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Why do the second row transition metal atoms prefer $5s^1 4d^{m+1}$ to $5s^2 4d^m$?

Numerical Hartree–Fock studies

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Abstract. Numerical Hartree–Fock (NHF) calculations have been performed for 332 ground and low-lying excited states of the fifth period atoms Rb through Xe, with our special interest in the states arising from the $5s^2 4d^m$, $5s^1 4d^{m+1}$, and $5s^0 4d^{m+2}$ configurations of the second row transition metal atoms. Among various properties, orbital energies and mean values of r of the outermost orbitals of each symmetry are presented as well as total energies. It is discussed in some detail why the second row transition metal atoms have a tendency to prefer $s^1 d^{m+1}$ as the ground configuration in contrast to the preferred $s^2 d^m$ configuration in the first row transition metal atoms. Our systematic NHF computations reported in this and the previous papers conclude that the Hartree–Fock method correctly predicts the experimental ground state of the atoms He through Xe with the sole exception for Zr.

Key words: Transition metal atoms – Ground and low-lying excited states – Numerical Hartree–Fock approximation

1. Introduction

Numerical Hartree–Fock (NHF) calculations have been performed for the ground states of many neutral atoms, cations [1–9], and anions [9]. In contrast to the ground state, few NHF results have been published [4, 5, 10–12] for excited states of atoms and atomic ions. Recently, we reported systematic NHF results for low-lying excited states of the atoms He to Ar [13], K to Kr [14], and cationic species from the lanthanide atoms [15]. In the present study, we consider the fifth period atoms Rb through Xe with the following configurations:

Rb:	$5s^1$, $5p^1$, and $4d^1$;
Sr:	$5s^2$, $5s^1 5p^1$ and $5s^1 4d^1$;
Y to Ag:	$5s^2 4d^m$, $5s^1 4d^{m+1}$, and $5s^0 4d^{m+2}$;
Cd:	$4d^{10} 5s^2$, $4d^{10} 5s^1 5p^1$, and $4d^{10} 5s^1 5d^1$;
In to I:	$5s^2 5p^m$ and $5s^1 5p^{m+1}$;
Xe:	$5s^2 5p^6$, $5s^2 5p^5 6s^1$, $5s^2 5p^5 6p^1$, and $5s^2 5p^5 5d^1$.

All the present NHF calculations were performed with an enhanced version of MCHF72 [16], and care was taken to ensure that the total energies are accurate to nine or more significant figures. Although we have calculated total 332 states arising from the above configurations, we give the information on the ground state, and the lowest and highest excited states of the respective configurations.

2. Results and discussion

Table 1 summarizes the total energies, excitation energies, orbital energies ε_i, and mean electron–nucleus distances, $\langle r \rangle_i$, for the outermost orbitals of each symmetry i (= s, p, d). All values are given in Hartree atomic units.

2.1. *Atoms Rb and Sr*

In the Rb atom, the ground electron configuration is [Kr]$5s^1$, where the $5s$ orbital is diffuse reflecting a large screening effect of the Kr core. As an angular momentum of the orbital increases, in which the excited electron moves, the diffuseness largely increases. In Sr, the $5p$ orbital of $5s^1 5p^1 {}^1P$ is fairly diffuse in comparison with that of $5s^1 5p^1 {}^3P$. The broadness of the $5p$ atomic orbital (AO) in Sr ${}^1P$ arises from a repulsive exchange potential between the $5s$ and $5p$ electrons as in cases of Be $2s^1 2p^1 {}^1P$ [5, 10, 11, 17, 18], Mg $3s^1 3p^1 {}^1P$ [13], and Ca $4s^1 4p^1 {}^1P$ [14].

2.2. *Atoms Y through Cd*

In Fig. 1, we plot the total energy difference (ΔE) between the lowest state arising from $ns^1(n-1)d^{m+1}$ and that from $ns^2(n-1)d^m$:

$$\Delta E = \mathrm{TE}[ns^1(n-1)d^{m+1}] - \mathrm{TE}[ns^2(n-1)d^m], \tag{1}$$

where TE stands for the total energy and n is a principal quantum number of AOs; $n = 4$ for the first row transition atoms and $n = 5$ for the second row transition atoms. It is seen that for the first row transition metal atoms the lowest state from $4s^2 3d^m$ is lower than that from $4s^1 3d^{m+1}$ except for Cr and Cu. The ground state therefore arises from $4s^2 3d^m$ except these two atoms. For the second row transition metal atoms, however, the lowest state from $5s^1 3d^{m+1}$ is lower than that from $5s^2 4d^m$ except for Y and Mn and the ground state has the configuration of $5s^1 4d^{m+1}$ except for Y, Tc, and Pd: the ground configuration for Pd is $5s^0 4d^{10}$. The reason is discussed below for the different preference of the ground configurations between the first and second row transition metal atoms.

In Fig. 2, we give the d orbital energies of the lowest states arising from the $4s^2 3d^m$, $4s^1 3d^{m+1}$, $5s^2 4d^m$, and $5s^1 4d^{m+1}$ configurations. It is interesting that the $4d$ orbital energies of $5s^1 4d^{m+1}$ are nearly equal to the $3d$ orbital energies of $4s^1 3d^{m+1}$. Then the Koopmans' theorem suggests the similarity of the d ionization energies in the $5s^1 4d^{m+1}$ and $4s^1 3d^{m+1}$ configurations, but this is not true. We have calculated ionization energies (IEs) using ΔSCF method:

$$\mathrm{IE} = \mathrm{TE}[ns^1(n-1)d^m] - \mathrm{TE}[ns^1(n-1)d^{m+1}]. \tag{2}$$

Results are shown in Fig. 3 where IEs for K, Ca, Rb, and Sr are defined as

$$\mathrm{IE} = \mathrm{TE}[ns^{m-1}] - \mathrm{TE}[ns^{m-1}(n-1)d^1] \quad (m = 1, 2). \tag{3}$$

Table 1. Numerical Hartree–Fock results for low-lying electronic states of the atoms Rb through Xe (all in a.u.)

