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Atomic Negative Ions: The Iron Series

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Results of the Hartree-Fock calculations on the ground state for the ions K$^-$(^1S), Sc$^-$(^3F), Ti$^-$(^4F), V$^-$(^5D), Cr2$^-$(^6S), Mn$^-$(^5D), Fe$^-$(^4F), Co$^-$(^3F), Ni$^-$(^2D), and Cu$^-$(^1S) are reported. By first-order perturbation calculation on the Hartree-Fock functions, the relativistic energy has been computed. The relativistic and the Hartree-Fock energies now available, and the correlation energy of the corresponding neutral atoms, previously obtained, make it feasible to obtain accurate estimate of the electron affinities for the above series of negative ions. These are 0.92, −0.14, 0.40, 0.94, 0.98, −1.07, 0.58, 0.94, 1.28, 1.80 eV for K$^-$, Sc$^-$, Ti$^-$, V$^-$, Cr$^-$, Mn$^-$, Fe$^-$, Co$^-$, Ni$^-$, and Cu$^-$, respectively, for the states above indicated. The uncertainty on the above data is estimated to be from 0.1 to 0.35 eV.

I. INTRODUCTION

IN this third paper on the negative ions,[1,2] we extend the theoretical analysis of the stability of the negative ions to the elements of the iron series. As done previously we have computed the Hartree-Fock energy and wave functions. A careful optimization of the orbital exponents for the basis set, although somewhat laborious and expensive in terms of the required computer time, was necessitated by the fact that the computed total energies must be accurate to within a few parts in 10^7. Indeed only with such an accuracy can we draw meaningful conclusions about the stability of the negative ions in the third period of the atomic system. A simple example can illustrate the need for such accuracy. Let us consider F(^2P state), F$^-$(^1S state), Cu (^2D state), and Cu$^-$(^1S state): the corresponding Hartree-Fock total energies are -99.409293 a.u., -99.459360 a.u., -1638.9606 a.u., and -1638.9624 a.u. The relative stabilities of F$^-$ to F and Cu$^-$ to Cu are therefore (considering only the Hartree-Fock energy for the moment) 0.050077 a.u. and 0.0018 a.u., respectively. In the first case (F and F$^-$) an uncertainty of ±1 in the seventh decimal figure corresponds to 0.003 eV uncertainty, in the second case (Cu and Cu$^-$) the same uncertainty of ±1 in the seventh figure corresponds to 0.03 eV uncertainty. Since the electron affinities are at the most on the order of a few electron volts, it is clear that an uncertainty of 0.03 eV can not be neglected if one wishes to obtain an accurate prediction of the stability of the negative ions. To make this above consideration even more stringent, we note that we heavily rely on such accuracy since we have to compute small differences between large quantities, as the Cu and Cu$^-$ example illustrates. For this reason, although more work has been devoted to this computation than to the preceding one,[1,2] the results might be less accurate.

On the other hand, our experimental knowledge[3] on the stability of the negative ions in the third period is so limited at present that our prediction, even if less accurate than those for the first two periods of the atomic system, should be extremely useful.

II. THE HARTREE-FOCK FUNCTIONS

The computation of the Hartree-Fock functions for the negative ions is not simply a by product in the analysis of the stability of the negative ions. Indeed these functions are of intrinsic value in that they furnish the first required information in order to com-

TABLE I. Potassium negative ion (^1S).

