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Atomic Negative Ions. Second Period

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Results of Hartree-Fock calculations on the ions Na^-, Al^-, Si^-, P^-, and Cl^- in states of the lowest electronic configuration, along with correlation and relativistic corrections, are given. The data are used to compute electron affinities for the atoms of the second row of the periodic table, and the stability of the excited states of the ions relative to the neutral ground-state atoms. The computed electron affinities for atoms on which experimental determinations are not available are 0.78 eV for Na, 0.52 eV for Al, 1.39 eV for Si, and 0.78 eV for P. The computed electron affinities for S and Cl are 2.12 and 3.56 eV in fair agreement with the experimental values of 2.07±0.07 and 3.613±0.003 eV, respectively. For the second-row negative ions, several excited states are lower in energy than the corresponding ground-state neutral atoms; the computed stabilities for the species $Al^-(^1D)$, $Si^-(^2D)$ and $Si^-(^2P)$ are 0.23, 0.58, and 0.08 eV, respectively. While the ^1D state of P^- is estimated to be very close to that of $P(^4S)$, our estimates are not accurate enough to say definitely whether it is above or below.

INTRODUCTION

In this work we extend the analysis of the location of the states of negative ions to the second-period elements. For a more general discussion on the negative ions we refer to the first paper of this series,[1] hereafter referred to as I. In addition, we refer to I for more general references on the problems related to negative ions, and we list here only those references directly related to the second-row negative ions.

Table I. Orbital exponents of the basis functions[a] used in constructing Hartree-Fock orbitals for second-row negative ions.

	$Na^-(^2S)$	$Al^-(^3P)$	$Al^-(^1D)$	$Al^-(^1S)$	$Si^-(^4S)$	$Si^-(^2D)$
1*s*[a]	11.1267	13.7557	13.8427	13.7700	14.6022	14.6187
1*s*	18.2412	21.3600	22.8326	21.3617	23.2138	22.6505
2*s*	4.1271	4.5468	4.5680	4.5449	5.2937	5.2922
2*s*	10.0000	12.4000	12.4542	12.4338	13.1500	13.1501
3*s*	0.9640	1.7945	1.7345	1.6827	2.0020	1.9936
3*s*	0.4181	0.9780	0.9781	0.9735	1.1304	1.1323
3*s*	3.1358	3.1209	3.2919	3.1984	4.3809	4.3815
2*p*	2.3617	5.4804	5.4843	5.4906	6.1700	6.1552
2*p*	4.3037	10.9301	10.8609	10.6617	12.4000	12.3542
3*p*	8.0065[b]	1.7300	1.6665	1.7083	2.0414	1.7591
3*p*	1.4586[b]	0.4833	0.3742	0.2741	0.6893	0.5215
3*p*		3.9109	3.9135	3.9304	4.4869	4.4592
3*p*		1.0118	0.8938	0.8402	1.2940	0.9780
	$Si^-(^2P)$	$P^-(^3P)$	$P^-(^1D)$	$P^-(^1S)$	$S^-(^2P)$	$Cl^-(^1S)$
1*s*	14.5440	15.9262	16.1731	16.0130	15.7319	17.2875
1*s*	23.8972	22.7375	23.7373	23.0000	24.0889	28.4472
2*s*	5.2962	5.6066	5.5961	5.5837	6.7552	6.8172
2*s*	13.1096	14.4286	14.5001	14.5107	13.9271	15.3682
3*s*	1.9822	2.3276	2.3119	2.3285	2.5561	2.8669
3*s*	1.1526	1.3331	1.3262	1.3378	1.4846	1.6723
3*s*	4.3930	4.6875	4.6777	4.6937	5.7191	5.9503
2*p*	6.1575	6.5098	6.5045	6.4864	7.0824	7.6419
2*p*	12.4000	12.1689	12.1773	12.0684	13.1000	13.9763
3*p*	1.8190	2.2125	2.3381	2.3893	2.6076	2.8985
3*p*	0.4999	0.7525	0.7217	0.7050	0.9096	1.0374
3*p*	4.4624	4.8990	4.8974	4.8933	5.4204	5.9321
3*p*	1.0264	1.3719	1.4389	1.4450	1.6767	1.8615

[a] In this table the notation 1*s*, 2*s*, 3*s*, 2*p*, 3*p* refers to Slater-type basis functions. In Table II the notation 1*s*, 2*s*, 3*s*, 2*p*, 3*p* refers to Hartree-Fock atomic orbitals.

