbit operators have also been derived. Atomic excitation and ionization energies from numerical HF as well as from SCF pseudopotential calculations using the derived basis sets differ in most cases by less than 0.1 eV from corresponding numerical all-electron results. Spin-orbit splittings for low-lying states are in reasonable agreement with corresponding all-electron Dirac–Fock (DF) results.

Key words: Pseudopotentials — Spin-orbit operator — Transition metals

1. Introduction

Pseudopotentials [1–4] provide a simple but efficient technique for reducing the computational effort and, even more importantly, accounting for relativistic effects [5] in *ab initio* SCF and subsequent CI calculations on transition metal compounds [6, 7]. Although accurate pseudopotentials for transition metals have already been published by various authors [8, 9, 11, 12] we wish to present in this paper new pseudopotentials for all second row transition metals and for the third row transition metals Hf through Hg (for La through Lu see [13, 14]; for Au see also [15]), following our previous work for first row transition metals [10]. The pseudopotentials published for these elements by other groups were adjusted to orbital properties of a single chosen atomic reference state with only one occupied subshell per angular momentum quantum number. These orbital properties, e.g. orbital energies or the shape of the orbitals themselves, are not quantum mechanical observables. In contrast to that approach, the pseudopotentials presented here are adjusted to total valence energies of a multitude of atomic reference states, which are quantum mechanical observables, without any restrictions imposed on the electron configurations by the fitting procedure. The required reference valence energies can be taken from nonrelativistic or (quasi)relativistic *ab initio* all-electron calculations as well as from empirical data — providing a possibility for alternatively generating *ab initio* or semi-empirical pseudopotentials. The former way was chosen to generate the pseudopotentials presented here, because suitable experimental data for transition metals are rare, and the adjustment (to these data) would require very accurate atomic valence CI calculations.

An important decision concerns the way of separating the core and the valence space for the pseudopotentials. Due to the underlying frozen-core approximation, this separation influences the quality achievable for the pseudopotentials [6, 10, 14]. In view of the experiences of several authors with the first row transition elements [8–11, 28] we decided to include the *ns*, *np*, *nd*, and $(n+1)s$ orbitals ($n = 4, 5$) in the valence space. Thus we present here pseudopotentials which substitute the $M^{(Z-28)+}$-core orbitals of the second row transition metal atoms and the $M^{(Z-60)+}$-core orbitals of the third row transition metal atoms, together with the corresponding spin-orbit operators.

2. Method

The atomic valence model Hamiltonian (in atomic units) used in this work is

$$H = -\frac{1}{2}\sum_i \Delta_i + \sum_i V(r_i) + \sum_{i<j} \frac{1}{r_{ij}},$$

where $V(r_i)$ is a semilocal nonrelativistic or one-component quasirelativistic pseudopotential of the form

$$V(r_i) = -\frac{Q}{r_i} + \sum_l \sum_k A_{lk} \exp(-\alpha_{lk} r_i^2) P_l.$$

Q is the charge of the core, i and j are electron indices and P_l is the projection operator onto the Hilbert subspace with angular symmetry l

$$P_l = \sum_{m_l} |lm_l\rangle\langle lm_l|.$$

The pseudopotential parameters, i.e. the coefficients A_{lk} and the exponential parameters α_{lk} were adjusted to total valence energies derived from numerical all-electron calculations in the following way. First, nonrelativistic Hartree–Fock (HF) and quasirelativistic Wood–Boring (WB) calculations [16, 17] for the core-systems and for several low-lying neutral and ionic states of the atoms were performed by considering all electrons variationally. In the quasirelativistic calculations, the mass-velocity term and the (averaged) Darwin-spin-orbit term were taken into account, being the major relativistic corrections. The form of the one-component Hamiltonian was suggested by Wood and Boring [18] and its implementation into the HF scheme is similar to the HFR treatment of Cowan and Griffin [19]. Excitation and ionization energies from both methods agree to within 0.1 eV, as can be verified by comparing our all-electron results from Table 3 (AE: HF, WB) with the corresponding results from Martin and Hay [20]. Further details of the quasirelativistic method are discussed in [13].

In the next step preliminary values for the parameters A_{lk} and α_{lk} were obtained in a single electron fit (SEFIT [17]) to the HF and WB valence energies [16] of the $M^{(Q-1)+}nl^1\,{}^2L$ valence substates ($n = 4$, 5 for second row and $n = 5$, 6 for third row transition elements; $l = s, p, d, f$, but $l = g$ only for WB pseudopotentials of the third row transition elements; $L = S, P, D, F, G$). These values have been improved in a multi electron fit (MEFIT [17]) by adjusting them in a least-squares sense to the HF and WB total valence energies of 7–11 low-lying states of the neutral atoms M and the monovalent ions M^+ (for Cd and Hg, the divalent ions M^{2+} nave also been considered). This improvement has not been carried out for the parameters of the term(s) with the highest l-value(s) ($l \geqslant 3$) in the pseudopotentials, since the occupation of the corresponding valence orbitals in the neutral atoms usually leads to states lying near or above the ionization limit.

Among several effects which influence atomic and molecular energy levels and which are not accounted for in the pseudopotentials presented above, the spin-orbit coupling is the major one. A convenient form of the spin-orbit operator to be used in addition to the one-component valence model Hamiltonian for calculations on molecules containing heavier atoms has recently been proposed by Pitzer and Winter [21],

$$H_{SO} = \sum_i \sum_{l>0} [2\Delta V_l(r_i)/(2l+1)] P_l \mathbf{l s} P_l$$

with

$$\Delta V_l(r_i) = V_{l,l+1/2}(r_i) - V_{l,l-1/2}(r_i),$$

following partly earlier suggestions by Hafner and Schwarz [27]. $\mathbf{l}$ and $\mathbf{s}$ are orbital angular momentum and spin operators. The difference, $\Delta V_l(r)$, of the relativistic potentials may be parametrized in the form

$$\Delta V_l(r_i) = \sum_k B_{lk} \exp(-\beta_{lk} r_i^2).$$

Since the exponential parameters β_{lk} have been set equal to the exponential parameters α_{lk} of the quasirelativistic WB-MEFIT pseudopotentials, a quasirelativistic semilocal pseudopotential

$$V(r_i) = -\frac{Q}{r_i} + \sum_l \sum_j \sum_k C_{ljk} \exp(-\alpha_{ljk} r_i^2) P_{lj}$$

Table 1. Parameters (in atomic units) of the quasirelativistic (WB) pseudopotentials and the corresponding spin-orbit (SO) operators for second and third row transition metals (TM)