	S basis	$1s$	$2s$	$3s$	$4s$		P basis	$2p$	$3p$
$1s$	19.06810	+0.93330	−0.27169	+0.09046	+0.01243	$2p$	8.63410	+0.66861	−0.20571
$1s$	30.84670	+0.01816	−0.00348	+0.00068	−0.00001	$2p$	15.20120	+0.04211	−0.01263
$2s$	16.87060	+0.05955	−0.14146	+0.04934	+0.00641	$3p$	6.91269	+0.34538	−0.13525
$2s$	7.51000	+0.00462	+0.98301	−0.35132	−0.04711	$3p$	3.48000	+0.01382	+0.42887
$3s$	6.54286	−0.00273	+0.15045	−0.19797	−0.03200	$3p$	2.28513	−0.00465	+0.50698
$3s$	3.95350	+0.00209	+0.00151	+0.48726	+0.08399	$3p$	1.65156	+0.00140	+0.18452
$3s$	2.61230	−0.00225	+0.00602	+0.61958	+0.08092				
$4s$	2.54324	+0.00116	−0.00289	+0.08752	+0.01425				
$4s$	0.34514	−0.00001	+0.00004	+0.00094	−0.37571				
$4s$	1.26173	−0.00010	+0.00034	+0.01040	−0.25517				
$4s$	0.6152	+0.00004	−0.00014	−0.00331	−0.57465				
	$-\epsilon$[a]	133.41312	14.37001	1.62894	0.01021			11.39934	0.83454

[a] The orbital energies ϵ, are given in atomic units.

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[1] E. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964).

[2] E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).

[3] L. M. Branscomb, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962).

TABLE II. Scandium negative ion (^3F).

S basis		1*s*	2*s*	3*s*	4*s*	*P* basis		2*p*	3*p*	*D* basis		3*d*
1*s*	20.87910	+0.94520	−0.28690	+0.10151	−0.01520	2*p*	9.58918	+0.68533	−0.22979	3*d*	3.26577	+0.30758
1*s*	33.10000	+0.02056	−0.00104	−0.00038	−0.00024	2*p*	16.47600	+0.04662	−0.01504	3*d*	8.54690	+0.02229
2*s*	18.00780	+0.04345	−0.15327	+0.05636	−0.00982	3*p*	7.86514	+0.31769	−0.14425	3*d*	4.87290	+0.07922
2*s*	8.60000	+0.00309	+0.98276	−0.37075	+0.06040	3*p*	4.14168	+0.01444	+0.43160	3*d*	1.62554	+0.54356
3*s*	7.37980	−0.00181	+0.18253	−0.25419	+0.03597	3*p*	2.83910	−0.00470	+0.48038	3*d*	0.73442	+0.28721
3*s*	4.73540	+0.00168	−0.02527	+0.51908	−0.05405	3*p*	2.06791	+0.00142	+0.21725			
3*s*	3.20865	−0.00193	+0.03497	+0.52737	−0.18082							
4*s*	3.22655	+0.00100	−0.01773	+0.19450	+0.04329							
4*s*	1.52776	−0.00007	+0.00123	+0.01799	+0.22627							
4*s*	0.96025	+0.00003	−0.00061	−0.00687	+0.48331							
4*s*	0.49289	−0.00001	+0.00015	+0.00158	+0.47270							
	$-\epsilon$[a]	165.61011	18.76899	2.26563	0.01553			15.36041	1.28758			0.05999

[a] See footnote to Table I.

TABLE III. Titanium negative ion (^4F).

S basis		1*s*	2*s*	3*s*	4*s*	*P* basis		2*p*	3*p*	*D* basis		3*d*
1*s*	21.78320	+0.95032	−0.29233	+0.10611	−0.01515	2*p*	10.00560	+0.69304	−0.23102	3*d*	1.88584	+0.51194
1*s*	34.57420	+0.02148	−0.00056	−0.00114	−0.00012	2*p*	16.79230	+0.05359	−0.01995	3*d*	9.10000	+0.02858
2*s*	18.70590	+0.03562	−0.15771	+0.05631	−0.00944	3*p*	8.32711	+0.29913	−0.16469	3*d*	4.40390	+0.24042
2*s*	9.30981	+0.00438	+0.93714	−0.35118	+0.05477	3*p*	4.73525	+0.01303	+0.40944	3*d*	3.17000	+0.17625
3*s*	8.23718	−0.00278	+0.22925	−0.25517	+0.03511	3*p*	2.86334	−0.00100	+0.70805	3*d*	0.92696	+0.25473
3*s*	4.83162	+0.00318	−0.00664	+0.58409	−0.05059	3*p*	1.34176	+0.00023	+0.03661			
3*s*	3.37930	−0.00450	+0.02228	+0.37318	−0.18178							
4*s*	3.48770	+0.00244	−0.01202	+0.26203	+0.05490							
4*s*	1.53912	−0.00008	+0.00054	+0.01542	+0.29321							
4*s*	0.88168	+0.00004	−0.00026	−0.00566	+0.51785							
4*s*	0.44922	−0.00001	+0.00008	+0.00160	+0.39046							
	$-\epsilon$[a]	182.95594	21.08303	2.54613	0.01576			17.45537	1.48341			0.11734