[b] This basis function is of 2*p*-type for the Na^- calculation.

The term splittings in the second-row negative ions are known to be smaller than in the corresponding members of the first row because of the decreased electrostatic interactions in the valence electrons. The electron affinities of the second-row neutral atoms are higher than those of the corresponding members of the first row. Because of these two experimental facts, we might expect to have excited states of the second-row negative ions which are stable relative to the ground-state neutral atoms, in comparison with the first row where there are no stable excited states. The physical reason why the electron affinity increases from first to second row presumably involves a balance of factors such as shielding and penetration effects, correlation effects, and the average distance of the valence electrons from the nucleus.

As previously done in I, we shall be concerned in this paper (a) with states of the lowest electronic configuration, and (b) with those ionic species in which the electron added to the neutral atom is assigned to an orbital with the same principal and azimuthal quantum numbers as the orbital of some other electron in the neutral atom.

HARTREE-FOCK ENERGY, CORRELATION AND RELATIVISTIC ENERGY, AND ELECTRON AFFINITIES

Programs developed at the Laboratory of Molecular Structure and Spectra under the direction of C. C. J. Roothaan were used in the computation of the Hartree-Fock functions.[2] We refer to I for a discussion on the stability of Hartree-Fock solutions for the negative ions.

In Table I the basis set of Slater-type orbitals and the corresponding orbital exponents are given; in Table II the expansion coefficients are reported for the basis set of Table I. In Table III the total and orbital energies are given; in this table we have added neutral-atom data

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

[2] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960). C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Pergamon Press, Inc., New York, 1963), Vol. II (to be published).

TABLE II. Expansion coefficients of the Slater-type basis set of Table I in Hartree-Fock atomic orbitals.[a]