Q			TM	WB	SO	WB, SO	TM	WB	SO	WB, SO
	l	k		A_{lk}	B_{lk}	α_{lk}, β_{lk}		A_{lk}	B_{lk}	α_{lk}, β_{lk}
11	0	1	Y	135.153844		7.4880	La–Lu[a]			
	0	2		15.552441		3.7440				
	1	1		87.784992	−1.155289	6.4454				
	1	2		11.564066	2.253093	3.2227				
	2	1		29.701001	−0.151309	4.6584				
	2	2		5.539968	0.280853	2.3292				
	3	1		−19.122198		6.5842				
	3	2		−2.436375		3.2921				
12	0	1	Zr	150.267591		8.2000	Hf	1499.284711		14.7700
	0	2		18.976217		4.0897		40.282101		7.3850
	1	1		99.622124	−1.595745	7.1100		397.733005	−56.417076	9.8495
	1	2		14.168733	2.796074	3.5968		19.316406	31.166005	4.9247
	2	1		35.045124	−0.088451	5.3500		101.329805	−1.074500	6.0968
	2	2		6.111259	0.284156	2.4918		5.873438	2.427565	3.0484
	3	1		−21.093776		7.5400		10.046723		1.7858
	3	2		−3.080694		3.7700				
	4	1						−9.558244		2.6324
13	0	1	Nb	165.179143		8.9000	Ta	1345.880647		14.5464
	0	2		21.992974		4.4300		36.766806		7.2732
	1	1		111.794414	−1.971852	7.7700		378.425301	−42.890508	9.9356
	1	2		16.633483	3.349342	3.9600		22.293091	30.087431	4.9678
	2	1		38.112249	−0.188397	6.0500		104.883956	−1.696498	6.3474
	2	2		8.039167	0.364478	2.8400		8.755848	2.762333	3.1737
	3	1		−22.929550		8.4900		12.017961		2.0179
	3	2		−3.666310		4.2500				
	4	1						−11.728933		3.0403
14	0	1	Mo	180.103109		9.7146	W	1192.395882		14.3229
	0	2		24.997228		4.6805		32.522933		7.1614
	1	1		123.772752	−3.699359	8.1421		359.031967	−31.069859	10.0216
	1	2		19.530228	5.046170	4.6260		24.030380	28.788539	5.0108
	2	1		48.375022	−0.224975	6.6184		108.301349	−1.996811	6.5980
	2	2		8.892053	0.476908	3.2488		10.982528	3.013506	3.2990
	3	1		−24.805177		9.4500		14.152579		2.2589
	3	2		−4.153782		4.7200				
	4	1						−14.056435		3.4641
15	0	1	Tc	195.159166		10.4223	Re	1038.951572		14.0993
	0	2		28.092603		5.0365		29.561738		7.0497
	1	1		135.284566	−3.421505	8.9504		339.543510	−21.564247	10.1077
	1	2		21.806504	5.119169	4.8544		24.913696	27.423178	5.0539
	2	1		54.329729	−0.628307	6.9457		111.699653	−2.946779	6.8486
	2	2		11.155068	0.821279	3.9706		12.624329	3.402527	3.4243
	3	1		−26.562447		10.4000		16.449852		2.5087
	3	2		−4.585681		5.2000				
	4	1						−16.501120		3.9012

Table 1 (continued)

Q			TM	WB	SO	WB, SO	TM	WB	SO	WB, SO
	l	k		A_{lk}	B_{lk}	α_{lk}, β_{lk}		A_{lk}	B_{lk}	α_{lk}, β_{lk}
16	0	1	Ru	209.822971		11.1053	Os	885.405719		13.8758
	0	2		30.654726		5.4147		25.967040		6.9379
	1	1		146.336182	−3.280102	9.7713		320.083902	−17.161319	10.1938
	1	2		24.127877	5.251066	5.0740		26.148765	26.682449	5.0969
	2	1		67.515897	−0.328444	7.6714		115.044843	−1.824068	7.0992
	2	2		9.870104	0.762830	4.1366		13.622575	3.297332	3.5496
	3	1		−28.340616		11.3600		18.909457		2.7671
	3	2		−4.944629		5.6800				
	4	1						−19.027595		4.3499
17	0	1	Rh	225.347754		11.7200	Ir	732.269200		13.6522
	0	2		32.823189		5.8200		26.484721		6.8261
	1	1		158.709412	−3.729370	10.4200		299.489474	−12.882766	10.2799
	1	2		26.444100	5.998808	5.4500		26.466234	25.569217	5.1399
	2	1		62.758626	−0.025179	8.8200		124.457595	−1.327232	7.3499
	2	2		10.978719	0.530740	3.8700		14.035995	3.419030	3.6749
	3	1		−30.093456		12.3100		21.531031		3.0341
	3	2		−5.218482		6.1600				
	4	1						−21.607597		4.8089
18	0	1	Pd	240.229040		12.4300	Pt	579.223861		13.4287
	0	2		35.171943		6.1708		29.669491		6.7143
	1	1		170.417276	−4.090561	11.0800		280.860774	−10.649196	10.3659
	1	2		28.472133	6.727831	5.8296		26.745382	24.737114	5.1830
	2	1		69.013845	0.020069	9.5100		120.396444	−1.741056	7.6005
	2	2		11.750862	0.583815	4.1398		15.810921	3.567054	3.8002
	3	1		−31.929554		13.2700		24.314376		3.3096
	3	2		−5.398217		6.6300				
	4	1						−24.218675		5.2773
19	0	1	Ag	255.139365		13.1300	Au	426.846679		13.2051
	0	2		36.866122		6.5100		37.007083		6.6026
	1	1		182.181869	−4.423733	11.7400		261.199580	−9.905079	10.4520
	1	2		30.357751	7.465561	6.2000		26.962496	23.965601	5.2260
	2	1		73.719261	0.069435	10.2100		124.790666	−1.493823	7.8511
	2	2		12.502117	0.625406	4.3800		16.300726	3.662935	3.9256
	3	1		−33.689920		14.2200		30.490089		4.7898
	3	2		−5.531120		7.1100		5.171074		2.3949
20	0	1	Cd	270.009483		13.8359	Hg	275.737212		12.9815
	0	2		38.767308		6.8573		49.089212		6.4908
	1	1		193.829629	−4.641130	12.4050		241.540074	−10.680271	10.5381
	1	2		31.896525	8.174615	6.5678		27.396591	23.412453	5.2690
	2	1		79.193647	0.119351	10.8969		127.867008	−1.260836	8.1017
	2	2		13.230827	0.678452	4.6412		16.608312	3.729792	4.0509
	3	1		−35.476626		15.1848		30.364996		3.8858
	3	2		−5.617677		7.5924				
	4	1						−29.473118		6.2410