[a] See footnote to Table I.

TABLE IV. Vanadium negative ion (^5D).

S basis		1*s*	2*s*	3*s*	4*s*	*P* basis		2*p*	3*p*	*D* basis		3*d*
1*s*	22.77630	+0.95177	−0.29623	+0.10576	−0.01494	2*p*	10.53300	+0.66059	−0.21206	3*d*	1.77900	+0.40026
1*s*	36.05340	+0.02115	+0.00020	+0.00014	−0.00013	2*p*	16.60760	+0.07195	−0.03122	3*d*	9.90720	+0.02732
2*s*	19.54100	+0.03440	−0.15797	+0.06385	−0.00960	3*p*	9.04882	+0.30355	−0.19509	3*d*	4.77520	+0.28121
2*s*	9.37400	+0.00409	+1.04089	−0.41496	+0.06088	3*p*	5.50616	+0.02327	+0.33494	3*d*	2.85268	+0.32610
3*s*	7.90503	−0.00353	+0.12516	−0.26028	+0.03877	3*p*	3.18858	−0.00157	+0.78740	3*d*	0.94564	+0.16928
3*s*	5.12985	+0.00514	−0.02156	+0.78223	−0.09940	3*p*	1.47490	+0.00041	+0.05007			
3*s*	3.87759	−0.00530	+0.02608	+0.05962	−0.06786							
4*s*	3.75000	+0.00202	−0.00910	+0.45486	−0.02706							
4*s*	1.65760	−0.00009	+0.00046	+0.01312	+0.28985							
4*s*	0.90074	+0.00004	−0.00019	−0.00381	+0.55091							
4*s*	0.44708	−0.00001	+0.00006	+0.00108	+0.37483							
	$-\epsilon$[a]	201.16366	23.51204	2.83469	0.01628			19.66408	1.68653			0.16150

[a] See footnote to Table I.

TABLE V. Chromium negative ion (^6S).

S basis		1*s*	2*s*	3*s*	4*s*	*P* basis		2*p*	3*p*	*D* basis		3*d*
1*s*	23.53540	+0.94322	−0.28716	+0.10796	−0.01505	2*p*	10.66740	+0.65794	−0.19320	3*d*	1.92376	+0.45143
1*s*	34.98000	+0.03648	−0.00853	+0.00078	−0.00004	2*p*	16.36250	+0.10558	−0.05155	3*d*	10.35870	+0.02875
2*s*	21.28350	+0.02372	−0.14749	+0.05199	−0.00705	3*p*	9.63424	+0.25404	−0.23309	3*d*	5.22640	+0.25903
2*s*	9.91772	+0.00983	+0.98205	−0.37047	+0.05108	3*p*	6.64010	+0.03599	+0.27956	3*d*	3.29019	+0.33025
3*s*	9.48828	−0.00701	+0.14817	−0.22755	+0.03565	3*p*	3.54736	+0.00053	+0.85988	3*d*	0.95000	+0.13007
3*s*	5.80330	+0.00359	+0.02745	+0.32073	−0.04976	3*p*	1.61428	+0.00010	+0.07120			
3*s*	4.02510	−0.00248	−0.00586	+0.76330	−0.12921							
4*s*	3.28393	+0.00083	+0.00173	+0.12483	+0.00688							
4*s*	1.68870	−0.00017	−0.00017	+0.00435	+0.30352							
4*s*	0.90349	+0.00007	+0.00006	−0.00111	+0.55104							
4*s*	0.44948	−0.00002	−0.00002	+0.00033	+0.36120							
	$-\epsilon$[a]	220.22237	26.04511	3.12346	0.01668			21.97562	1.88959			0.21121

[a] See footnote to Table I.