	Hartree-Fock atomic orbitals				
Ion	1*s*	2*s*	3*s*	2*p*	3*p*
Na$^-$(^1S)	+0.89279	−0.21546	+0.02026	+0.54654	
	+0.02586	−0.00759	+0.00196	+0.44673	
	+0.00447	+0.79854	−0.09503	+0.06221	
	+0.09907	−0.11376	+0.01550	+0.02402	
	+0.00012	+0.00154	+0.50712		
	−0.00005	−0.00045	+0.63179		
	−0.00070	+0.33328	−0.03017		
Al$^-$(^3P)	+0.85238	−0.21802	+0.04698	+0.63664	−0.08861
	+0.01897	−0.00672	+0.00211	+0.03401	−0.00503
	+0.00496	+0.99251	−0.24299	+0.01567	+0.15392
	+0.15296	−0.12468	+0.03072	+0.00089	+0.46497
	+0.00095	−0.02386	+0.62005	+0.41322	−0.06334
	−0.00030	+0.00623	+0.52889	−0.00377	+0.54328
	−0.00190	+0.12454	−0.08977		
Al$^-$(^1D)	+0.85232	−0.21764	+0.04715	+0.63481	−0.08322
	+0.01347	−0.00532	+0.00201	+0.03452	−0.00512
	+0.00552	+0.98151	−0.24536	+0.01486	+0.20759
	+0.15906	−0.12640	+0.03224	+0.00094	+0.44058
	+0.00095	−0.01522	+0.64445	+0.41523	−0.06306
	−0.00035	+0.00466	+0.48056	−0.00338	+0.56630
	−0.00213	+0.12891	−0.07144		
Al$^-$(^1S)	+0.85001	−0.21774	+0.04636	+0.62950	−0.07495
	+0.01953	−0.00667	+0.00338	+0.03644	−0.00543
	+0.00522	+0.99061	−0.25570	+0.01554	+0.20433
	+0.15489	−0.12425	+0.03397	+0.00076	+0.51450
	+0.00092	−0.01738	+0.70106	+0.41785	−0.06306
	−0.00035	+0.00558	+0.41236	−0.00267	+0.57729
	−0.00194	+0.11965	−0.05982		
Si$^-$(^4S)	+0.87604	−0.22584	+0.05456	+0.62873	−0.11545
	+0.01698	−0.00824	+0.00245	+0.02638	−0.00502
	+0.00484	+0.89441	−0.24112	+0.01764	+0.18819
	+0.12769	−0.13363	+0.03596	+0.00101	+0.39863
	+0.00031	+0.00058	+0.65693	+0.42217	−0.08566
	−0.00013	+0.00042	+0.46686	−0.00507	+0.54868
	−0.00141	+0.22380	−0.10265		
Si$^-$(^2D)	+0.87279	−0.22441	+0.05445	+0.63192	−0.11510
	+0.01850	−0.00909	+0.00283	+0.02663	−0.00466
	+0.00443	+0.89510	−0.24396	+0.01367	+0.40717
	+0.12993	−0.13440	+0.03672	+0.00164	+0.24013
	+0.00023	+0.00068	+0.67311	+0.42194	−0.07975
	−0.00009	+0.00035	+0.44913	−0.00468	+0.51396
	−0.00116	+0.22303	−0.10242		
Si$^-$(^2P)	+0.88280	−0.22948	−0.05547	+0.63187	−0.11320
	+0.01561	−0.00682	−0.00253	+0.02635	−0.00467
	+0.00525	+0.89324	+0.24705	+0.01403	+0.35858
	+0.12126	−0.13113	−0.03706	+0.00139	+0.30085
	+0.00041	+0.00104	−0.67374	+0.42173	−0.08043
	−0.00018	+0.00020	−0.44160	−0.00392	+0.52271
	−0.00168	+0.22474	+0.09847		
P$^-$(^3P)	+0.84531	−0.21011	+0.05413	+0.65072	−0.13747
	+0.02469	−0.01822	+0.00594	+0.03983	−0.00845
	+0.00542	+0.94626	−0.27849	+0.01241	+0.32521
	+0.15374	−0.14676	+0.04312	+0.00093	+0.31615
	+0.00047	+0.00105	+0.66545	+0.38170	−0.09112
	−0.00018	+0.00047	+0.47416	−0.00307	+0.50812
	−0.00195	+0.16481	−0.10859		
P$^-$(^1D)	+0.84153	−0.21057	+0.05430	+0.65165	−0.13675
	+0.01440	−0.01416	+0.00494	+0.03986	−0.00854
	+0.00490	+0.94847	−0.28107	+0.01210	+0.25727
	+0.17027	−0.15018	+0.04449	+0.00078	+0.34324
	+0.00035	+0.00097	+0.68036	+0.38001	−0.09278
	−0.00013	+0.00048	+0.45780	−0.00144	+0.56244
	−0.00160	+0.16162	−0.10584		

TABLE II (*continued*)

	Hartree-Fock atomic orbitals				
Ion	1*s*	2*s*	3*s*	2*p*	3*p*
$P^-(^1S)$	+0.84036	−0.20889	+0.05461	+0.65208	−0.13524
	+0.02318	−0.01764	+0.00565	+0.04151	−0.00914
	+0.00594	+0.95043	−0.28178	+0.01216	+0.24973
	+0.16093	−0.14732	+0.04336	+0.00104	+0.36964
	+0.00059	+0.00244	+0.67768	+0.37730	−0.09500
	−0.00022	−0.00006	+0.46238	−0.00053	+0.55630
	−0.00230	+0.15754	−0.10888		
$S^-(^2P)$	+0.92758	−0.26302	+0.07506	+0.65298	−0.15235
	+0.03684	−0.00658	+0.00139	+0.03797	−0.00883
	+0.00480	+0.79254	−0.24100	+0.01284	+0.29446
	+0.04456	−0.13313	+0.03965	+0.00091	+0.34500
	+0.00023	+0.00680	+0.69648	+0.37609	−0.10281
	−0.00011	−0.00084	+0.43761	−0.00210	+0.51322
	−0.00127	+0.35864	−0.17315		
$Cl^-(^1S)$	+0.91793	−0.25652	+0.07523	+0.65625	−0.16376
	+0.01495	−0.00460	+0.00152	+0.03696	−0.00908
	+0.00355	+0.89068	−0.28724	+0.01249	+0.32880
	+0.08173	−0.13956	+0.04485	+0.00051	+0.32345
	+0.00012	+0.00630	+0.69590	+0.37039	−0.11084
	−0.00006	−0.00038	+0.45212	−0.00271	+0.50195
	−0.00097	+0.24136	−0.15224		

[a] See Ref. a in Table I.

for comparison, and draw attention to the expected decrease of valence orbital energies in going from neutral atom to negative ion. For all reported functions the ratio of potential to total energy is in the range 2 ± 10^{-6} indicating that optimization of the orbital exponents was sufficiently extensive.