[a] Pseudopotentials for rare earth elements are given in [13, 14]

Table 2. Contraction coefficients and exponents of the $(8s7p6d)/[6s5p3d]$-GTO valence basis sets for the quasirelativistic pseudopotentials

	No.	TM	Coefficients	Exponents	TM	Coefficients	Exponents
s	1	Y	−1.3875107	5.132958	La–Lu[a]		
			1.9445128	4.240192			
			0.4416434	1.298280			
	2		1.	0.832113			
	3		1.	0.349905			
	4		1.	0.066551			
	5		1.	0.028659			
	6		1.	0.010			
p	1		−3.5841846	2.727920			
			3.0212057	1.979050			
	2		0.4638586	0.873476			
			0.5708554	0.441067			
	3		1.	0.183815			
	4		1.	0.060567			
	5		1.	0.022236			
d	1		−0.0838205	2.900709			
			0.1525870	2.099792			
			0.4792681	0.618252			
			0.6007504	0.200184			
	2		1.	0.061189			
	3		1.	0.020			
s	1	Zr	−0.9736630	5.873789	Hf	−0.7993444	14.592485
			1.7091822	4.287270		1.5201548	11.547491
			0.2438310	1.464137		−1.6453640	4.911194
	2		1.	0.831245		1.	0.808518
	3		1.	0.362335		1.	0.350285
	4		1.	0.079357		1.	0.101282
	5		1.	0.033920		1.	0.039336
	6		1.	0.011		1.	0.01
p	1		−4.2181013	2.874224		3.2662549	6.726531
			4.0479431	2.119901		−4.2015628	5.959979
	2		0.5709451	0.851364		0.3248424	1.301958
			0.4621080	0.437292		0.7010145	0.693136
	3		1.	0.202904		1.	0.279759
	4		1.	0.063259		1.	0.077695
	5		1.	0.022523		1.	0.026952
d	1		−0.0932131	2.580137		−0.0591620	3.721641
			0.2213570	1.855396		0.1495139	1.584120
			0.4684427	0.680754		0.4373137	0.633510
			0.5391950	0.256691		0.5887587	0.230564
	2		1.	0.089400		1.	0.074951
	3		1.	0.030		1.	0.025
s	1	Nb	−0.8582654	6.566301	Ta	−1.4929085	13.951105
			1.3041672	4.586438		2.2820146	12.010241
			0.5069043	3.753770		−1.7133405	5.166446
	2		1.	0.889871		1.	0.856315

Table 2 (continued)

	No.	TM	Coefficients	Exponents	TM	Coefficients	Exponents
	3		1.	0.407138		1.	0.364281
	4		1.	0.094271		1.	0.125494
	5		1.	0.039879		1.	0.046213
	6		1.	0.011		1.	0.015
p	1		−3.9044315	3.070063		1.2668099	7.418872
			4.0688070	2.237964		−2.2049615	5.698410
	2		0.6713910	0.852255		0.3927202	1.318072
			0.3474365	0.504436		0.6380526	0.682169
	3		1.	0.266800		1.	0.282172
	4		1.	0.068732		1.	0.079685
	5		1.	0.023444		1.	0.026770
d	1		−0.0204201	4.053563		−0.0668976	3.791671
			0.2089854	1.652600		0.1669000	1.649302
			0.4705515	0.706859		0.4642789	0.664925
			0.4758860	0.286367		0.5488671	0.246655
	2		1.	0.108757		1.	0.082724
	3		1.	0.033		1.	0.025
s	1	Mo	−0.8262973	7.203380	W	−1.4086099	14.290729
			1.4675616	5.052295		2.1936470	12.241249
			0.3189549	2.913533		−1.7108013	5.312240
	2		1.	1.028993		1.	0.949626
	3		1.	0.469534		1.	0.431118
	4		1.	0.110014		1.	0.126931
	5		1.	0.046115		1.	0.046539
	6		1.	0.015		1.	0.015
p	1		−4.7381435	3.151866		2.0610138	7.249657
			5.0190400	2.453482		−3.0002471	6.084876
	2		0.7493629	0.878773		0.2133964	1.694089
			0.2705697	0.490791		0.8069039	0.891144
	3		1.	0.284714		1.	0.348328
	4		1.	0.071182		1.	0.084670
	5		1.	0.023607		1.	0.027028
d	1		−0.0239430	5.034770		−0.1932562	3.442248
			0.2194576	1.802149		0.2079329	2.667151
			0.4611714	0.807250		0.4423852	0.947109
			0.4671210	0.339005		0.6159882	0.365384
	2		1.	0.128342		1.	0.120903
	3		1.	0.043		1.	0.04
s	1	Tc	−1.1125180	7.434402	Re	−1.1410382	14.781862
			1.8144998	5.551327		1.9371450	12.324075
			0.2569292	3.023086		−1.7232745	5.497478
	2		1.	1.084669		1.	1.026052
	3		1.	0.492585		1.	0.469009
	4		1.	0.113896		1.	0.131184
	5		1.	0.046887		1.	0.047857
	6		1.	0.016		1.	0.015

Table 2 (continued)

	No.	TM	Coefficients	Exponents	TM	Coefficients	Exponents
p	1		−4.8161381	3.449005		2.3698360	7.404005
			5.0866054	2.692737		−3.3105542	6.350206
	2		0.7449072	0.959484		0.1821961	1.888599
			0.2826863	0.485213		0.8363077	0.983485
	3		1.	0.281490		1.	0.383410
	4		1.	0.068371		1.	0.070460
	5		1.	0.022613		1.	0.022028
d	1		−0.0332376	5.122268		−0.3626707	3.434482
			0.2467387	1.954015		0.3761696	2.980781
			0.4802380	0.854756		0.4578332	1.017394
			0.4288664	0.360581		0.5995702	0.395060
	2		1.	0.141275		1.	0.130111
	3		1.	0.047		1.	0.04
s	1	Ru	−1.1196656	7.936570	Os	−1.0664147	15.286736
			1.4453293	5.984245		1.8430761	12.700638
			0.6261653	4.882220		−1.7059002	5.687295
	2		1.	1.144624		1.	1.118087
	3		1.	0.523017		1.	0.520733
	4		1.	0.117573		1.	0.136378
	5		1.	0.048050		1.	0.049592
	6		1.	0.016		1.	0.015
p	1		−4.7226565	3.754609		1.4190452	7.936279
			4.9909084	2.916571		−2.3624495	6.303641
	2		0.7285467	1.048675		0.2064020	1.970323
			0.3039043	0.507320		0.8142959	1.020547
	3		1.	0.267398		1.	0.400593
	4		1.	0.069748		1.	0.087127
	5		1.	0.022927		1.	0.026657
d	1		−0.0327160	6.009913		−0.4670808	3.580815
			0.2657392	2.104280		0.4794806	3.196165
			0.4812398	0.921500		0.4649147	1.105825
			0.4099778	0.388598		0.5893576	0.436032
	2		1.	0.152836		1.	0.144332
	3		1.	0.051		1.	0.05
s	1	Rh	−2.4155775	7.917744	Ir	−1.6750339	15.293709
			3.0987382	6.841207		2.3934648	13.573682
			0.2821256	2.959840		−1.6504979	5.816274
	2		1.	1.334341		1.	1.195521
	3		1.	0.598810		1.	0.565776
	4		1.	0.121894		1.	0.140527
	5		1.	0.049452		1.	0.050820
	6		1.	0.016		1.	0.015
p	1		−3.3443545	4.136079		0.8677142	8.669796
			3.7037440	2.946281		−1.8144826	6.245614
	2		0.7462258	1.122304		0.2709454	1.966384
			0.2698833	0.666177		0.7540443	1.020206
	3		1.	0.365743		1.	0.406580