TABLE VI. Manganese negative ion (^5D).

S basis		1s	2s	3s	4s	P basis		2p	3p	D basis		3d
1s	24.60960	+0.95313	−0.30382	+0.11249	−0.01587	2p	9.58940	+0.85705	−0.33981	3d	3.53372	+0.31622
1s	37.60670	+0.02706	+0.00055	−0.00102	+0.00035	2p	16.26990	+0.14813	−0.04256	3d	11.17720	+0.02669
2s	21.11770	+0.02485	−0.16251	+0.06237	−0.00798	3p	6.08000	+0.01849	−0.16547	3d	5.61570	+0.26819
2s	10.66850	+0.00560	+0.96989	−0.37978	+0.05114	3p	5.28000	+0.01164	+0.69116	3d	2.11562	+0.43659
3s	9.75659	−0.00369	+0.19202	−0.23928	+0.03969	3p	3.43000	−0.00909	+0.41386	3d	1.05601	+0.15609
3s	5.73348	+0.00269	+0.02111	+0.46406	−0.08033	3p	2.60000	+0.00406	+0.17873			
3s	4.14800	−0.00238	−0.00712	+0.59485	−0.09164							
4s	3.65000	+0.00084	+0.00238	+0.15611	−0.00945							
4s	1.81690	−0.00011	−0.00016	+0.00632	+0.30545							
4s	0.94167	+0.00004	+0.00006	−0.00158	+0.56438							
4s	0.46670	−0.00001	−0.00002	+0.00048	+0.35499							
	$-\epsilon^{a}$	240.18541	28.74044	3.45333	0.01778			24.44740	2.13065			0.21354

[a] See footnote to Table I.

TABLE VII. Iron negative ion (^4F).

S basis		1s	2s	3s	4s	P basis		2p	3p	D basis		3d
1s	25.87820	+0.95055	−0.31123	+0.11569	−0.01609	2p	10.09080	+0.85985	+0.34628	3d	2.65000	+0.43340
1s	38.73300	+0.02055	+0.00638	−0.00299	+0.00065	2p	17.02370	+0.14309	+0.04066	3d	11.50000	+0.02764
2s	21.33300	+0.04065	−0.18072	+0.07178	−0.00896	3p	6.07960	+0.04426	+0.24371	3d	6.09290	+0.24144
2s	11.01230	−0.00494	+1.04045	−0.41687	+0.05494	3p	5.46805	−0.01638	−0.83640	3d	4.16000	+0.23945
3s	9.50024	+0.00639	+0.14508	−0.31096	+0.05400	3p	3.32897	−0.00331	−0.45476	3d	1.37669	+0.25609
3s	6.99020	−0.00533	+0.00138	+0.37788	−0.06852	3p	2.55178	+0.00220	−0.07263			
3s	4.67090	+0.00255	+0.00433	+0.73550	−0.11125							
4s	3.92345	−0.00085	−0.00034	+0.20282	−0.01984							
4s	1.92680	+0.00013	+0.00007	+0.00836	+0.29883							
4s	0.97817	−0.00005	−0.00002	−0.00218	+0.57819							
4s	0.47310	+0.00001	+0.00001	+0.00066	+0.35663							
	$-\epsilon^{a}$	260.99733	31.53787	3.78210	0.01849			27.02015	2.36998			0.23025

[a] See footnote to Table I.

TABLE VIII. Cobalt negative ion (^3F).