					Orbital energies of outermost s, p, and d orbitals			Mean value of r for outermost s, p, and d orbitals		
Atom	Configuration	State[a]	$-$TE	ΔE	$-\varepsilon_s$	$-\varepsilon_p$	$-\varepsilon_d$	$\langle r \rangle_s$	$\langle r \rangle_p$	$\langle r \rangle_d$
37 Rb	[Kr] 5*s*(1)	^2S	2938.35745	0.00000	0.13787	0.81007	4.73229	5.63187	1.73495	0.52133
	[Kr] 5*p*(1)	^2P	2938.31008	0.04737	1.57141	0.09016	4.78179	1.49963	7.64549	0.52132
	[Kr] 4*d*(1)	^2D	2938.28005	0.07740	1.58293	0.87083	0.06018	1.50001	1.73034	8.90492
38 Sr	[Kr] 5*s*(2)	^1S	3131.54569	0.00000	0.17846	1.09816	5.69440	4.63297	1.57762	0.49501
	[Kr] 5*s*(1)5*p*(1)	^3P	3131.51075	0.03494	0.23679	0.14051	5.72781	4.49152	5.62903	0.49501
		^1P	3131.45490	0.09079	0.23074	0.08131	5.77229	4.05118	8.33687	0.49499
	[Kr] 5*s*(1)4*d*(1)	^3D	3131.48454	0.06115	0.18079	1.04728	0.12246	4.74531	1.58842	3.81369
		^1D	3131.45530	0.09039	0.14555	1.04182	0.10799	5.22088	1.59115	3.41910
39 Y	[Kr] 5*s*(2)4*d*(1)	^2D	3331.68417	0.00000	0.19614	1.30119	0.24985	4.30000	1.47117	2.43521
	[Kr] 5*s*(1)4*d*(2)	^4F	3331.66876	0.01541	0.19399	1.21792	0.19518	4.41822	1.48418	2.75212
		^2S	3331.56025	0.12392	0.19877	1.26827	0.11113	4.37182	1.47778	3.19552
	[Kr] 5*s*(0)4*d*(3)	^4F	3331.58402	0.10015	2.01664	1.16833	0.14184	1.32596	1.49276	3.09849
		$^2D_1$	3331.50071	0.18346	2.07029	1.21887	0.10728	1.32333	1.48671	3.42097
40 Zr	[Kr] 5*s*(1)4*d*(3)	^5F	3539.00960	0.00000	0.20568	1.38749	0.25049	4.17531	1.39797	2.33224
		^5P	3538.97245	0.03715	0.20951	1.39735	0.22931	4.14341	1.39661	2.37613
		$^1D[d(^2D_1)]$	3538.85353	0.15607	0.17510	1.42513	0.18278	4.54116	1.39480	2.41337
	[Kr] 5*s*(2)4*d*(2)	^3F	3538.99506	0.01454	0.20729	1.48760	0.33676	4.09185	1.38557	2.10449
		^1S	3538.86396	0.14564	0.21611	1.51721	0.21259	4.00620	1.38131	2.31028
	[Kr] 5*s*(0)4*d*(4)	^5D	3538.93212	0.07748	2.22627	1.31643	0.17602	1.25973	1.40740	2.57102
		$^1S_0$	3538.74675	0.26285	2.30860	1.39350	0.12265	1.25578	1.39907	2.85819
41 Nb	[Kr] 5*s*(1)4*d*(4)	^6D	3753.59773	0.00000	0.21559	1.55699	0.30065	3.98545	1.32429	2.07123
		$^4D[d(^5D)]$	3753.54987	0.04786	0.16148	1.56900	0.31036	4.77856	1.32577	2.00285
		$^2S[d(^1S_0)]$	3753.33043	0.26730	0.20681	1.61441	0.20614	4.07778	1.31872	2.20301
	[Kr] 5*s*(0)4*d*(5)	^6S	3753.55453	0.04320	2.43154	1.46251	0.21554	1.20202	1.33447	2.23568
		^2P	3753.32143	0.27630	2.50386	1.52977	0.15990	1.19859	1.32774	2.39282

Table 1. (Continued)