Table 2 (continued)

	No.	TM	Coefficients	Exponents	TM	Coefficients	Exponents
	4		1.	0.076686		1.	0.090116
	5		1.	0.024170		1.	0.027364
d	1		−0.0161604	7.032892		−0.5973104	3.699485
			0.2763987	2.309819		0.6112252	3.361743
			0.4850026	0.998228		0.4732939	1.174525
			0.3930199	0.417057		0.5755302	0.470176
	2		1.	0.164447		1.	0.157678
	3		1.	0.055		1.	0.05
s	1	Pd	−2.1642497	8.475640	Pt	−0.8849447	16.559563
			2.8928286	7.165717		1.5011228	13.892440
			0.2339564	3.182110		−1.5529012	5.853608
	2		1.	1.406357		1.	1.287320
	3		1.	0.623921		1.	0.604732
	4		1.	0.123303		1.	0.142783
	5		1.	0.049360		1.	0.050969
	6		1.	0.016		1.	0.015
p	1		−5.2503025	4.246097		4.9530757	7.925175
			5.5527850	3.392594		−5.8982100	7.341538
	2		0.7577315	1.216185		0.3047425	1.912515
			0.2660046	0.639624		0.7164894	1.071545
	3		1.	0.372657		1.	0.437917
	4		1.	0.079175		1.	0.093621
	5		1.	0.024754		1.	0.027802
d	1		−0.0185004	7.169612		−0.5826439	3.939531
			0.2769690	2.561263		0.5922576	3.587777
			0.4859035	1.109669		0.4736921	1.286231
			0.3930651	0.462296		0.5765202	0.519814
	2		1.	0.181525		1.	0.174715
	3		1.	0.060		1.	0.05
s	1	Ag	−1.9648132	9.088442	Au	−0.1597614	20.115299
			2.7332194	7.540731		0.7893559	12.193477
			0.1991148	2.794005		−1.5714057	6.039626
	2		1.	1.480158		1.	1.373721
	3		1.	0.653851		1.	0.650010
	4		1.	0.124488		1.	0.145816
	5		1.	0.049264		1.	0.051484
	6		1.	0.016		1.	0.015
p	1		−6.0833780	4.451240		2.0982231	8.609665
			6.4168543	3.675263		−3.0458670	7.335326
	2		0.7539735	1.291288		0.3791452	1.912970
			0.2730597	0.652578		0.6456428	1.057695
	3		1.	0.367036		1.	0.443060
	4		1.	0.075694		1.	0.090144
	5		1.	0.023723		1.	0.026811
d	1		−0.0163876	7.994730		−0.4058458	4.143949
			0.2814107	2.784773		0.4275070	3.568257

Table 2 (continued)

	No.	TM	Coefficients	Exponents	TM	Coefficients	Exponents
			0.4863264	1.209744		0.4755405	1.344324
			0.3867258	0.505393		0.5610972	0.555289
	2		1.	0.198851		1.	0.189675
	3		1.	0.066		1.	0.06
s	1	Cd	−1.7864259	9.727011	Hg	−0.0282477	26.842049
			2.5778948	7.837523		0.8202914	10.320909
			0.1601171	5.089194		−1.7406770	6.344923
	2		1.	1.553326		1.	1.450305
	3		1.	0.714079		1.	0.708215
	4		1.	0.150784		1.	0.167606
	5		1.	0.057467		1.	0.059066
	6		1.	0.019		1.	0.02
p	1		−6.2311994	4.742716		0.8855369	9.772990
			6.5741920	3.936655		−1.8364564	7.169095
	2		0.7497265	1.380391		−0.4904267	1.868009
			0.2811082	0.668485		0.5415630	0.973301
	3		1.	0.363423		1.	0.421997
	4		1.	0.106253		1.	0.125213
	5		1.	0.036644		1.	0.040190
d	1		−0.0163606	8.469341		−0.1428567	4.911447
			0.2864728	3.024231		0.1988172	3.049550
			0.4868518	1.316367		0.4885401	1.344501
			0.3794111	0.556393		0.5143447	0.576618
	2		1.	0.223856		1.	0.210245
	3		1.	0.075		1.	0.07

[a] Basis sets and pseudopotentials for rare earth elements see [13]

with the projection operator onto the Hilbert subspace of symmetry j

$$P_{lj} = \sum_{m_j} |ljm_j\rangle\langle ljm_j|$$

for use in two-component atomic or molecular calculations may be derived by using the relations:

$$C_{ljk} = A_{lk} - B_{lk}(l+1)/(2l+1), \quad \text{for } j = l - 1/2$$

$$C_{ljk} = A_{lk} + B_{lk}l/(2l+1), \quad \text{for } j = l + 1/2.$$

The coefficients B_{lk} have been adjusted in numerical pseudopotential calculations for the one-valence-electron ions [17] to reproduce the spin-orbit splittings obtained from the corresponding all-electron DF calculations [22]. No parameters have been derived for the highest l-values $(1 \geqslant 3)$ since in those cases the spin-orbit splittings are of the same order as or smaller than the remaining errors in the potentials.

The parameters of the derived quasirelativistic WB-MEFIT pseudopotentials and the corresponding spin-orbit operators are listed in Table 1. The corresponding parameters of the nonrelativistic HF-MEFIT pseudopotentials may be obtained by writing to the authors.