In paper I we extrapolated correlation-energy data available for neutral atoms and positive ions[3] to estimate the correlation energies in the negative ions for the first row of the periodic table. Then, together with Hartree-Fock data and computed relativistic data we were able to predict a table of first-row electron affinities and negative ion stabilities. In the case of the second row, correlation-energy data of equivalent accuracy is not available[4]; and so here we use a different approach in which correlation and relativistic corrections taken together are computed for systems with accurately known ionization potentials, and these same corrections are applied to systems involving negative ions. The procedure can best be presented by use of an example.

The ionization potential of argon can be written

$$\begin{aligned}\text{I.P.}(\text{Ar}) &= \Delta E_{\text{ex}}(\text{Ar}\rightarrow\text{Ar}^+)\\ &= \Delta E_{\text{H.F.}}(\text{Ar}\rightarrow\text{Ar}^+)+\Delta E_{\text{C+R}}(\text{Ar}\rightarrow\text{Ar}^+)\,, \quad (1)\end{aligned}$$

where $\Delta E_{\text{ex}}(\text{Ar}\rightarrow\text{Ar}^+)$ is the difference in exact energies between Ar^+ and Ar, $\Delta E_{\text{H.F.}}(\text{Ar}\rightarrow\text{Ar}^+)$ is the difference in the Hartree-Fock energies of the two systems, and $\Delta E_{\text{C+R}}(\text{Ar}\rightarrow\text{Ar}^+)$ is the difference in the correlation and relativistic corrections. With experimentally observed ionization potentials and excitation energies, Eq. (1) can be used to determine $\Delta E_{\text{C+R}}(\text{Ar}\rightarrow\text{Ar}^+)$. The systems Cl^-, Cl should be rather similar to the systems Ar, Ar^+ since the number of electrons and the electronic states are the same, the only change being that the nuclear charge has decreased from 18 to 17. We use the argument that the difference in correlation and relativistic corrections for $\text{Ar}\rightarrow\text{Ar}^+$ process should be close to the difference in correlation and relativistic corrections for the $\text{Cl}^-\rightarrow\text{Cl}$ process, i.e., we make the approximation

$$\Delta E_{\text{C+R}}(\text{Ar}\rightarrow\text{Ar}^+)=\Delta E_{\text{C+R}}(\text{Cl}^-\rightarrow\text{Cl})\,.$$

This approximation, in which the $\Delta E_{\text{C+R}}$ for the ionization of a neutral atom is made equal to the $\Delta E_{\text{C+R}}$ for the detachment of the electron from a negative ion, should be better in the second row than in the first, primarily because of the smaller percentage change in atomic number in the two comparable processes; for instance in the example above the change in atomic number from Ar to Cl is from 18 to 17, whereas in the first row the change in atomic number from Ne to F is from 10 to 9. However, in view of the dependence of the relativistic energy on the fourth power of the atomic number, a further comment should be made. For instance, in the above example, since the atomic number in Ar is the same as in Ar^+, the change in relativistic energy in going from Ar to Ar^+ is small (≈0.002 au). Again, since the atomic number in Cl^- is the same as in Cl, the change in relativistic energy in going from Cl^- to Cl is small (≈0.002 au); and the relativistic contribution to $\Delta E_{\text{C+R}}$ for the ionization of neutral argon and the detachment of an electron from Cl^- will be the same to within the accuracy needed for this work. The final column of Table III lists computed

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[3] E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

[4] E. Clementi, J. Chem. Phys. **39**, 175 (1963).