Atom	Configuration	State[a]	− TE	ΔE	Orbital energies of outermost s, p, and d orbitals			Mean value of r for outermost s, p, and d orbitals		
					$-\varepsilon_s$	$-\varepsilon_p$	$-\varepsilon_d$	$\langle r\rangle_s$	$\langle r\rangle_p$	$\langle r\rangle_d$
	[Kr] 5*s*(2)4*d*(3)	^4F	3753.55203	0.04570	0.21660	1.67227	0.40587	3.92840	1.31263	1.89972
		$^2D_1$	3753.40186	0.19587	0.22252	1.69553	0.31431	3.87073	1.30966	1.98610
42 Mo	[Kr] 5*s*(1)4*d*(5)	^7S	3975.54950	0.00000	0.22273	1.72363	0.35792	3.84193	1.26042	1.87516
		^5S	3975.49783	0.05167	0.16505	1.74085	0.37295	4.67620	1.26158	1.82678
		^1P	3975.21897	0.33053	0.18944	1.77891	0.27290	4.22196	1.25654	1.92860
	[Kr] 5*s*(2)4*d*(4)	^5D	3975.44332	0.10618	0.22466	1.85737	0.47001	3.79381	1.24904	1.74696
		$^1S_0$	3975.14689	0.40261	0.23378	1.89561	0.34055	3.71062	1.24489	1.83934
	[Kr] 5*s*(0)4*d*(6)	^5D	3975.40565	0.14385	2.66769	1.63868	0.23048	1.14935	1.26797	2.04573
		$^1S_0$	3975.16020	0.38930	2.73067	1.69724	0.18460	1.14663	1.26288	2.14367
43 Tc	[Kr] 5*s*(2)4*d*(5)	^6S	4204.78874	0.00000	0.23127	2.04122	0.54395	3.68481	1.19303	1.62024
		^4G	4204.68030	0.10844	0.23343	2.05198	0.50607	3.66418	1.19198	1.63756
		^2P	4204.44968	0.33906	0.23849	2.07543	0.42676	3.61909	1.18974	1.67666
	[Kr] 5*s*(1)4*d*(6)	^6D	4204.78135	0.00739	0.22333	1.91368	0.37851	3.77697	1.20217	1.74562
		$^4D[d(^5D)]$	4204.73930	0.04944	0.17671	1.92866	0.39148	4.40476	1.20291	1.71689
		$^2S[d(^1S_0)]$	4204.46438	0.32436	0.21246	1.96045	0.30811	3.89060	1.19878	1.79350
	[Kr] 5*s*(0)4*d*7)	^4F	4204.69215	0.09659	2.89685	1.80954	0.25371	1.10244	1.20982	1.88212
		$^2D_1$	4204.54212	0.24662	2.92776	1.83822	0.22938	1.10119	1.20758	1.91709
44 Ru	[Kr] 5*s*(1)4*d*(7)	^5F	4441.53949	0.00000	0.22243	2.10125	0.41278	3.73560	1.15057	1.63011
		$^3F[d(^4F)]$	4441.50732	0.03217	0.18702	2.11387	0.42385	4.19313	1.15102	1.61357
		$^1D[d(^2D_1)$	4441.33610	0.20339	0.19837	2.13069	0.38254	4.01876	1.14930	1.63896
	[Kr] 5*s*(2)4*d*(6)	^5D	4441.48735	0.05214	0.23990	2.24151	0.56902	3.56547	1.14161	1.53320
		$^1S_0$	4441.14388	0.39561	0.24634	2.27335	0.47389	3.51028	1.13897	1.57236
	[Kr] 5*s*(0)4*d*(8)	^3F	4441.47729	0.06220	3.12667	1.98197	0.27852	1.06001	1.15786	1.74692
		^1S	4441.31475	0.22474	3.15516	2.00842	0.25585	1.05895	1.15603	1.77169
45 Rh	[Kr] 5*s*(1)4*d*(8)	^4F	4685.88170	0.00000	0.22162	2.29115	0.45020	3.70246	1.10403	1.53146
		^2F	4685.85867	0.02303	0.19643	2.30101	0.45896	4.01766	1.10429	1.52227
		^2S	4685.68447	0.19723	0.21662	2.31357	0.41858	3.75782	1.10277	1.54441

Table 1. (Continued)

					Orbital energies of outermost s, p, and d orbitals			Mean value of r for outermost s, p, and d orbitals		
Atom	Configuration	State[a]	$-$ TE	ΔE	$-\varepsilon_s$	$-\varepsilon_p$	$-\varepsilon_d$	$\langle r\rangle_s$	$\langle r\rangle_p$	$\langle r\rangle_d$
	[Kr] $5s(0)4d(9)$	^2D	4685.84699	0.03471	3.35800	2.15662	0.30465	1.02132	1.11098	1.63289
	[Kr] $5s(2)4d(7)$	^4F	4685.80125	0.08045	0.24711	2.44092	0.61135	3.46718	1.09555	1.45117
		$^2D_1$	4685.59994	0.28176	0.25011	2.45705	0.56421	3.44194	1.09436	1.46617
46 Pd	[Kr] $5s(0)4d(10)$	^1S	4937.92102	0.00000	3.58731	2.33009	0.33600	0.98596	1.06857	1.53306
	[Kr] $5s(1)4d(9)$	^3D	4937.89347	0.02755	0.22097	2.48385	0.49001	3.67481	1.06174	1.44600
		^1D	4937.87881	0.04221	0.20503	2.49064	0.49612	3.86910	1.06187	1.44136
	[Kr] $5s(2)4d(8)$	^3F	4937.78303	0.13799	0.25365	2.64286	0.65735	3.38086	1.05371	1.37785
		^1S	4937.57086	0.35016	0.25635	2.65825	0.61483	3.35894	1.05271	1.38904
47 Ag	[Kr] $5s(1)4d(10)$	^2S	5197.69847	0.00000	0.21998	2.67682	0.53740	3.65649	1.02321	1.36980
	[Kr] $5s(2)4d(9)$	^2D	5197.51789	0.18058	0.25965	2.84773	0.70606	3.30399	1.01545	1.31211
48 Cd	[Kr] $4d(10)5s(2)$	^1S	5465.13314	0.00000	0.26486	3.05350	0.76366	3.23749	0.98039	1.25209
	[Kr] $4d(10)5s(1)5p(1)$	^3P	5465.05353	0.07961	0.35194	0.17948	0.81460	3.12580	4.13932	1.24745
		^1P	5464.97862	0.15452	0.35166	0.10019	0.88182	2.86943	6.46130	1.24500
	[Kr] $4d(10)5s(1)5d(1)$	^3D	5464.93511	0.19803	0.43591	3.24390	0.05655	2.91782	0.97998	10.21767
		^1D	5464.93286	0.20028	0.44243	3.25131	0.05426	2.89355	0.97999	10.93826
49 In	[Kr] $4d(10)5s(2)5p(1)$	^2P	5740.16916	0.00000	0.37266	0.19728	1.06314	2.84449	3.77795	1.15692
	[Kr] $4d(10)5s(1)5p(2)$	^4P	5740.08334	0.08582	0.48895	0.24443	1.09857	2.79734	3.50110	1.15422
		^2P	5739.91665	0.25251	0.37930	0.17227	1.15921	2.60323	4.16178	1.15202
50 Sn	[Kr] $4d(10)5s(2)5p(2)$	^3P	6022.93170	0.00000	0.47643	0.26504	1.36905	2.58591	3.24826	1.08040
		^1D	6022.89692	0.03478	0.48233	0.23259	1.37819	2.58079	3.32586	1.08017
		^1S	6022.84697	0.08473	0.49217	0.18759	1.39304	2.57214	3.46307	1.07982
	[Kr] $4d(10)5s(1)5p(3)$	^5S	6022.85068	0.08102	0.63498	0.31128	1.39628	2.55719	3.09622	1.07868
		^1P	6022.56359	0.36811	0.48221	0.20788	1.46222	2.46414	3.44414	1.07673
51 Sb	[Kr] $4d(10)5s(2)5p(3)$	^4S	6313.48532	0.00000	0.58177	0.33471	1.68787	2.39017	2.90114	1.01640
		^2D	6313.42622	0.05910	0.58894	0.29925	1.69937	2.38590	2.95188	1.01615
		^2P	6313.38765	0.09767	0.59399	0.27657	1.70735	2.38286	2.98866	1.01599