For use in atomic and subsequent molecular SCF calculations, GTO valence basis sets have been optimized for the HF- and WB-MEFIT pseudopotentials. In the first step of this procedure the exponential parameters of a ($7s5p5d$) basis set have been energy-optimized [23] for the lowest states of the $d^{n+1}s^1$-configuration of the transition metal atoms, except for Cd and Hg, where the $d^{10}s^2\,{}^1S$ ground states were used. These basis sets were augmented by two p functions whose exponential parameters have been energy-optimized for the lowest states of the $d^{n+1}p^1$ configuration, except for Cd and Hg, were the $d^{10}s^1p^1\,{}^3P$ states were used. Finally these basis sets were completed to yield the ($8s7p6d$) basis sets by adding a diffuse s and a diffuse d function without energy-optimization. Their exponential parameters were taken as a third of the next higher exponential parameter in the corresponding symmetry. To get a good and balanced description of the low-lying atomic and ionic states involved in the adjustment of the MEFIT pseudopotentials it turned out to be suitable to take the contraction coefficients for the ($8s7p6d$)/[$6s5p3d$] basis sets from calculations for the lowest states of the d^ns^2 configuration. This is in contrast to the experience made by other authors [29] and ourselves [10] for the first row transition metals. Contraction coefficients and exponential parameters for the ($8s7p6d$)/[$6s5p3d$]-GTO valence basis sets for the quasirelativistic WB-MEFIT pseudopotentials are collected in Table 2. As with the HF pseudopotential parameters, the parameters for the basis sets corresponding to the HF-MEFIT pseudopotentials may be obtained by writing to the authors.

3. Results

The derived nonrelativistic and quasirelativistic pseudopotentials were tested in numerical HF calculations [17] and in SCF calculations [23] using the optimized valence basis sets. The excitation and ionization energies obtained in these calculations for low-lying atomic and ionic states are summarized in Table 3. In all cases, the results from numerical pseudopotential calculations (HF- or WB-MEFIT-PP: HF in Table 3) [17] differ by less than 0.1 eV from the values obtained in numerical all-electron calculations (AE: HF or WB in Table 3). In most cases the deviations are significantly smaller than 0.05 eV. These differences, which are due to errors left in the pseudopotential and caused mainly by the inherent frozen-core approximation and the applied semilocal form, are much smaller than the influence of the major relativistic effects, neglecting spin-orbit coupling, which contribute several eV in some cases (compare, e.g., AE, HF with AE, WB in Table 3 for Rh, Ag and the third row transition elements). Therefore our nonrelativistic and quasirelativistic pseudopotentials are reliable tools for the investigation of relativistic effects in molecular calculations. For the total valence energies obtained with the derived HF- and WB-MEFIT pseudopotentials in numerical calculations, the deviations from corresponding all-electron results are in most cases much smaller than 0.004 a.u., with maxima occurring around the center of the rows at ruthenium and rhenium, respectively. Despite the energy adjustment of our pseudopotentials, orbital properties such as radius expectation values $\langle r \rangle$, orbital energies ε and the shape of the pseudo-orbitals are in excellent agreement with corresponding all-electron data — the deviations for $\langle r \rangle$ values and orbital energies are less than 5%.

Additional information about the quality of our pseudopotentials is provided by the comparison of atomic excitation and ionization energies from numerical calculations [17] with our pseudopotentials and comparable ones taken from the literature. This was done with the WB-MEFIT pseudopotentials for Ru and Os and with pseudopotentials taken from [8] (p. 302 for Ru, p. 303 for Os) and [11] (p. 2814 for Ru, no data for Os). The total valence energies as well as the atomic excitation and ionization energies obtained in these numerical calculations are given in Table 4 (HF: PP [8], PP [11] or WB-MEFIT-PP), together with the atomic excitation and ionization energies from numerical all-electron WB calculations and the corresponding values from [20] (AE: WB or [20]). Excitation and ionization energies from numerical all-electron calculations are well reproduced by the pseudopotentials from [11] and from this work, whereas the pseudopotentials from [8] are not able to reproduce these values within 0.1 eV.

When the derived pseudopotentials are used in atomic SCF calculations [23] together with the corresponding basis sets (HF- or WB-MEFIT-PP: SCF in Table 3), the deviations in excitation and ionization energies from the all-electron results (AE: HF or WB, respectively) still remain smaller than 0.1 eV for nearly all low-lying atomic and ionic states. The same holds true for the differential basis set errors, as can be seen by comparing numerical HF with SCF pseudopotential results. Deviations greater than 0.1 eV may be avoided by successively uncontracting the basis sets. Experimental values for the excitation and ionization energies are not given in Table 3 because these should be compared to results from CI calculations including at least *f* functions in the basis sets.

As a first test for the derived spin-orbit operators small CI calculations (by means of generating all *jj*-coupled configurations corresponding to the nonrelativistic configuration of the *LS* state under consideration and subsequent diagonalization of the Hamiltonian matrix) have been carried out [26] for several low-lying atomic and ionic states of the second and third row transition metal atoms; these utilized the quasirelativistic WB-MEFIT pseudopotentials together with the spin-orbit operators and numerical one-electron functions derived from *LS*-coupled calculations [17]. In Table 5 some of the spin-orbit splittings obtained from these calculations are summarized together with all-electron [22, 31] and experimental [24] results. The values derived with the WB pseudopotentials and the corresponding spin-orbit operators (PP: WB, SO) and with all-electron calculations (multi-configuration Dirac–Fock optimized-level calculations corresponding to a single nonrelativistic configuration, AE, DF, OL [22]; Hartree–Fock calculations with consideration of the Breit–Pauli operator in first order perturbation theory, AE, HF + BP [31]) agree rather well in their magnitude and their change within a multiplet. In some cases differences up to 40%

Table 3. Atomic excitation and ionization energies (in eV) for the second and third row transition metals (TM) from numerical all-electron HF and WB calculations (AE: HF, WB) in comparison with HF and SCF pseudopotential results using the non-relativistic HF- and the quasirelativistic WB-MEFIT pseudopotentials (HF-MEFIT-PP, WB-MEFIT-PP: HF, SCF)

