

## Atomic Negative Ions: The Iron Series

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Results of the Hartree-Fock calculations on the ground state for the ions  $K^- (^1S)$ ,  $Sc^- (^3F)$ ,  $Ti^- (^4F)$ ,  $V^- (^6D)$ ,  $Cr^- (^6S)$ ,  $Mn^- (^6D)$ ,  $Fe^- (^4F)$ ,  $Co^- (^3F)$ ,  $Ni^- (^2D)$ , 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,<sup>1,2</sup> 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  $\pm 1$  in the seventh decimal figure corresponds to 0.003 eV uncertainty, in the second case ( $Cu$  and  $Cu^-$ ) the same uncertainty of

$\pm 1$  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,<sup>1,2</sup> the results might be less accurate.

On the other hand, our experimental knowledge<sup>3</sup> 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 ( $^1S$ ).

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

<sup>a</sup> The orbital energies  $\epsilon$ , are given in atomic units.

<sup>1</sup> E. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964).

<sup>2</sup> E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).

<sup>3</sup> L. M. Branscomb, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962).

TABLE II. Scandium negative ion (<sup>3</sup>F).

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

<sup>a</sup> See footnote to Table I.

TABLE III. Titanium negative ion (<sup>4</sup>F).

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

<sup>a</sup> See footnote to Table I.

TABLE IV. Vanadium negative ion (<sup>5</sup>D).

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

<sup>a</sup> See footnote to Table I.

TABLE V. Chromium negative ion (<sup>6</sup>S).

S basis	1s	2s	3s	4s	P basis	2p	3p	D basis	3d			
1s	23.53540	+0.94322	-0.28716	+0.10796	-0.01505	2p	10.66740	+0.65794	-0.19320	3d	1.92376	+0.45143
1s	34.98000	+0.03648	-0.00853	+0.00078	-0.00004	2p	16.36250	+0.10558	-0.05155	3d	10.35870	+0.02875
2s	21.28350	+0.02372	-0.14749	+0.05199	-0.00705	3p	9.63424	+0.25404	-0.23309	3d	5.22640	+0.25903
2s	9.17172	+0.00983	+0.98205	-0.37047	+0.05108	3p	6.64010	+0.03599	+0.27956	3d	3.29019	+0.33025
3s	9.48828	-0.00701	+0.14817	-0.22755	+0.03565	3p	3.54736	+0.00053	+0.85988	3d	0.95000	+0.13007
3s	5.80330	+0.00359	+0.02745	+0.32073	-0.04976	3p	1.61428	+0.00010	+0.07120			
3s	4.02510	-0.00248	-0.00586	+0.76330	-0.12921							
4s	3.28393	+0.00083	+0.00173	+0.12483	+0.00688							
4s	1.68870	-0.00017	-0.00017	+0.00435	+0.30352							
4s	0.90349	+0.00007	+0.00006	-0.00111	+0.55104							
4s	0.44948	-0.00002	-0.00002	+0.00033	+0.36120							
-e <sup>a</sup>	220.22237	26.04511	3.12346	0.01668		21.97562	1.88959				0.21121	

<sup>a</sup> See footnote to Table I.

TABLE VI. Manganese negative ion ( ${}^6D$ ).

	<i>S</i> basis	1 <i>s</i>	2 <i>s</i>	3 <i>s</i>	4 <i>s</i>	<i>P</i> basis	2 <i>p</i>	3 <i>p</i>	<i>D</i> basis	3 <i>d</i>		
1 <i>s</i>	24.60960	+0.95313	-0.30382	+0.11249	-0.01587	2 <i>p</i>	9.58940	+0.85705	-0.33981	3 <i>d</i>	3.53372	+0.31622
1 <i>s</i>	37.60670	+0.02706	+0.00055	-0.00102	+0.00035	2 <i>p</i>	16.26990	+0.14813	-0.04256	3 <i>d</i>	11.17720	+0.02669
2 <i>s</i>	21.11770	+0.02485	-0.16251	+0.06237	-0.00798	3 <i>p</i>	6.08000	+0.01849	-0.16547	3 <i>d</i>	5.61570	+0.26819
2 <i>s</i>	10.66850	+0.00560	+0.96989	-0.37978	+0.05114	3 <i>p</i>	5.28000	+0.01164	+0.69116	3 <i>d</i>	2.11562	+0.43659
3 <i>s</i>	9.75659	-0.00369	+0.19202	-0.23928	+0.03969	3 <i>p</i>	3.43000	-0.00909	+0.41386	3 <i>d</i>	1.05601	+0.15609
3 <i>s</i>	5.73348	+0.00269	+0.02111	+0.46406	-0.08033	3 <i>p</i>	2.60000	+0.00406	+0.17873			
3 <i>s</i>	4.14800	-0.00238	-0.00712	+0.59485	-0.09164							
4 <i>s</i>	3.65000	+0.00084	+0.00238	+0.15611	-0.00945							
4 <i>s</i>	1.81690	-0.00011	-0.00016	+0.00632	+0.30545							
4 <i>s</i>	0.94167	+0.00004	+0.00006	-0.00158	+0.56438							
4 <i>s</i>	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

<sup>a</sup> See footnote to Table I.