Table 1. (Continued)

Atom	Configuration	State[a]	− TE	ΔE	Orbital energies of outermost s, p, and d orbitals			Mean value of r for outermost s, p, and d orbitals		
					$-\varepsilon_s$	$-\varepsilon_p$	$-\varepsilon_d$	$\langle r\rangle_s$	$\langle r\rangle_p$	$\langle r\rangle_d$
	[Kr] $4d(10)5s(1)5p(4)$	^4P	6313.23804	0.24728	0.72771	0.32194	1.73825	2.36043	2.88659	1.01451
		^2P	6313.01768	0.46764	0.53600	0.28104	1.77696	2.30138	3.01120	1.01353
52 Te	[Kr] $4d(10)5s(2)5p(4)$	^3P	6611.78406	0.00000	0.70056	0.35983	2.03829	2.22797	2.69137	0.96118
		^1D	6611.74140	0.04266	0.70488	0.34146	2.04529	2.22607	2.71099	0.96106
		^1S	6611.67829	0.10577	0.71161	0.31471	2.05606	2.22309	2.74211	0.96088
	[Kr] $4d(10)5s(1)5p(5)$	^3P	6611.45555	0.32851	0.81616	0.35478	2.09107	2.20164	2.68072	0.95959
		^1P	6611.29499	0.48907	0.67144	0.33211	2.11393	2.17732	2.72833	0.95911
53 I	[Kr] $4d(10)5s(2)5p(5)$	^2P	6917.98090	0.00000	0.82112	0.40318	2.40121	2.09443	2.50175	0.91303
	[Kr] $4d(10)5s(1)5p(6)$	^2S	6917.56518	0.41572	0.90035	0.39993	2.45638	2.07051	2.49706	0.91168
54 Xe	[Kr] $4d(10)5s(2)5p(6)$	^1S	7232.13836	0.00000	0.94441	0.45729	2.77788	1.98096	2.33798	0.87045
	[Kr] $4d(10)5s(2)5p(5)6s(1)$	^3P	7231.82958	0.30878	0.12108	0.61595	2.97178	6.44840	2.23555	0.86956
		^1P	7231.82424	0.31412	0.11531	0.62092	2.97713	6.75497	2.22915	0.86957
	[Kr] $4d(10)5s(2)5p(5)6p(1)$	^3S	7231.80035	0.33801	1.11896	0.09167	2.99997	1.93230	7.81434	0.86953
		^1P	7231.78756	0.35080	1.13432	0.07861	3.01497	1.93206	8.86498	0.86954
	[Kr] $4d(10)5s(2)5p(5)5d(1)$	^3P	7231.79117	0.34719	1.05329	0.58644	0.08438	1.94118	2.25416	5.47615
		^1P	7231.76552	0.37284	1.15107	0.67499	0.05658	1.93178	2.22106	10.41388

[a] The symbol in the brackets denotes the coupling in the $4d$ shell

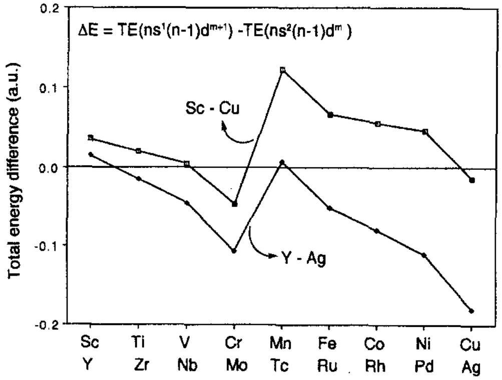

Fig. 1. Total energy difference between the lowest states from $ns^2(n-1)d^m$ and $ns^1(n-1)d^{m+1}$ configurations

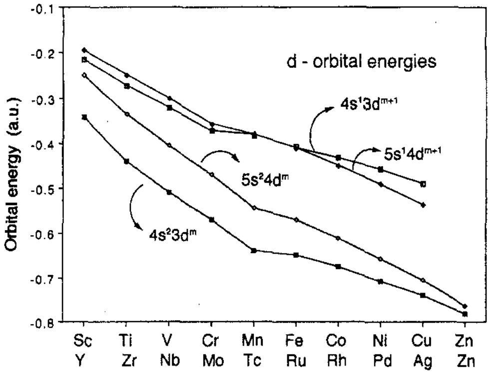

Fig. 2. The d orbital enegies for $ns^2(n-1)d^m$ and $ns^1(n-1)d^{m+1}$ configurations

In Fig. 3, we find that the IEs for the second row transition metal atoms are always larger than those of the corresponding atoms in the first row transition series. The IE difference between the two series of the transition metal atoms increases as we move along the period. Thus, the electron in $4d$ AO is stabler than that in the $3d$ AO in the s^1d^{m+1} configuration. The sudden decrease of IE at Mn and Tc is due to the fact that all the spins of the outermost s and d electrons are parallel in the ionic states and the precorrelation effect is larger for the ions than for the corresponding neutral atoms.