State	TM	AE	HF-MEFIT-PP		AE	WB-MEFIT-PP	
		HF	HF	SCF	WB	HF	SCF
d^1s^2 ^2D	Y	0.00	0.00	0.00	0.00	0.00	0.00
d^2s^1 ^4F		0.42	0.41	0.43	0.75	0.74	0.76
d^3 ^4F		2.73	2.71	2.76	3.32	3.32	3.35
d^1s^1 ^3D	Y$^+$	4.92	4.93	4.93	5.03	5.04	5.05
d^2 ^3F		5.48	5.48	5.49	6.02	6.04	6.06
d^2s^2 ^3F	Zr	0.00	0.00	0.00	0.00	0.00	0.00
d^3s^1 ^5F		−0.40	−0.40	−0.39	−0.01	−0.02	−0.01
d^4 ^5D		1.71	1.71	1.73	2.44	2.44	2.46
d^2s^1 ^4F	Zr$^+$	5.06	5.06	5.06	5.18	5.18	5.18
d^3 ^4F		4.99	5.00	5.02	5.65	5.66	5.67
d^3s^2 ^4F	Nb	0.00	0.00	0.00	0.00	0.00	0.00
d^4s^1 ^6D		−1.24	−1.25	−1.24	−0.80	−0.80	−0.80
d^5 ^6S		−0.07	−0.08	−0.05	0.81	0.80	0.82
d^3s^1 ^5F	Nb$^+$	5.15	5.16	5.16	5.29	5.29	5.29
d^4 ^5D		4.42	4.44	4.46	5.18	5.20	5.22
d^4s^2 ^5D	Mo	0.00	0.00	0.00	0.00	0.00	0.00
d^5s^1 ^7S		−2.89	−2.93	−2.95	−2.37	−2.42	−2.41
d^6 ^5D		1.03	1.06	1.03	1.99	2.03	2.03
d^4s^1 ^6D	Mo$^+$	5.23	5.23	5.23	5.37	5.37	5.37
d^5 ^6S		2.98	2.97	2.95	3.86	3.85	3.87
d^5s^2 ^6S	Tc	0.00	0.00	0.00	0.00	0.00	0.00
d^6s^1 ^6D		0.20	0.26	0.25	0.76	0.81	0.81
d^7 ^4F		2.63	2.70	2.68	3.69	3.76	3.78
d^5s^1 ^7S	Tc$^+$	5.29	5.29	5.29	5.43	5.42	5.43
d^6 ^5D		6.12	6.21	6.20	7.05	7.14	7.16
d^6s^2 ^5D	Ru	0.00	0.00	0.00	0.00	0.00	0.00
d^7s^1 ^5F		−1.42	−1.42	−1.41	−0.74	−0.75	−0.74
d^8 ^3F		0.27	0.27	0.31	1.50	1.48	1.52
d^6s^1 ^6D	Ru$^+$	5.68	5.68	5.68	5.88	5.88	5.88
d^7 ^4F		4.50	4.52	4.55	5.57	5.60	5.62
d^7s^2 ^4F	Rh	0.00	0.00	0.00	0.00	0.00	0.00
d^8s^1 ^4F		−2.19	−2.19	−2.17	−1.40	−1.40	−1.38
d^9 ^2D		−1.24	−1.24	−1.18	0.13	0.15	0.20
d^7s^1 ^5F	Rh$^+$	6.03	6.04	6.04	6.28	6.28	6.28
d^8 ^3F		3.73	3.74	3.78	4.93	4.93	4.96
d^8s^2 ^3F	Pd	0.00	0.00	0.00	0.00	0.00	0.00
d^9s^1 ^3D		−3.01	−2.99	−2.97	−2.10	−2.08	−2.07
d^{10} ^1S		−3.76	−3.76	−3.70	−2.21	−2.20	−2.15
d^8s^1 ^4F	Pd$^+$	6.36	6.37	6.36	6.66	6.66	6.66
d^9 ^2D		2.91	2.94	2.98	4.24	4.26	4.29

Table 3 (continued)

State		TM	AE	HF-MEFIT-PP		AE	WB-MEFIT-PP	
			HF	HF	SCF	WB	HF	SCF
d^9s^2	^2D	Ag	0.00	0.00	0.00	0.00	0.00	0.00
$d^{10}s^1$	^2S		−4.91	−4.93	−4.91	−3.88	−3.89	−3.87
d^9s^1	^3D	Ag^+	6.66	6.67	6.67	7.02	7.03	7.02
d^{10}	^1S		0.99	0.99	1.04	2.46	2.46	2.50
$d^{10}s^2$	^1S	Cd	0.00	0.00	0.00	0.00	0.00	0.00
$d^{10}s^1$	^2S	Cd^+	6.93	6.94	6.94	7.35	7.35	7.35
d^9s^2	^2D		17.50	17.53	17.63	16.41	16.43	16.53
d^1s^2	^2D	La–Lu[a]						
d^2s^1	^4F							
d^3	^4F							
d^1s^1	^3D	La^+–Lu^+						
d^2	^3F							
d^2s^2	^3F	Hf	0.00	0.00	0.00	0.00	0.00	0.00
d^3s^1	^5F		−0.38	−0.37	−0.41	0.95	0.96	0.92
d^4	^5D		1.72	1.73	1.69	4.36	4.38	4.30
d^2s^1	^4F	Hf^+	5.07	5.05	5.05	5.62	5.59	5.57
d^3	^4F		5.12	5.11	5.07	7.54	7.51	7.45
d^3s^2	^4F	Ta	0.00	0.00	0.00	0.00	0.00	0.00
d^4s^1	^6D		−1.28	−1.27	−1.33	0.20	0.21	0.15
d^5	^6S		−0.18	−0.19	−0.25	2.92	2.92	2.82
d^3s^1	^5F	Ta^+	5.13	5.12	5.11	5.71	5.69	5.67
d^4	^5D		4.51	4.50	4.44	7.28	7.26	7.17
d^4s^2	^5D	W	0.00	0.00	0.00	0.00	0.00	0.00
d^5s^1	^7S		−2.95	−2.97	−3.00	−1.29	−1.31	−1.36
d^6	^5D		0.73	0.76	0.71	4.15	4.17	4.08
d^4s^1	^6D	W^+	5.17	5.16	5.16	5.78	5.76	5.75
d^5	^6S		3.06	3.02	3.00	6.19	6.16	6.08
d^5s^2	^6S	Re	0.00	0.00	0.00	0.00	0.00	0.00
d^6s^1	^6D		−0.04	0.01	−0.02	1.76	1.80	1.75
d^7	^4F		2.05	2.11	2.07	5.78	5.83	5.74
d^5s^1	^7S	Re^+	5.19	5.17	5.17	5.81	5.77	5.77
d^6	^5D		5.98	6.01	5.99	9.34	9.36	9.29
d^6s^2	^5D	Os	0.00	0.00	0.00	0.00	0.00	0.00
d^7s^1	^5F		−1.63	−1.65	−1.68	0.53	0.52	0.47
d^8	^3F		−0.40	−0.43	−0.47	3.82	3.79	3.70
d^6s^1	^6D	Os^+	5.58	5.57	5.58	6.42	6.39	6.38
d^7	^4F		4.37	4.35	4.32	8.16	8.13	8.06
d^7s^2	^4F	Ir	0.00	0.00	0.00	0.00	0.00	0.00
d^8s^1	^4F		−2.43	−2.44	−2.47	0.07	0.07	0.02
d^9	^2D		−2.08	−2.09	−2.14	2.59	2.58	2.49
d^7s^1	^5F	Ir^+	5.94	5.93	5.93	6.98	6.96	6.95
d^8	^3F		3.55	3.54	3.51	7.72	7.71	7.65
d^8s^2	^3F	Pt	0.00	0.00	0.00	0.00	0.00	0.00
d^9s^1	^3D		−3.28	−3.27	−3.31	−0.42	−0.42	−0.47