S basis		1s	2s	3s	4s	P basis		2p	3p	D basis		3d
1s	26.82720	+0.95651	−0.31021	+0.11687	−0.01548	2p	11.11190	+0.89058	−0.35251	3d	2.33789	+0.49292
1s	41.36000	+0.01824	+0.00422	−0.00262	+0.00028	2p	19.95740	+0.07682	−0.02026	3d	12.07030	+0.03074
2s	22.00000	+0.03556	−0.19747	+0.07618	−0.01058	3p	7.16122	+0.11035	−0.13405	3d	6.56390	+0.18767
2s	12.16050	−0.00308	+0.94455	−0.37352	+0.05097	3p	5.67893	−0.05554	+0.72240	3d	4.52420	+0.37022
3s	10.54700	+0.00283	+0.27318	−0.29637	+0.04156	3p	3.47914	+0.01574	+0.43569	3d	1.09462	+0.12389
3s	6.28224	−0.00435	−0.02555	+0.62255	−0.06724	3p	2.70842	−0.00564	+0.07798			
3s	5.20835	+0.00392	+0.03105	+0.21304	−0.07763							
4s	4.55000	−0.00084	−0.00614	+0.42074	−0.03236							
4s	2.01586	+0.00006	+0.00056	+0.01490	+0.28048							
4s	1.05393	−0.00003	−0.00023	−0.00449	+0.55388							
4s	0.51285	+0.00001	+0.00007	+0.00135	+0.39407							
	$-\epsilon^{a}$	282.67423	34.45397	4.12084	0.01938			29.71005	2.61790			0.24891

[a] See footnote to Table I.

pute cross-section scattering and transition probabilities of the negative ions. It is known that there are important parameters in the interpretation of the data which leads to the experimental electron affinity.[3] As was done for the first,[4] second,[5] and third[6] row isoelectronic series of neutral and positive ions, the basis set, in which the Hartree-Fock atomic orbitals are expanded, was chosen to consist of Slater type functions of the form

$$\chi = N r^{n-1} e^{-\zeta r} P_l^{|m|}(\cos\theta) e^{im\phi},$$

where N is a normalizing factor; n, l, m are integers, ζ is a variational parameter, and r, θ, ϕ are the spherical polar coordinates centered at the nucleus.

The expansion coefficients for the basis set of a given Hartree-Fock atomic orbital are obtained variationally and the number of the basis set as well as the values of the parameters ζ are tentatively assumed and finally

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[4] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962). E. Clementi, J. Chem. Phys. **38**, 996 (1963).

[5] E. Clementi, J. Chem. Phys. **38**, 1001 (1963).

[6] E. Clementi, J. Chem. Phys. **40**, 1944 (1964).

TABLE IX. Nickel negative ion (^2D).

S basis		*1s*	*2s*	*3s*	*4s*	*P* basis		*2p*	*3p*	*D* basis		*3d*
1s	27.78100	+0.95286	−0.31399	+0.11861	−0.01389	*2p*	11.34410	+0.77060	−0.27908	*3d*	2.40323	+0.47493
1s	40.98670	+0.02299	+0.00534	−0.00294	−0.00060	*2p*	18.00300	+0.15814	−0.05975	*3d*	12.67910	+0.03049
2s	22.66670	+0.03502	−0.20540	+0.08151	−0.01436	*3p*	11.35750	+0.08351	−0.09638	*3d*	6.87180	+0.20784
2s	12.65000	−0.00462	+0.96677	−0.38917	+0.05897	*3p*	6.30257	+0.03094	+0.50178	*3d*	4.63000	+0.37846
3s	10.71570	+0.00454	+0.27429	−0.31953	+0.02631	*3p*	4.13333	−0.01475	+0.38195	*3d*	1.13064	+0.11402
3s	6.77220	−0.00697	−0.06393	+0.60995	+0.02479	*3p*	3.32861	+0.00704	+0.27257			
3s	5.51882	+0.00598	+0.05931	+0.23951	−0.19065							
4s	4.80234	−0.00135	−0.01204	+0.43811	+0.01427							
4s	2.13400	+0.00015	+0.00136	+0.02054	+0.18026							
4s	1.36272	−0.00008	−0.00070	−0.00814	+0.43775							
4s	0.65772	+0.00002	+0.00016	+0.00167	+0.57280							
	$-\epsilon^{a}$	305.20260	37.48017	4.46255	0.01801			32.50837	2.86762			0.26335

[a] See footnote to Table I.