We define a screening constant S by

$$\mathrm{IE} = (Z - S)^2/2n^2, \tag{4}$$

where Z stands for the nuclear charge. We consider S for $5s$ and $4d$ in the field generated by $5s^14d^m$ and S for $4s$ and $3d$ in the field of $4s^13d^m$. The IE and S obtained from NHF and experiment [19] are given in Fig. 4 and Table 2, where the S values are subtracted by 18 and 36 for the first and second row transition metal atoms, respectively. We express the screening constant of $4s$ in $4s^23d^m$ as $S_{4s}(4s^23d^m)$ or S_{4s} and that of $5s$ in $5s^24d^m$ as $S_{5s}(5s^24d^m)$ or S_{5s}. In Fig. 4, the screening constants S_{4s} and S_{5s} are almost parallel and increase linearly as the number of the d electrons increases. The smaller values of S_{5s}-36 than S_{4s}-18

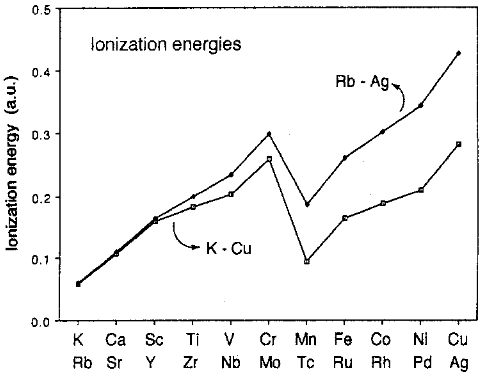

Fig. 3. The d ionization energies for $ns^1(n-1)d^{m+1}$ configurations calculated with ΔSCF

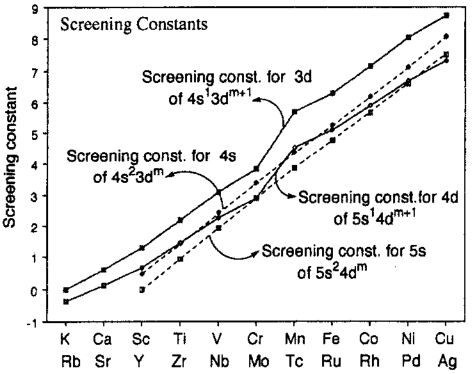

Fig. 4. Screening constants for d orbitals of $ns^1(n-1)d^{m+1}$ and for s orbitals of $ns^2(n-1)d^m$ calculated from the ΔSCF ionization energies. The values 18 and 36 are subtracted, respectively, for the fourth- and fifth-period atoms

indicate the incomplete screening of the Kr core compared with that of the Ar core. The NHF screening constants for 4s and 5s are described by

$$S_{4s}(4s^2 3d^m) = 17.58 + 0.95m \quad (m = 1\text{–}9) \tag{5}$$

and

$$S_{5s}(5s^2 4d^m) = 35.11 + 0.94m \quad (m = 1\text{–}9) \tag{6}$$

Next we express the screening constant of 3d in $4s^1 3d^{m+1}$ as S_{3d} $(4s^1 3d^{m+1})$ or S_{3d} and that of 4d in $5s^1 4d^{m+1}$ as $S_{4d}(5s^1 4d^{m+1})$ or S_{4d}. The behaviors of S_{3d} and S_{4d} are more complicated than S_{4s} and S_{5s}. It is seen in Fig. 4 that the difference between S_{5s} and S_{4d} is much smaller than that between S_{4s} and S_{3d}. At the Mo, Pd, and Ag atoms, S_{4d} is almost equal or smaller than S_{5s}, reflecting a larger binding (i.e., IE) of the 4d electrons than the 5s electrons. In Fig. 5, we give the differences $S_{3d} - S_{4s}$ and $S_{4d} - S_{5s}$. It is seen that $S_{3d} - S_{4s}$ oscillates around 0.8 and the changes in $S_{3d} - S_{4s}$ are approximately independent of the increase in the nuclear charge. On the other hand, $S_{4d} - S_{5s}$ has a trend to decrease as the nuclear charge increases. We found that NHF S_{3d} and S_{4d} are roughly expressed as

$$S_{3d}(4s^1 3d^{m+1}) = S_{4s} + 0.84 \quad (m = 1\text{–}9) \tag{7}$$

Table 2. d electron ionization energies from $ns^1\,(n-1)d^{m+1}$, s electron ionization energies from $ns^2(n-1)d^m$, and screening constants by experiment and ΔSCF