Table 3 (continued)

State	TM	AE	HF-MEFIT-PP		AE	WB-MEFIT-PP	
		HF	HF	SCF	WB	HF	SCF
d^{10} ^1S		−4.69	−4.72	−4.78	0.46	0.43	0.34
d^8s^1 ^4F	Pt^+	6.26	6.26	6.13	7.52	7.51	7.47
d^9 ^2D		2.68	2.68	2.65	7.24	7.25	7.20
d^9s^2 ^2D	Au	0.00	0.00	0.00	0.00	0.00	0.00
$d^{10}s^1$ ^2S		−5.15	−5.13	−5.19	−1.89	−1.92	−1.96
d^9s^1 ^3D	Au^+	6.57	6.56	6.57	8.03	8.03	8.03
d^{10} ^1S		0.78	0.78	0.74	5.77	5.74	5.71
$d^{10}s^2$ ^1S	Hg	0.00	0.00	0.00	0.00	0.00	0.00
$d^{10}s^1$ ^2S	Hg^+	6.83	6.84	6.83	8.52	8.52	8.52
d^9s^2 ^2D		16.82	16.83	16.90	14.05	14.07	14.11

[a] See [13, 14]

Table 4. Total valence energies (in a.u.) and atomic excitation and ionization energies (in eV) for Ru and Os from numerical HF pseudopotential calculations (HF), using the WB-MEFIT pseudopotentials (WB-MEFIT-PP, this work) and comparable ones taken from [8] and [11] (PP [8], PP [11]), in comparison with results from numerical all-electron calculations (AE: WB, [20])

State	TM	HF			AE	
		PP [8]	PP [11][a]	WB-MEFIT-PP	WB	[20]
1. Total valence energies (in a.u.)						
d^6s^2 ^5D	Ru	−93.1790372	−93.7489495	−94.0886399		
d^7s^1 ^5F		−93.2085402	−93.7765238	−94.1163569		
d^8 ^3F		−93.1286555	−93.6943678	−94.0340888		
d^6s^1 ^6D	Ru^+	−92.9638775	−93.5332869	−93.8724335		
d^7 ^4F		−92.9773049	−93.5442821	−93.8830372		
d^6s^2 ^5D	Os	−90.3322978		−89.8268259		
d^7s^1 ^5F		−90.2952694		−89.8077590		
d^8 ^3F		−90.1583599		−89.6873757		
d^6s^1 ^6D	Os^+	−90.0925803		−89.5919860		
d^7 ^4F		−90.0053062		−89.5282089		
2. Atomic excitation and ionization energies (in eV)						
d^6s^2 ^5D	Ru	0.00	0.00	0.00	0.00	0.00
d^7s^1 ^5F		−0.80	−0.75	−0.75	−0.74	−0.74
d^8 ^3F		1.37	1.49	1.48	1.50	1.50
d^6s^1 ^6D	Ru^+	5.85	5.87	5.88	5.88	5.87
d^7 ^4F		5.49	5.57	5.60	5.57	5.57
d^6s^2 ^5D	Os	0.00		0.00	0.00	0.00
d^7s^1 ^5F		1.01		0.52	0.53	0.55
d^8 ^3F		4.73		3.79	3.82	3.85
d^6s^1 ^6D	Os^+	6.52		6.39	6.42	6.40
d^7 ^4F		8.90		8.13	8.16	8.17

[a] No data for Os pseudopotential

Table 5. Spin-orbit splittings (in cm^{-1}) for low-lying states of some second and third row transition metals (TM). Results obtained from numerical pseudopotential calculations (PP: WB, SO [26]), from numerical all-electron multiconfiguration Dirac–Fock optimized-level calculations corresponding to a single nonrelativistic configuration (AE, DF, OL [22]), and from all-electron Hartree-Fock calculations adding the Breit-Pauli operator as a first order perturbation (AE, HF + BP [31]). Experimental data were taken from [24]

Configuration		TM	PP WB, SO	AE, DF, OL	AE, HF +BP	Exp.
d^1s^2	$^2D_{3/2}-{}^2D_{5/2}$	Y	643	467		530
d^2s^2	$^3F_2-{}^3F_3$	Zr	627	533	622	570
	$^3F_3-{}^3F_4$		767	620	762	670
d^3s^2	$^4F_{3/2}-{}^4F_{5/2}$	Nb	483	437	477	444
	$^4F_{5/2}-{}^4F_{7/2}$		633	566	626	567
	$^4F_{7/2}-{}^4F_{9/2}$		750	658	741	651
d^4s^2	$^5D_0-{}^5D_1$	Mo	215	198	211	177
	$^5D_1-{}^5D_2$		395	368	389	312
	$^5D_2-{}^5D_3$		534	502	526	404
	$^5D_3-{}^5D_4$		641	595	632	488
d^5s^2	$^4P_{1/2}-{}^4P_{3/2}$	Tc	−371	−328	−379	[a]
	$^4P_{3/2}-{}^4P_{5/2}$		−288	−250	−290	[a]
d^6s^1	$^6D_{1/2}-{}^6D_{3/2}$		−203	−163		−176
	$^6D_{3/2}-{}^6D_{5/2}$		−348	−288		−302
	$^6D_{5/2}-{}^6D_{7/2}$		−512	−443		−450
	$^6D_{7/2}-{}^6D_{9/2}$		−728	−663		−678
d^6s^2	$^5D_0-{}^5D_1$	Ru	−221	−177	−218	−419
	$^5D_1-{}^5D_2$		−457	−380	−450	−15
	$^5D_2-{}^5D_3$		−715	−629	−704	−482
	$^5D_3-{}^5D_4$		−1149	−1081	−1135	−1092
d^7s^1	$^5F_1-{}^5F_2$		−430	−387		−392
	$^5F_2-{}^5F_3$		−672	−610		−622
	$^5F_3-{}^5F_4$		−946	−872		−901
	$^5F_4-{}^5F_5$		−1237	−1166		−1191
d^7s^2	$^4F_{3/2}-{}^4F_{5/2}$	Rh	−890	−807	−875	−825
	$^4F_{5/2}-{}^4F_{7/2}$		−1382	−1281	−1361	−1331
	$^4F_{7/2}-{}^4F_{9/2}$		−2095	−1999	−2066	−2065
d^8s^1	$^4F_{3/2}-{}^4F_{5/2}$		−879	−832		−875
	$^4F_{5/2}-{}^4F_{7/2}$		−1372	−1299		−1068
	$^4F_{7/2}-{}^4F_{9/2}$		−1615	−1578		−1529
d^8s^2	$^3F_2-{}^3F_3$	Pd	−1706	−1626	−1673	−1498
	$^3F_3-{}^3F_4$		−3148	−3053	−3115	−3112
d^9s^1	$^3D_1-{}^3D_2$		−2106	−2053		−2339
	$^3D_2-{}^3D_3$		−1409	−1435		−1191
d^9s^2	$^2D_{3/2}-{}^2D_{5/2}$	Ag	−4482	−4454		−4472
$d^{10}s^1p^1$	$^3P_0-{}^3P_1$	Cd	461	525		542
	$^3P_1-{}^3P_2$		928	1046		1171