TABLE III. Hartree-Fock total energy, orbital energies, and relativistic energy.[a]

System	Total energy[b]	$-\epsilon(1s)$	$-\epsilon(2s)$	$-\epsilon(3s)$	$-\epsilon(2p)$	$-\epsilon(3p)$	$-E_R$[c]
Na(^2S)[d]	−161.85889	40.47849	2.79702	0.18211	1.51813		0.2007
Na$^-(^1S)$	−161.85464	40.33166	2.64986	0.01255	1.37095		0.2009
Al(^2P)[d]	−241.87665	58.50129	4.91094	0.39348	3.21858	0.21017	0.4219
Al$^-(^3P)$	−241.87771	58.30692	4.71540	0.20799	3.02428	0.01977	0.4214
Al$^-(^1D)$	−241.85643	58.33595	4.74416	0.23083	3.05264	0.00534	0.4220
Al$^-(^1S)$	−241.82999	58.38485	4.79292	0.27178	3.10087	−0.00570	0.4216
Si(^3P)[d]	−288.85428	68.81244	6.15659	0.53991	4.25611	0.29709	0.5856
Si$^-(^4S)$	−288.88942	68.55306	5.89655	0.30148	3.99768	0.06156	0.5846
Si$^-(^2D)$	−288.84141	68.58098	5.92363	0.31997	4.02441	0.03846	0.5843
Si$^-(^2P)$	−288.81105	68.60123	5.94313	0.33383	4.04365	0.02518	0.5852
P(^4S)[d]	−340.71868	79.96980	7.51118	0.69645	5.40105	0.39170	0.7927
P$^-(^3P)$	−340.69866	79.69247	7.23214	0.43640	5.12341	0.07693	0.7917
P$^-(^1D)$	−340.65976	79.70990	7.24871	0.44733	5.13981	0.06432	0.7915
P$^-(^1S)$	−340.60314	79.73376	7.27138	0.46228	5.16220	0.04552	0.7920
S(^3P)[e]	−397.50476	92.00462	9.00446	0.87963	6.68268	0.43739	1.053
S$^-(^2P)$	−397.53819	91.67599	8.67518	0.57937	6.35494	0.10742	1.052
Cl(^2P)[e]	−459.48197	104.88447	10.60754	1.07288	8.07231	0.50637	1.375
Cl$^-(^1S)$[f]	−459.57668	104.50528	10.22890	0.73290	7.69531	0.14988	1.373

[a] All energies are in atomic units.
[b] The total energy is not mass corrected.
[c] The relativistic energies of the neutral species are taken from E. Clementi, J. Mol. Spectry. (to be published).
[d] Unpublished data of E. Clementi.
[e] Unpublished data of G. L. Malli.
[f] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961), computed an energy of −459.5750 au.

relativistic energies for the systems of interest in this paper.

A measure of validity of the approximation can be obtained by comparing the values of $\Delta E_{\mathrm{C+R}}$ for detachment of negative ions of the first row obtained by the approximation discussed above and by the more accurate methods of I. This comparison is given in Table IV, where we observe fair agreement between the two sets of results with the exceptions of the Li$^-$ and F$^-$ detachment processes. Also, with the exceptions of the Li$^-(^1S) \rightarrow$ Li(^2S) process, the correction for the dissociation of the neutral atom is always lower than for the negative ion. In going to the second row, we expect the magnitude of the differences between the accurate values of $\Delta E_{\mathrm{C+R}}$ and those estimated by the method of this paper to decrease.

TABLE IV. Correlation+relativistic corrections for first-row systems.

Process	$\Delta E_{\mathrm{C+R}}$[a]	Process	$\Delta E_{\mathrm{C+R}}$[b]
Be$(^1S) \rightarrow$ Be$^+(^2S)$	0.0468	Li$^-(^1S) \rightarrow$ Li(^2S)	0.026±0.002
C$(^3P) \rightarrow$ C$^+(^2P)$	0.0173	B$^-(^3P) \rightarrow$ B(^2P)	0.021±0.002
C$(^1D) \rightarrow$ C$^+(^2P)$	0.0285	B$^-(^1D) \rightarrow$ B(^2P)	0.031±0.002
C$(^1S) \rightarrow$ C$^+(^2\mathrm{P})$	0.0581	B$^-(^1S) \rightarrow$ B(^2P)	0.052±0.003
N$(^4S) \rightarrow$ N$^+(^3P)$	0.0211	C$^-(^4S) \rightarrow$ C(^3P)	0.023±0.002
N$(^2D) \rightarrow$ N$^+(^3P)$	0.0390	C$^-(^2D) \rightarrow$ C(^3P)	0.043±0.002
N$(^2P) \rightarrow$ N$^+(^3P)$	0.0632	C$^-(^2P) \rightarrow$ C(^3P)	0.063±0.002
O$(^3P) \rightarrow$ O$^+(^4S)$	0.0636	N$^-(^3P) \rightarrow$ N(^4S)	0.069±0.004
O$(^1D) \rightarrow$ O$^+(^4S)$	0.0716	N$^-(^1D) \rightarrow$ N(^4S)	0.079±0.004
O$(^1S) \rightarrow$ O$^+(^4S)$	0.1082	N$^-(^1S) \rightarrow$ N(^4S)	0.109±0.005
F$(^2P) \rightarrow$ F$^+(^3P)$	0.0625	O$^-(^2P) \rightarrow$ O(^3P)	0.065±0.005
Ne$(^1S) \rightarrow$ Ne$^+(^2P)$	0.0630	F$^-(^1S) \rightarrow$ F(^2P)	0.074±0.003