TABLE X. Copper negative ion (^1S).

S basis		*1s*	*2s*	*3s*	*4s*	*P* basis		*2p*	*3p*	*D* basis		*3d*
1s	28.74260	+0.95368	−0.31974	+0.12161	−0.01469	*2p*	12.11030	+0.74691	−0.25451	*3d*	4.73170	+0.30474
1s	42.11330	+0.02397	+0.00758	−0.00398	−0.00003	*2p*	19.00000	+0.14460	−0.06111	*3d*	13.00000	+0.02662
2s	23.33300	+0.03287	−0.20573	+0.08124	−0.01248	*3p*	12.18720	+0.11297	−0.13748	*3d*	7.34375	+0.23842
2s	13.14530	−0.00468	+0.96833	−0.38914	+0.05443	*3p*	7.48146	+0.03786	+0.31550	*3d*	3.06659	+0.37446
3s	11.41790	+0.00403	+0.25735	−0.29605	+0.03239	*3p*	4.62620	−0.00563	+0.71488	*3d*	1.62434	+0.25444
3s	6.66320	−0.00869	−0.02090	+0.87316	−0.01477	*3p*	2.84094	+0.00182	+0.14391			
3s	5.83970	+0.00816	+0.02740	−0.09108	−0.13158							
4s	5.03278	−0.00126	−0.00378	+0.48426	−0.01288							
4s	2.14219	+0.00009	+0.00035	+0.01630	+0.26578							
4s	1.15760	−0.00004	−0.00015	−0.00538	+0.52421							
4s	0.55896	+0.00001	+0.00004	+0.00154	+0.43598							
	$-\epsilon^{a}$	328.59633	40.62345	4.81586	0.02031			35.42222	3.12809			0.29411

[a] See footnote to Table I.

TABLE XI. Copper (^2S).

S basis		*1s*	*2s*	*3s*	*4s*	*P* basis		*2p*	*3p*	*D* basis		*3d*
1s	28.74260	+0.95331	−0.32022	+0.11945	−0.01740	*2p*	12.11030	+0.74696	−0.25454	*3d*	5.03170	+0.31049
1s	42.11330	+0.02418	+0.00785	−0.00276	−0.00135	*2p*	19.00000	+0.14459	−0.06105	*3d*	13.00000	+0.02938
2s	23.33300	+0.03354	−0.20473	+0.08571	−0.02206	*3p*	12.18720	+0.11292	−0.13729	*3d*	7.34375	+0.20893
2s	13.14530	−0.00596	+0.96623	−0.39847	+0.08500	*3p*	7.48146	+0.03787	+0.31523	*3d*	3.06659	+0.38617
3s	11.41790	+0.00702	+0.26346	−0.27171	+0.00229	*3p*	4.62620	−0.00564	+0.71456	*3d*	1.70984	+0.25756
3s	8.02300	−0.00959	−0.02451	−0.04254	+0.18178	*3p*	2.84094	+0.00183	+0.14448			
3s	6.64662	+0.00659	+0.02452	+0.83877	−0.34309							
4s	5.03278	−0.00110	−0.00212	+0.43364	−0.01019							
4s	3.16106	+0.00029	+0.00069	+0.02962	+0.01705							
4s	1.75420	−0.00007	−0.00014	−0.00071	+0.65070							
4s	0.86248	+0.00002	+0.00003	+0.00021	+0.46716							
	$-\epsilon^{a}$	328.78967	40.81586	5.00921	0.23525			35.61491	3.32224			0.48963

[a] See footnote to Table I.

fixed via a laborious (for a large set) process of trials. Since we have started with smaller and easier systems[1–4] we are confident, on the basis of our previous experience, that the Hartree-Fock functions reported are accurate to at least three decimal places and the corresponding energies are accurate to about 7 figures.