Table 5 (continued)

Configuration		TM	PP WB, SO	AE, DF, OL	AE, HF +BP	Exp.
d^2s^2	$^3F_2-{}^3F_3$	Hf	2357	1831	2908	2357
	$^3F_3-{}^3F_4$		2432	1892	2903	2411
d^3s^2	$^4F_{3/2}-{}^4F_{5/2}$	Ta	1937	1586	2244	2010
	$^4F_{5/2}-{}^4F_{7/2}$		2101	1777	2367	1954
	$^4F_{7/2}-{}^4F_{9/2}$		2020	1795		1657
d^4s^2	$^5D_0-{}^5D_1$	W	1355	1084	1594	1670
	$^5D_1-{}^5D_2$		1681	1414	1897	1655
	$^5D_2-{}^5D_3$		1698	1528	1864	1504
	$^5D_3-{}^5D_4$		1621	1540	1738	1389
d^5s^2	$^4P_{1/2}-{}^4P_{3/2}$	Re	−1796	−1499	−1924	−1340
	$^4P_{3/2}-{}^4P_{5/2}$		−3724	−3289	−3932[b]	−2242
d^6s^1	$^6D_{1/2}-{}^6D_{3/2}$		−595	−466		−911
	$^6D_{3/2}-{}^6D_{5/2}$		−1012	−807		−557
	$^6D_{5/2}-{}^6D_{7/2}$		−1290	−1132		−1554
	$^6D_{7/2}-{}^6D_{9/2}$		−2629	−2166		−2462
d^6s^2	$^5D_0-{}^5D_1$	Os	−464	−407	−467	−327
	$^5D_1-{}^5D_2$		−1744	−1372	−1925	−3026
	$^5D_2-{}^5D_3$		−852	−846	−763	1419
	$^5D_3-{}^5D_4$		−4122	−3588	−4405	−4159
d^7s^1	$^5F_1-{}^5F_2$		−957	−880		−2854
	$^5F_2-{}^5F_3$		−1596	−1467		1212
	$^5F_3-{}^5F_4$		−2785	−2458		−2635
	$^5F_4-{}^5F_5$		−3930	−3608		−3599
d^7s^2	$^4F_{3/2}-{}^4F_{5/2}$	Ir	−1041	−1037	−897	1706
	$^4F_{5/2}-{}^4F_{7/2}$		−2545	−2371	−2515	539
	$^4F_{7/2}-{}^4F_{9/2}$		−7001	−6348	−7381	−6324
d^8s^1	$^4F_{3/2}-{}^4F_{5/2}$		−1137	−1193		−1954
	$^4F_{5/2}-{}^4F_{7/2}$		−3784	−3413		−2771
	$^4F_{7/2}-{}^4F_{9/2}$		−4269	−4206		−4272
d^8s^2	$^3F_2-{}^3F_3$	Pt	931	840	1319	[a]
	$^3F_3-{}^3F_4$		−9376	−8740	−9772	[a]
d^9s^1	$^3D_1-{}^3D_2$		−7046	−6566		−9356
	$^3D_2-{}^3D_3$		−3017	−3134		−776
d^9s^2	$^2D_{3/2}-{}^2D_{5/2}$	Au	−12326	−11832		−12274
$d^{10}s^1p^1$	$^3P_0-{}^3P_1$	Hg	1537	1967		1767
	$^3P_1-{}^3P_2$		3916	4271		4631

[a] Corresponding levels experimentally not observed [24]

[b] Calculated with level-assignment differing from that proposed in [31]

occur between these results, but these do not change the overall picture given for the spin-orbit coupling by the three methods mentioned above. All three methods show fairly good agreement with experimental values in those cases where a single nonrelativistic configuration yields a sufficient description for the considered state, i.e. especially for the beginning and the end of the rows. However, large deviations from experimental data are found for those cases where mixing of several low-lying nonrelativistic configurations becomes important, i.e. in the center of the rows, where multiplets from the $d^n s^2$ and the $d^{n+1}s^1$ configurations lie close together. It is evident that in the case of the pseudopotential method these differences are caused mainly by the very limited CI calculations, i.e. are due to the neglect of the mixing of several low-lying states of other configurations to the state under consideration. In contrast with the numerical all-electron DF results the pseudopotential calculation may easily be improved by large-scale CI calculations in the intermediate coupling scheme, applying existing programs [30] and the analytical form of the spin-orbit operator proposed by Pitzer and Winter [21]. Calculations utilizing the presented MEFIT pseudopotentials and spin-orbit operators for molecules containing transition-metal atoms are underway in our laboratory.

4. Conclusion

Atomic excitation and ionization energies obtained from calculatons with the nonrelativistic and quasirelativistic *ab initio* pseudopotentials for transition elements presented in this paper are in good agreement with corresponding results from all-electron calculations. Computational savings and, even more importantly, easy treatment of the major relativistic effects are the main advantages of these pseudopotentials. In addition to this, their analytical form is less complicated than for the pseudopotentials previously published by other groups, due to the different fitting procedure. Spin-orbit potentials, to be used in connection with the quasirelativistic pseudopotentials, are also presented. Calculated atomic spin-orbit splittings are in good agreement with all-electron results and acceptable in comparison with experimental data in those cases where the small valence CI employed is a reasonable approximation.

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