Fourth period atoms					Fifth period atoms				
Atom	IE(ΔSCF)	S(ΔSCF)-18	IE(Exptl)	S(Exptl)-18	Atom	IE(ΔSCF)	S(ΔSCF)-36	IE(Exptl)	S(Exptl)-36
d-electron									
K	0.05813 a.u.	− 0.02293	0.06143 a.u.	− 0.05151	Rb	0.06012 a.u.	− 0.38703	0.06535 a.u.	− 0.44614
Ca	0.10725	0.061059	0.13197	0.45876	Sr	0.11076	0.11736	0.12615	− 0.00918
Sc	0.15964	1.30484	0.18880	1.15651	Y	0.16551	0.69863	0.19405	0.50811
Ti	0.18275	2.18629	0.22175	2.00215	Zr	0.20030	1.46828	0.23420	1.26238
V	0.20337	3.08671	0.25069	2.87576	Nb	0.23510	2.25715	0.26150	2.10722
Cr	0.25928	3.83967	0.30472	3.65799	Mo	0.29845	2.90963	0.31939	2.80305
Mn	0.09458	5.69522	0.19447	5.12904	Tc	0.18699	4.55384	0.25266	4.15656
Fe	0.16461	6.27867	0.25828	5.84382	Ru	0.26088	5.11068	0.31109	4.84486
Co	0.18764	7.16220	0.28918	6.71848	Rh	0.30214	5.89058	0.35333	5.63750
Ni	0.20968	8.05726	0.32004	7.59986	Pd	0.34405	6.68193	0.39545	6.44271
Cu	0.28259	8.74465	0.38734	8.35952	Ag	0.42521	7.31127	0.46368	7.14803
s electron									
Sc	0.19657	0.49194	0.24127	0.22139	Y	0.18092	− 0.00766	0.24401	− 0.49290
Ti	0.20260	1.45381	0.25137	1.16382	Zr	0.18576	0.95238	0.25581	0.42364
V	0.20793	2.42054	0.25970	2.11724	Nb	0.18940	1.92266	0.25473	1.43118
Cr	0.21272	3.39097	0.26784	3.07239	Mo	0.19227	2.89944	0.26545	2.35684
Mn	0.21687	4.36564	0.27334	4.04247	Tc	0.19438	3.88247	0.26760	3.34213
Fe	0.23066	5.28318	0.29045	4.95131	Ru	0.20874	4.76937	0.27919	4.26383
Co	0.24381	6.20681	0.30452	5.87835	Rh	0.22169	5.67066	0.29336	5.17011
Ni	0.25656	7.13470	0.31894	6.80530	Pd	0.23361	6.58233	0.30624	6.08697
Cu	0.26893	8.06644	0.33254	7.73788	Ag	0.24463	7.50264	0.31766	7.01468

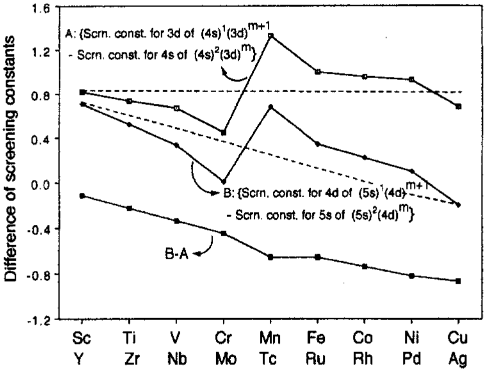

Fig. 5. Differences of screening constants between 4*d* and 5*s* and those between 3*d* and 4*s* given by $ns^1(n-1)d^m$ core

and

$$S_{4d}(5s^1 4d^{m+1}) = S_{5s} + 0.70 - 0.08m \quad (m = 1\text{–}9). \tag{8}$$

The 3*d* electron moves in the field of effective charge which is smaller than that of 4*s* by a constant amount, while the 4*d* electron moves in the field of effective nuclear charge which increases faster than that for 5*s* as the number of the *d* electrons increases. Since the 4*d* AO is more diffuse than the 3*d* AO, the screening effect for a 4*d* electron by the other 4*d* electrons is smaller than that for a 3*d* by the other 3*d*s; the screening for 4*d* increases more slowly than that for 3*d*, when the number of *d* electrons increases. Thus, the difference between S_{3d} and S_{4d} shown in Eqs. (7) and (8) is natural. (See also the line A–B in Fig. 5 which shows the difference of the *Z* dependence between S_{3d} and S_{4d} since that between S_{4s} and S_{5s} is almost the same.) The growing effective nuclear charge for 4*d* is expected to reverse the energetic order of $5s^2 4d^m$ and $5s^1 4d^{m+1}$ at some value of *m*. We here note that the effective charge as well as the principal quantum number determines the ionization energies. From Eq. (4) one obtains the nuclear charge which reverses the energetic order of $ns^1(n-1)d^{m+1}$ and $ns^2(n-1)d^m$:

$$Z > nS_{(n-1)d} - (n-1)S_{ns}. \tag{9}$$

Using Eqs. (6), (8), $m = Z - 38$, and the relation (9), one may find that the energetic order reverses at an atom with $Z = 39.3$ and it actually happens at the Zr atom ($Z = 40$) in Fig. 1. Using (5), (6), $m = Z - 20$, and (9), on the other hand, one may see that $4s^1 3d^{m+1}$ never becomes lower than $4s^2 3d^m$ so far as we consider the neutral first row transition metal atoms.

The screening constants for *s* electrons given by experimental IEs in Table 2 are described by

$$S_{4s}(4s^2 3d^m\text{: exptl}) = 17.30 + 0.94m \quad (m = 1\text{–}9) \tag{10}$$

and

$$S_{5s}(5s^2 4d^m\text{: exptl}) = 34.59 + 0.94m \quad (m = 1\text{–}9), \tag{11}$$

and those for *d* electrons are roughly expressed as

$$S_{3d}(4s^1 3d^{m+1}\text{: exptl}) = S_{4s} + 0.82 \quad (m = 1\text{–}9) \tag{12}$$

and

$$S_{4d}(5s^14d^{m+1}\text{: exptl}) = S_{5s} + 1.02 - 0.09m \quad (m = 1\text{–}9). \tag{13}$$

Using Eqs. (11), (13), $m = Z - 38$, and the relation (9), we find that the energetic order reverses at an atom with $Z = 41.3$ and it actually happens at the Nb atom ($Z = 41$; see [19]). The agreement between the NHF calculations and experiments is rather well. We thus confirmed the argument given by the NHF calculations.

In order to develop clear discussion, we have above fitted the screening constants given in Table 2 to a linear function of the number of electrons m. However, the screening constants in Table 2 can be directly used to derive the critical nuclear charge. Such results are discussed in the appendix.

Table 2 shows that the screening from the Ar core is almost complete but that from the Kr core is not. We thus summarize the reasons why the second row transition metal atoms prefer the configuration $5s^14d^{m+1}$:

a) the incomplete screening of the Kr core, and
b) the smaller screening for $4d$ which is proportional to the number of $4d$ electrons in the $5s^14d^m$ core.