[a] Computed from observed ionization potentials and computed Hartree-Fock energies. Ionization potentials from C. E. Moore, *Atomic Energy Levels* (U. S. Department of Commerce National Bureau of Standards, Washington, D. C.), Circular 467, Vol. I (1949) and Vol. III (1958); Hartree-Fock energies from E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962); E. Clementi, J. Chem. Phys. **38**, 996, 1001 (1963).
[b] From Paper I.

In Table V, using the values of $\Delta E_{\mathrm{C+R}}$ obtained from the ionization of neutral atoms, we have listed the predicted electron affinities of the second row atoms. For Cl it will be noticed that the predicted affinity lies close to the accurate experimental value of 0.133 au obtained by Berry *et al.*,[5] thus illustrating a previous point that the method of this paper improves from first to second row of the periodic table.

For a few cases sufficient data on the correlation energy in the neutral atoms and positive ions is available to extrapolate to the negative ions and thus further check the approximation of this paper.[4] For the Na$^-$ dissociation we would obtain $\Delta E_{\mathrm{C+R}}(\mathrm{Na}^- \rightarrow \mathrm{Na}) = 0.033 \pm 0.002$ au in fair agreement with the value 0.0376 of Table V. Notice that the discrepancy between these two numbers is in the same direction, but less in absolute magnitude than the values for the corresponding first row case (Li$^-$) given in Table IV. For the case of Al$^-(^3P)$ direct extrapolation of correlation energy tables[4] gives 0.017±0.005 au for $\Delta E_{\mathrm{C+R}}[\mathrm{Al}^-(^3P) \rightarrow \mathrm{Al}(^2P)]$ in agreement with the value of 0.018 au used in Table V.

Figure 1, which is drawn from the data of Table V, shows the decreased multiplet splittings and the lower absolute magnitude of the states of the negative ions relative to the ground states of the neutral atoms for the second row as compared with the first. The stability of the excited states Si$^-(^2D)$, Al$^-(^1D)$, and Si$^-(^2P)$ relative to the ground-state neutral atom is clearly shown. Our

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[5] R. S. Berry, C. W. Reimann, and G. N. Spokes, J. Chem. Phys. **37**, 2278 (1962); R. S. Berry and C. W. Reimann, *ibid.* **38**, 1540 (1963).

TABLE V. Electron affinities for second-row atoms computed using correlation+relativistic corrections obtained from ionization processes.[a]