In Tables I to X we give the basis set, expansion coefficients, and orbital energies for the negative ions K$^-$(^2S), Sc$^-$(^3F), Ti(^4F), V$^-$(^5D), Cr$^-$(^6S), Mn$^-$(^5D), Fe$^-$(^4F), Co$^-$(^3F), Ni$^-$(^2D), and Cu$^-$(^1S). The program we have used was kindly supplied to us by Professor C. C. J. Roothaan and information about this program is available in a number of papers.[7] The ground-state Hartree-Fock functions for the corresponding neutral atoms are given elsewhere,[6] with the exception of Cu(^2S) which is reported in Table XI. In Table XII we list the Hartree-Fock total energies of the ground-state atoms, the corresponding energies for the negative ions ions and their differences, hereafter referred to as

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[7] C. C. J. Roothaan and P. Bogus, *Methods in Computational Physics* (Pergamon Press, New York, 1963), Vol. I; see also C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

TABLE XII. Hartree-Fock total energies (in a.u.).

Atoms		Ions		Δ(HF)[a]
K(^2S)	-599.16447	K$^-$(^1S)	-599.16177	-0.073
Sc(^2D)	-759.73554	Sc$^-$(^3F)	-759.68830	-1.285
Ti(^3F)	-848.40526	Ti$^-$(^4F)	-848.37165	-0.915
V(^4F)	-942.88266	V$^-$(^5D)	-942.86109	-0.587
Cr(^5D)	-1043.3061	Cr$^-$(^6S)	-1043.3326	$+0.721$
Mn(^6S)	-1149.8651	Mn$^-$(^5D)	-1149.7277	-3.739
Fe(^5D)	-1262.4424	Fe$^-$(^4F)	-1262.3658	-2.084
Co(^4F)	-1381.4134	Co$^-$(^3F)	-1381.3488	-1.758
Ni(^3F)	-1506.8689	Ni$^-$(^2D)	-1506.8158	-1.445
Cu(^2S)	-1638.9606	Cu$^-$(^1S)	-1638.9624	$+0.049$
Cu(^2D)	-1638.9490	Cu$^-$(^1S)	-1638.9624	$+0.365$

[a] In eV.

Δ(HF). With exception of Cr$^-$ and Cu$^-$, all the negative ions given in Table XII are unstable in the Hartree-Fock model. It should be noted that the Δ(HF) of -0.731 eV for the chromium case is computed with reference to the Cr(^5D) state which lies 0.9608 eV above the ground state of the Cr ground state. Hence the reported value of Δ(HF) for Cr does not indicate that Cr$^-$ is stable in the Hartree-Fock model.

III. CORRELATION AND RELATIVISTIC ENERGY

As known, the correlation energy[8–10] is the main factor in the stability of the negative ions[1,2] at least for the cases where the electrons added to the neutral atoms create a new electron pair in the negative ion. This is the case of K$^-$(^1S), Cr$^-$(^6S), Mn$^-$(^5D), Fe$^-$(^4F), Co$^-$(^3F), Ni$^-$(^2D), and Cu$^-$(^1S). For the K$^-$ negative ion the electron pair formed is the $4s^2$; if we use for this case the same correlation energy obtained in the formation of the $4s^2$ pair in the Ca atom from the Ca$^+$ ion,[9] then we obtain for K a stabilization due to the correlation energy of 0.0365 a.u. = 0.993 eV. The computed value of Δ(HF) for potassium and the above value of the correlation stabilization gives an electron affinity of 0.920 eV for the K$^-$ ion.

The same arguments presented for the K$^-$(^1S) negative ion hold, in general, for the Cu$^-$(^1S) negative ion, but one should note that the use of the correlation stabilization from Ca$^+$(^2S) to Ca(^1S) is insufficient for the Cu$^-$(^1S) ion, because of the $4s$-$3d$ intra-pair correlation present[8,9] in Cu$^-$ but not in Ca$^-$. For this reason one should use the correlation stabilization from Zn$^+$(^2S) to Zn(^1S), which is computed to be 0.0644 a.u. = 1.752 eV. The computed value of Δ(HF) for copper (Table XI) and the above value for the correlation stabilization gives an electron affinity of 1.801 eV for Cu$^-$(^1S).