TABLE VII. Iron negative ion ( ${}^4F$ ).

	<i>S</i> basis	1 <i>s</i>	2 <i>s</i>	3 <i>s</i>	4 <i>s</i>	<i>P</i> basis	2 <i>p</i>	3 <i>p</i>	<i>D</i> basis	3 <i>d</i>		
1 <i>s</i>	25.87820	+0.95055	-0.31123	+0.11569	-0.01609	2 <i>p</i>	10.09080	+0.85985	+0.34628	3 <i>d</i>	2.65000	+0.43340
1 <i>s</i>	38.73300	+0.02055	+0.00638	-0.00299	+0.00065	2 <i>p</i>	17.02370	+0.14309	+0.04066	3 <i>d</i>	11.50000	+0.02764
2 <i>s</i>	21.33300	+0.04065	-0.18072	+0.07178	-0.00896	3 <i>p</i>	6.07960	+0.04426	+0.24371	3 <i>d</i>	6.09290	+0.24144
2 <i>s</i>	11.01230	-0.00494	+1.04045	-0.41687	+0.05494	3 <i>p</i>	5.46805	-0.01638	-0.83640	3 <i>d</i>	4.16000	+0.23945
3 <i>s</i>	9.50024	+0.00639	+0.14508	-0.31096	+0.05400	3 <i>p</i>	3.32897	-0.00331	-0.45476	3 <i>d</i>	1.37669	+0.23609
3 <i>s</i>	6.99020	-0.00533	+0.00138	+0.37788	-0.06852	3 <i>p</i>	2.55178	+0.00220	-0.07263			
3 <i>s</i>	4.67090	+0.00255	+0.00433	+0.73550	-0.11125							
4 <i>s</i>	3.92345	-0.00085	-0.00034	+0.20282	-0.01984							
4 <i>s</i>	1.92680	+0.00013	+0.00007	+0.00836	+0.29883							
4 <i>s</i>	0.97817	-0.00005	-0.00002	-0.00218	+0.57819							
4 <i>s</i>	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

<sup>a</sup> See footnote to Table I.

TABLE VIII. Cobalt negative ion ( ${}^3F$ ).

	<i>S</i> basis	1 <i>s</i>	2 <i>s</i>	3 <i>s</i>	4 <i>s</i>	<i>P</i> basis	2 <i>p</i>	3 <i>p</i>	<i>D</i> basis	3 <i>d</i>		
1 <i>s</i>	26.82720	+0.95651	-0.31021	+0.11687	-0.01548	2 <i>p</i>	11.11190	+0.89058	-0.35251	3 <i>d</i>	2.33789	+0.49292
1 <i>s</i>	41.36000	+0.01824	+0.00422	-0.00262	+0.00028	2 <i>p</i>	19.95740	+0.07682	-0.02026	3 <i>d</i>	12.07030	+0.03074
2 <i>s</i>	22.00000	+0.03556	-0.19747	+0.07618	-0.01058	3 <i>p</i>	7.16122	+0.11035	-0.13405	3 <i>d</i>	6.56390	+0.18767
2 <i>s</i>	12.16050	-0.00308	+0.94455	-0.37352	+0.05097	3 <i>p</i>	5.67893	-0.05554	+0.72240	3 <i>d</i>	4.52420	+0.37022
3 <i>s</i>	10.54700	+0.00283	+0.27318	-0.29637	+0.04156	3 <i>p</i>	3.47914	+0.01574	+0.43569	3 <i>d</i>	1.09462	+0.12389
3 <i>s</i>	6.28224	-0.00435	-0.02555	+0.62255	-0.06724	3 <i>p</i>	2.70842	-0.00564	+0.07798			
3 <i>s</i>	5.20835	+0.00392	+0.03105	+0.21304	-0.07763							
4 <i>s</i>	4.55000	-0.00084	-0.00614	+0.42074	-0.03236							
4 <i>s</i>	2.01586	+0.00006	+0.00056	+0.01490	+0.28048							
4 <i>s</i>	1.05393	-0.00003	-0.00023	-0.00449	+0.55388							
4 <i>s</i>	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

<sup>a</sup> 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.<sup>3</sup> As was done for the first,<sup>4</sup> second,<sup>5</sup> and third<sup>6</sup> 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,  $\zeta$  is a variational parameter, and  $r$ ,  $\theta$ ,  $\phi$  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  $\zeta$  are tentatively assumed and finally

<sup>4</sup> E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962). E. Clementi, J. Chem. Phys. **38**, 996 (1963).