Process	$\Delta E_{\text{H.F.}}$[b]	Ionization[c] potential	$\Delta E_{\text{C+R}}$[d]	Process	$\Delta E_{\text{H.F.}}$[e]	Electron affinity computed[f]
$\text{Mg}(^1S) \rightarrow \text{Mg}^+(^2S)$	0.2433	0.2809	0.0376	$\text{Na}^-(^1S) \rightarrow \text{Na}(^2S)$	−0.0043	0.0333
$\text{Al}(^2P) \rightarrow \text{Al}^+(^1S)$	0.2025	0.2199	0.0174	$\text{Mg}^-(^2P) \rightarrow \text{Mg}(^1S)$[g]		
$\text{Si}(^3P) \rightarrow \text{Si}^+(^2P)$	0.2815	0.2995	0.0180	$\text{Al}^-(^3P) \rightarrow \text{Al}(^2P)$	+0.0011	0.0191
$\text{Si}(^1D) \rightarrow \text{Si}^+(^2P)$	0.2422	0.2708	0.0286	$\text{Al}^-(^1D) \rightarrow \text{Al}(^2P)$	−0.0202	0.0084
$\text{Si}(^1S) \rightarrow \text{Si}^+(^2P)$	0.1856	0.2294	0.0438	$\text{Al}^-(^1S) \rightarrow \text{Al}(^2P)$	−0.0467	−0.0029
$\text{P}(^4S) \rightarrow \text{P}^+(^3P)$	0.3692	0.3853	0.0161	$\text{Si}^-(^4S) \rightarrow \text{Si}(^3P)$	+0.0351	0.0512
$\text{P}(^2D) \rightarrow \text{P}^+(^3P)$	0.2992	0.3335	0.0343	$\text{Si}^-(^2D) \rightarrow \text{Si}(^3P)$	−0.0129	0.0214
$\text{P}(^2P) \rightarrow \text{P}^+(^3P)$	0.2537	0.3000	0.0463	$\text{Si}^-(^2P) \rightarrow \text{Si}(^3P)$	−0.0432	0.0031
$\text{S}(^3P) \rightarrow \text{S}^+(^4S)$	0.3319	0.3806	0.0487	$\text{P}^-(^3P) \rightarrow \text{P}(^4S)$	−0.0200	0.0287
$\text{S}(^1D) \rightarrow \text{S}^+(^4S)$	0.2792	0.3386	0.0594	$\text{P}^-(^1D) \rightarrow \text{P}(^4S)$	−0.0589	0.0005
$\text{S}(^1S) \rightarrow \text{S}^+(^4S)$	0.2015	0.2797	0.0782	$\text{P}^-(^1S) \rightarrow \text{P}(^4S)$	−0.1155	−0.0373
$\text{Cl}(^2P) \rightarrow \text{Cl}^+(^3P)$	0.4336	0.4781	0.0445	$\text{S}^-(^2P) \rightarrow \text{S}(^3P)$	+0.0334	0.0779
$\text{Ar}(^1S) \rightarrow \text{Ar}^+(^2P)$	0.5431	0.5790	0.0359	$\text{Cl}^-(^1S) \rightarrow \text{Cl}(^2P)$	+0.0947	0.1306

[a] All energies in atomic units.
[b] From data in Table III, and in E. Clementi, J. Chem. Phys. **38**, 1001 (1963).
[c] From C. E. Moore, *Atomic Energy Levels* (United States, Department of Commerce National Bureau of Standards, Washington, D. C.), Circular Number 467, Vol. I (1949), and Vol. III (1958).
[d] $\Delta E_{\text{C+R}}$ = Ionization Potential − $\Delta E_{\text{H.F.}}$.
[e] From data in Table III.
[f] Sum of column $\Delta E_{\text{C+R}}$ and the column to the left.
[g] Hartree-Fock calculation for Mg^- not available (see Paper I).

prediction for $\text{P}^-(^1D)$ is not accurate enough to say whether it is stable, only that it is very close in energy to $\text{P}(^4S)$.

COMPARISON WITH OTHER DATA ON ELECTRON AFFINITIES

In obtaining electron affinities, the method used in I and the method of the current paper are basically extrapolation procedures, and should therefore be compared with the extrapolation method of Edlén[6] used to obtain this same data.

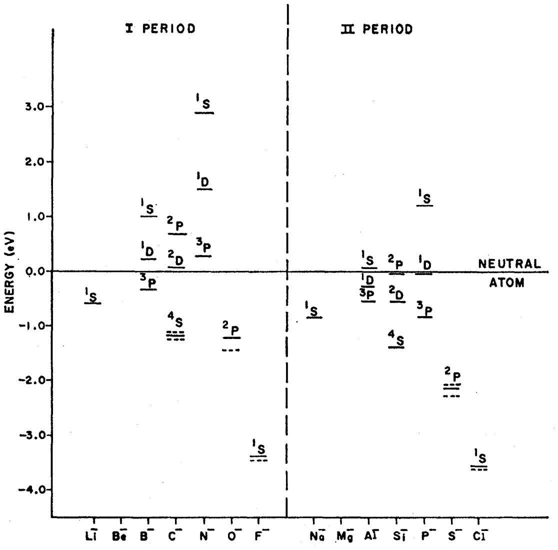

FIG. 1. Stability of the negative ions of the first and second rows of the periodic table. The energy scale along the ordinate is in eV, and the energies are given relative to the energy of the ground-state neutral atom. Dashed lines represent experimental data.