From previous work[9] the introduction of a $3d$ electron, brings about a variation in the correlation energy which is given in Table XII. Although these data were obtained for the neutral atoms, they should represent a reliable estimate for the case of negative ions as we have discussed in the case of second period negative ions.[2] It is gratifying to note that this independent estimate of the Cu electron affinity, obtained by considering the addition of one $3d$ electron to Cu in the ^2D state, with configuration $K(2)$, $L(2)$, $3s(s)$ $3p(2)$ $3d(9)$ $4s(1)$, leads to a value of 1.799 eV in nice agreement with the value of 1.801 eV obtained previously by adding a $4s$ electron to Cu in the ^2S state, with configuration $K(2)$, $L(8)$, $3s(2)$ $3p(6)$ $3d(10)$ $4s(1)$.

The limits of uncertainty for the correlation energy stabilization reported in Table XII are those given in our previous work on the correlation energy for the neutral atoms. Since this uncertainty is up to 0.35 eV, we have not included in this work the small effects due to the relativistic correction. It is noted that this correction is larger in the third row than in the second row, but smaller than the uncertainty we have given in Table XIII.

TABLE XIII. Electron affinity for III row elements (energies in eV).

Case	HF stability	Corr. stability	Elec. affinity[d]
K$^-$(^2S)	-0.073	0.993 ± 0.05	0.902 ± 0.05
Sc$^-$(^3F)	-1.285	1.143 ± 0.1	-0.142 ± 0.1
Ti$^-$(^4F)	-0.915	1.306 ± 0.2	0.391 ± 0.2
V$^-$(^5D)	-0.587	1.524 ± 0.25	0.937 ± 0.25
Cr$^-$(^6S)[a]	$+0.721$	1.220 ± 0.35	0.980 ± 0.35
Mn$^-$(^5D)	-3.739	2.666 ± 0.20	-1.073 ± 0.20
Fe$^-$(^4F)	-2.084	2.666 ± 0.20	0.582 ± 0.20
Co$^-$(^3F)	-1.758	2.694 ± 0.15	0.936 ± 0.15
Ni$^-$(^2D)	-1.445	2.721 ± 0.20	1.276 ± 0.20
Cu$^-$(^1S)[b]	$+0.049$	1.752 ± 0.10	1.801 ± 0.10
Cu$^-$(^1S)[c]	$+0.365$	2.823 ± 0.08	1.799 ± 0.08

[a] Subtract in the second column 0.961 eV due to excitation between the Cr(^2D) and Cr gound state.

[b] Hartree-Fock stability relative to the Cu(^2S) ground state.

[c] Hartree-Fock stability relative to the Cu(^2D) excited state; subtract 1.389 eV from second column due to electronic excitation.

[d] Neglecting relativistic effects.

IV. CONCLUSIONS

The computed stability of the negative ions in the third row might be somewhat in error as we have indicated, but it is worthwhile to note that by computations on the first and second row negative ions we have predicted electron affinities within a few percent of the experimental one. This gives us confidence in the above estimate.

In a forthcoming paper,[10] we shall discuss the negative ions from Ga$^-$ to Br$^-$. However, this will require some time, because we shall need, in addition, correlation data obtained from presently incomplete computations on the neutral and positive ions from Ga to Kr.

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[8] E. Clementi, J. Chem. Phys. **38**, 2248 (1963); **39**, 175 (1963); see also L. C. Allen, E. Clementi, and H. Gladney, Rev. Mod. Phys. **35**, 465 (1963).

[9] E. Clementi, J. Chem. Phys. **41**, 295 (1964).

[10] A collection of Hartree-Fock functions for the first three periods of the periodic system (He to Kr) will appear in or supplement to the IBM J. Res. Develop. This collection of about one thousand Hartree-Fock functions was previously reported, ***in part***, in several papers (Refs. 1, 2, 4–6).