<sup>5</sup> E. Clementi, J. Chem. Phys. **38**, 1001 (1963).

<sup>6</sup> E. Clementi, J. Chem. Phys. **40**, 1944 (1964).

TABLE IX. Nickel negative ion (<sup>2</sup>D).

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							
-e <sup>a</sup>	305.20260	37.48017	4.46255	0.01801		32.50837	2.86762				0.26335	

<sup>a</sup> See footnote to Table I.

TABLE X. Copper negative ion (<sup>1</sup>S).

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							
-e <sup>a</sup>	328.59633	40.62345	4.81586	0.02031		35.42222	3.12809				0.29411	

<sup>a</sup> See footnote to Table I.

TABLE XI. Copper (<sup>2</sup>S).

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							
-e <sup>a</sup>	328.78967	40.81586	5.00921	0.23525		35.61491	3.32224				0.48963	

<sup>a</sup> 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<sup>1-4</sup> 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<sup>-</sup>(<sup>2</sup>S), Sc<sup>-</sup>(<sup>3</sup>F), Ti(<sup>4</sup>F), V<sup>-</sup>(<sup>5</sup>D), Cr<sup>-</sup>(<sup>6</sup>S), Mn<sup>-</sup>(<sup>6</sup>D), Fe<sup>-</sup>(<sup>4</sup>F), Co<sup>-</sup>(<sup>3</sup>F), Ni<sup>-</sup>(<sup>2</sup>D), and Cu<sup>-</sup>(<sup>1</sup>S). 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.<sup>7</sup> The ground-state Hartree-Fock functions for the corresponding neutral atoms are given elsewhere,<sup>8</sup> with the exception of Cu(<sup>2</sup>S) 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 and their differences, hereafter referred to as

<sup>7</sup> 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		$\Delta(\text{HF})^a$
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 $^-$ ( $^6D$ )	-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

<sup>a</sup> In eV.

$\Delta(\text{HF})$ . 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  $\Delta(\text{HF})$  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  $\Delta(\text{HF})$  for Cr does not indicate that Cr $^-$  is stable in the Hartree-Fock model.

### III. CORRELATION AND RELATIVISTIC ENERGY

As known, the correlation energy<sup>8-10</sup> is the main factor in the stability of the negative ions<sup>1,2</sup> 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,<sup>9</sup> then we obtain for K a stabilization due to the correlation energy of 0.0365 a.u.=0.993 eV. The computed value of  $\Delta(\text{HF})$  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<sup>8,9</sup> 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  $\Delta(\text{HF})$  for copper (Table XI) and the above value for the cor-

relation stabilization gives an electron affinity of 1.801 eV for Cu $^-$ ( $^1S$ ).

From previous work<sup>9</sup> 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.<sup>2</sup> 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 <sup>d</sup>
K $^-$ ( $^2S$ )	-0.073	0.993 $\pm$ 0.05	0.902 $\pm$ 0.05
Sc $^-$ ( $^3F$ )	-1.285	1.143 $\pm$ 0.1	-0.142 $\pm$ 0.1
Ti $^-$ ( $^4F$ )	-0.915	1.306 $\pm$ 0.2	0.391 $\pm$ 0.2
V $^-$ ( $^5D$ )	-0.587	1.524 $\pm$ 0.25	0.937 $\pm$ 0.25
Cr $^-$ ( $^6S$ ) <sup>a</sup>	+0.721	1.220 $\pm$ 0.35	0.980 $\pm$ 0.35
Mn $^-$ ( $^6D$ )	-3.739	2.666 $\pm$ 0.20	-1.073 $\pm$ 0.20
Fe $^-$ ( $^4F$ )	-2.084	2.666 $\pm$ 0.20	0.582 $\pm$ 0.20
Co $^-$ ( $^3F$ )	-1.758	2.694 $\pm$ 0.15	0.936 $\pm$ 0.15
Ni $^-$ ( $^2D$ )	-1.445	2.721 $\pm$ 0.20	1.276 $\pm$ 0.20
Cu $^-$ ( $^1S$ ) <sup>b</sup>	+0.049	1.752 $\pm$ 0.10	1.801 $\pm$ 0.10
Cu $^-$ ( $^1S$ ) <sup>c</sup>	+0.365	2.823 $\pm$ 0.08	1.799 $\pm$ 0.08

<sup>a</sup> Subtract in the second column 0.961 eV due to excitation between the Cr( $^2D$ ) and Cr ground state.<sup>b</sup> Hartree-Fock stability relative to the Cu( $^2S$ ) ground state.<sup>c</sup> Hartree-Fock stability relative to the Cu( $^2D$ ) excited state; subtract 1.389 eV from second column due to electronic excitation.<sup>d</sup> 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,<sup>10</sup> 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.

<sup>8</sup> 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).

<sup>9</sup> E. Clementi, J. Chem. Phys. **41**, 295 (1964).

<sup>10</sup> 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).