The method of Paper I extrapolates correlation energies along an isoelectronic sequence in which the data for the neutral atom and positive ions is obtained from accurately computed energies and observed ionization potentials. Errors in this correlation-energy data on which the extrapolation is based are due to errors in observed high ionization potentials. If more accurate experiments to determine high ionization potentials are performed, then because of the subsequent improvement in the data which is used for the extrapolation, the predicted electron affinities will be more accurate. The important point here is that the correlation energy along an isoelectronic sequence is a smooth and slowly changing function of atomic number, and can be extrapolated accurately. With revised values of ionization potentials, this method is capable of high accuracy, considerably better than that reported in I.

The method of the current paper is less accurate than that of I. Here we simply equate the change in correlation and relativistic energies in an ionization process, to a similar change in a process involving the detachment of an electron from a negative ion. The systems involved in the two processes which are compared have the same numbers of electrons, but the atomic numbers differ. The procedure can be justified by the argument of the previous section.

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[6] B. Edlén, J. Chem. Phys. **33**, 98 (1960).

TABLE VI. Electron affinities of first- and second-row atoms (eV).

	Paper I[a]	Method of this paper[b]	Edlén[c]	Other data
Li	0.58±0.06	1.15	0.82	0.62[d]
Be			−0.19	
B	0.30±0.06	0.20	0.33	
C	1.17±0.06	1.12	1.24	1.25 ±0.03[e]
N	−0.27±0.11	−0.42	0.05	
O	1.22±0.14	1.16	1.47	1.465±0.005[f]
F	3.37±0.08	3.08	3.50	3.448±0.005[g]
Ne			−0.57	
Na	0.78±0.06	0.91	0.47[h]	0.84[i]
Mg			−0.32	
Al	0.49±0.14	0.52	0.52	
Si		1.39	1.46	
P		0.78	0.77	1.12[j]
S		2.12	2.15	2.07 ±0.007[k]
Cl		3.56	3.70	3.613±0.003[g]

[a] Reference 1. The only serious discrepancy in this column when compared with the fourth column is the case of oxygen. This probably reflects an error in our correlation energy data.

[b] As discussed in the text these estimates are not considered as reliable as column 1, although they should be considerably better for the second-row atoms than for the first.

[c] Reference 6.

[d] A. W. Weiss, Phys. Rev. **122**, 1826 (1961). On the basis of extensive configuration interaction calculations on 4-electron systems Weiss gives 0.48 eV as a lower limit, with a probable value of 0.62 eV.

[e] M. Seman and L. M. Branscomb, Phys. Rev. **125**, 1602 (1962).

[f] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltmen, Phys. Rev. **111**, 504 (1958).

[g] R. S. Berry and C. W. Reimann, J. Chem. Phys. **38**, 1540 (1963).

[h] This entry seems anomolous. For instance, notice that using Edlén's extrapolation in all other cases except sodium, the second row affinity is higher than the corresponding member of the first row.

[i] R. Gáspár and B. Molner, Acta Phys. Hungar. **5**, 75 (1955).

[j] P. Gombás and K. Ladányi, Z. Physik **158**, 261 (1960). This electron affinity, and also that for Na in Ref. i, is computed using statistical theory. It should be pointed out that Gombás and Ladányi also use this same theory to compute values of 1.25 eV for S and 3.10 eV for Cl, both significantly different from the more accurate values listed in this table. Thus it is likely that the agreement between columns 1 and 4 for Na is accidental.

[k] L. M. Branscomb and S. J. Smith, J. Chem. Phys. **25**, 598 (1956).

Edlén's method[6] extrapolates ionization potentials along an isoelectronic sequence using observed data for the neutral atom, and singly and doubly positive ions of a given isoelectronic sequence. The extrapolation formulation is based on a perturbation expansion. Since the ionization potentials in an isoelectronic sequence are basically Z^2-dependent, any small deficiency in the extrapolation formula can give large errors in the extrapolated result. The agreement reported by Edlén between his extrapolated results and observed values is indeed impressive, but it is our consideration that the method of paper I is potentially more accurate. In addition, the methods of I and the current paper involve the computation of negative-ion wave functions which will be of use in computing other properties of the ions.

Table VI offers a comparison of our estimates of the electron affinities of the first- and second-row atoms with those of Edlén, and with the most reliable observations or other calculations in those cases where they have been made.

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