Concerning s^1d^{m+1} and s^2d^m configurations, we finally comment that the calculated ground state for Zr is $5s^14d^3\,{}^5F$, but $5s^24d^2\,{}^3F$ is known to be the ground state experimentally [19]. This is only the case where the Hartree–Fock approximation fails to predict the true ground state among the atoms He through Xe.

2.3. *Atoms In through Xe*

From the atom In to Xe, the electronic configuration for the ground states is $5s^25p^m$. We compare the mean value of r, $\langle r\rangle$, of the outermost s and p orbitals of the atoms of the groups 1, 2, and 13–18 in Table 3. We see that $\langle r\rangle_s$ and $\langle r\rangle_p$ of the atoms in the same group increase as we move from the second to the fifth period with the sole exception of a small decrease in $\langle r\rangle_s$ and $\langle r\rangle_p$ at Ga compared with those of Al. We may briefly sum up the trend as

$$\langle r\rangle_{5s} > \langle r\rangle_{4s} > \langle r\rangle_{3s} \gg \langle r\rangle_{2s}, \tag{14}$$

$$\langle r\rangle_{5p} > \langle r\rangle_{4p} > \langle r\rangle_{3p} \gg \langle r\rangle_{2p} \tag{15}$$

and

$$\langle r\rangle_{5p} - \langle r\rangle_{5s} > \langle r\rangle_{4p} - \langle r\rangle_{4s} > \langle r\rangle_{3p} - \langle r\rangle_{3s} \gg \langle r\rangle_{2p} - \langle r\rangle_{2s}. \tag{16}$$

In Table 4 we list the excitation energies of the lower excited states of the second to the fifth period atoms. It is seen that the excitation energies from ns^2np^m to ns^1np^{m+1} of atoms in the groups 13 and 14 have a local maximum at the fourth period atoms as we move down the periodic table. In many cases, excitation energies of the remaining groups (1, 2, 15–18) decrease as the nuclear charge increases.

3. Concluding remarks

In this paper we developed numerical Hartree–Fock wave function from Rb to Xe. Total 332 states were calculated. We discussed why the second row transition metal

Table 3. Mean value of r for the atoms with the ground state configuration of ns^1np^m (all in a.u.)

		Period			
Group	Atoms	2nd	3rd	4th	5th
			$\langle r\rangle_{ns}$		
1	Li, Na, K, Rb	3.8737	4.2088	5.2437	5.6319
2	Be, Mg, Ca, Sr	2.6494	3.2529	4.2185	4.6330
13	B, Al, Ga, In	1.9771	2.5993	2.4889	2.8445
14	C, Si, Ge, Sn	1.5893	2.2071	2.2258	2.5859
15	N, P, As, Sb	1.3323	1.9327	2.0297	2.3902
16	O, S, Se, Te	1.1420	1.7207	1.8692	2.2280
17	F, Cl, Br, I	1.0011	1.5556	1.7389	2.0944
18	Ne, Ar, Kr, Xe	0.8921	1.4222	1.6294	1.9810
			$\langle r\rangle_{np}$		
13	B, Al, Ga, In	2.2048	3.4339	3.4243	3.7780
14	C, Si, Ge, Sn	1.7145	2.7522	2.8669	3.2483
15	N, P, As, Sb	1.4096	2.3227	2.5123	2.9011
16	O, S, Se, Te	1.2322	2.0607	2.2996	2.6914
17	F, Cl, Br, I	1.0848	1.8420	2.1116	2.5018
18	Ne, Ar, Kr, Xe	0.9653	1.6630	1.9516	2.3380
			$\langle r\rangle_{np} - \langle r\rangle_{ns}$		
13	B, Al, Ga, In	0.2277	0.8346	0.9354	0.9335
14	C, Si, Ge, Sn	0.1252	0.5451	0.6411	0.6624
15	N, P, As, Sb	0.0773	0.3900	0.4826	0.5109
16	O, S, Se, Te	0.0902	0.3400	0.4304	0.4634
17	F, Cl, Br, I	0.0837	0.2864	0.3727	0.4074
18	Ne, Ar, Kr, Xe	0.0732	0.2408	0.3222	0.3570

Table 4. Excitation energies from the ground configuration of $ns^1\,np^m$ (all in a.u.)

			Period				
Group	Atoms	States		2nd	3rd	4th	5th
1	Li, Na, K, Rb	$ns(1)$	^2S	0.00000	0.00000	0.00000	0.00000
		$np(1)$	^2P	0.06766	0.07250	0.05164	0.04737
		$(n-1)d(1)$	^2D			0.08908	0.07740
2	Be, Mg, Ca, Sr	$ns(2)$	^1S	0.00000	0.00000	0.00000	0.00000
		$ns(1)np(1)$	^3P	0.06152	0.06792	0.06243	0.03494
			^1P	0.17829	0.14351	0.10185	0.09079
		$ns(1)(n-1)d(1)$	^3D			0.08093	0.06115
			^1D			0.10724	0.09039
13	B, Al, Ga, In	$ns(2)np(1)$	^2P	0.00000	0.00000	0.00000	0.00000
		$ns(1)np(2)$	^4P	0.07840	0.08584	0.11237	0.08582
			^2D	0.21719	0.18502	0.21282	0.17677
			^2S	0.28097	0.23146	0.26013	0.22045
			^2P	0.35002	0.27063	0.29707	0.25251

Table 4. (Continued)

				Period			
Group	Atoms	States		2nd	3rd	4th	5th
14	C, Sl, Ge, Sn	$ns(2)np(2)$	^3P	0.00000	0.00000	0.00000	0.00000
			^1D	0.05729	0.03915	0.03838	0.03478
			^1S	0.13901	0.09528	0.09335	0.08473
		$ns(1)np(3)$	^5S	0.08940	0.09132	0.11446	0.08102
			^3D	0.29425	0.23426	0.25397	0.20488
			^3P	0.35090	0.27407	0.29317	0.24021
			^1D	0.51900	0.38795	0.40169	0.33501
			^3S	0.54650	0.40510	0.41626	0.34650
			^1P	0.57283	0.42519	0.43826	0.36811
15	N, P, As, Sb	$ns(2)np(3)$	^4S	0.00000	0.00000	0.00000	0.00000
			^2D	0.10476	0.06991	0.06649	0.05910
			^2P	0.17283	0.11548	0.10983	0.09767
		$ns(1)np(4)$	^4P	0.41265	0.30226	0.31127	0.24728
			^2D	0.61729	0.44114	0.44191	0.36131
			^2S	0.71752	0.50945	0.50705	0.41914
			^2P	0.81699	0.57578	0.56590	0.46764
16	O, S, Se, Te	$ns(2)np(4)$	^3P	0.00000	0.00000	0.00000	0.00000
			^1D	0.08013	0.05254	0.04865	0.04266
			^1S	0.19838	0.13022	0.12059	0.10577
		$ns(1)np(5)$	^3P	0.62549	0.42603	0.41609	0.32851
			^1P	0.93736	0.63364	0.60419	0.48907
17	F, Cl, Br, I	$ns(2)np(5)$	^2P	0.00000	0.00000	0.00000	0.00000
		$ns(1)np(6)$	^2S	0.87811	0.56531	0.52983	0.41572
18	Ne, Ar, Kr, Xe	$ns(2)np(6)$	^1S	0.00000	0.00000	0.00000	0.00000
		$ns(2)np(5)(n+1)s(1)$	^3P	0.55478	0.40077	0.35343	0.30878
			^1P	0.56089	0.40676	0.35958	0.31412
		$ns(2)np(5)(n+1)p(1)$	^3S	0.61509	0.44139	0.39058	0.33801
			^3D	0.62107	0.44906	0.39859	0.34626
			^1D	0.62283	0.45082	0.40031	0.34791
			^1S	0.62729	0.45335	0.40205	0.34889
			^3P	0.62442	0.45331	0.40300	0.35080
			^1P	0.62442	0.45331	0.40300	0.35080
		$ns(2)np(5)nd(1)$	^3P		0.47882	0.41963	0.34719
			^3F		0.48244	0.42466	0.35716
			^1F		0.48455	0.42788	0.36555
			^3D		0.48636	0.43029	0.36881
			^1D		0.48636	0.43029	0.36881
			^1P		0.48649	0.43102	0.37284

atoms prefer the configuration $5s^14d^{m+1}$. The reasons are: (a) the incomplete screening of the Kr core and (b) the smaller screening for $4d$ which is proportional to the number of $4d$ electrons in the $5s^14d^m$ core.

In atomic and molecular calculations, we often use analytical approximations of Hartree–Fock wave functions. The excitation energies, the mean distance of r given in this paper, the electron affinities, and the ionization energies given in

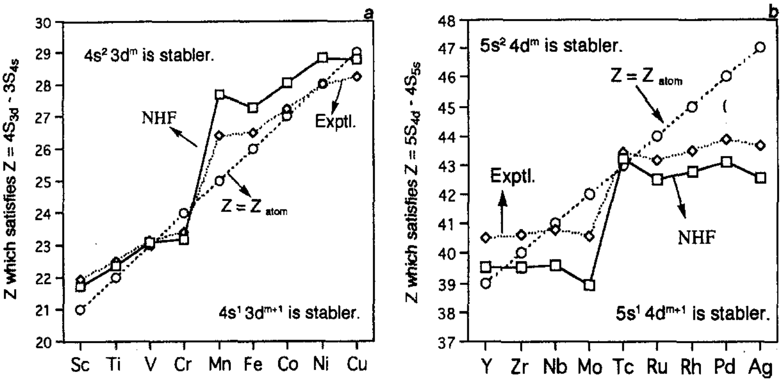

Fig. 6. Nuclear charge which gives $ns^1(n-1)d^{m+1}$ stabler than $ns^2(n-1)d^m$. a) For Sc to Cu. b) For Y to Ag

the previous papers [9, 13–15] would be useful for constructing the basis sets for molecules including the transition metal atoms. Full details of the present results are available on 3.5 in diskettes upon request to TK or HT.

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Appendix

The critical nuclear charge specified by the inequality (9) can also be directly calculated from the screening constants given in Table 2. The results are depicted in Fig. 6. For the first transition metal atoms, the NHF and experimental screening constants give the same stable configurations with the sole exception of Ni which will be explained below; in most cases $4s^2 3d^m$ is stabler than $4s^1 3d^{m+1}$. The results confirm what we have discussed in the main text. One may wonder why Ni $4s^1 3d^9$ is stabler than $4s^2 3d^8$ in experiment although the experimental ground configuration is $4s^2 3d^8$. Moore [19] gives the ground state as $4s^2 3d^8\,{}^3F_4$. Even if one adopts the gravity of the energetic states generated from the same spatial and spin configuration with different total angular momentum, ordinary the ground configuration does not change. In Ni, however, the gravity of $4s^2 3d^8\,{}^3F_4$, ${}^3F_3$, and ${}^3F_2$ in 240 cm^{-1} higher than that of $4s^1 3d^9\,{}^3D_3$, ${}^3D_2$, and ${}^3D_1$. So far as we discuss the electronic structure under the LS coupling scheme, we may change the experimental ground configuration from ${}^3F$ to ${}^3D$.

In the second row transition metal atoms, the calculated nuclear charge which satisfies the relation (9) always predicts that $5s^1 4d^{m+1}$ is stabler than $5s^2 4d^m$ except for Y and Tc (see Fig. 6b). Except for Tc, this is what we concluded in the main text based on a fitting of screening constants S to a linear function of number electrons m. We thus see good agreement between the NHF calculations and experiment, confirming again the discussion in the main text.

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