

## Atomic Negative Ions

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Results of Hartree-Fock calculations on the ions of  $\text{Li}^-$ ,  $\text{B}^-$ ,  $\text{C}^-$ ,  $\text{N}^-$ ,  $\text{O}^-$ ,  $\text{F}^-$ ,  $\text{N}^{--}$ ,  $\text{O}^{--}$  in states of the lowest electronic configuration, along with correlation and relativistic corrections, are given. These data are used to compute electron affinities for the atoms of the first row of the periodic table, and the stabilities of the excited states of the ions relative to the neutral atoms. Computed electron affinities for atoms on which experimental determinations are not available are  $0.58 \pm 0.05$  eV for lithium,  $0.3 \pm 0.05$  eV for boron, and  $-0.27 \pm 0.11$  eV for nitrogen. Computed electron affinities for other first row atoms are in agreement with experiment with the exception of oxygen, where the computed value of  $1.22 \pm 0.14$  eV is significantly less than the experimental determination of 1.47 eV. For the first row atoms, no excited states of the ground-state electronic configuration are lower in energy than the neutral atom, although  $\text{C}^- (^2D)$  is only  $0.08 \pm 0.05$  eV above.

### I. INTRODUCTION

**T**HEORETICAL computations of wave functions for negative ions are of interest for a number of reasons. For example, they provide the starting point for computations of photodetachment cross sections,<sup>1</sup> direct information on atomic electron affinities, and the possibility of more accurate work in solid-state computations where at present it is customary to use Hartree-Fock functions for the neutral atoms, although the relevant species approach ionic states in the solid.<sup>2</sup> In addition, a study of negative ions should be of interest in problems related to the spectra of high-temperature plasmas and stellar atmospheres. One of the dominant sources of spectral opacity is the photodetachment of negative ions,<sup>3</sup> since the binding energies of the negative ions correspond in general to radiation in the visible and infrared regions. The low-binding energy of the negative ions poses the interesting problem of the existence of excited states.<sup>4</sup> Previous theoretical computations on negative ions have been confined to very light atoms.<sup>5</sup>

In this work, we shall report Hartree-Fock functions for the ground and excited states of the lowest electronic configuration for  $\text{Li}^-$ ,  $\text{B}^-$ ,  $\text{C}^-$ ,  $\text{N}^-$ ,  $\text{O}^-$ ,  $\text{F}^-$ ,  $\text{N}^{--}$ , and  $\text{O}^{--}$ . The functions were computed with the atomic self-consistent field computer programs developed at the Laboratory of Molecular Structure and Spectra of the University of Chicago under the direction of Dr. Roothaan. These programs have already been extensively used in atomic calculations and, because of their flexibility and sophistication, it is now quite simple to obtain atomic Hartree-Fock functions.<sup>6</sup>

<sup>1</sup> L. M. Branscomb, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York and London, 1962), p. 100.

<sup>2</sup> See, for example, T. O. Woodruff, *Solid-State Phys.* **4**, 367 (1957).

<sup>3</sup> R. Woolley and D. W. Stibbs, *The Outer Layers of a Star* (Oxford University Press, London and New York, 1953).

<sup>4</sup> D. R. Bates and B. L. Moiseiwitch, *Proc. Phys. Soc. (London)* **A68**, 540 (1955).

<sup>5</sup> A. W. Weiss, *Phys. Rev.* **122**, 1826 (1961).

<sup>6</sup> E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1962); E. Clementi, *J. Chem. Phys.* **38**, 996, 1001 (1963).

Since the Hartree-Fock method does not include the correlation effects, we have made use of simple techniques<sup>7</sup> to obtain the correlation energy. Those techniques have been proven sufficiently reliable to ensure that a meaningful discussion on the stability of negative ions can be presented. In addition, to obtain the total energy of the negative ions, the relativistic correction has been computed with standard perturbation theory.<sup>8</sup> Thus, we are in a position to predict electron affinities and spectral transitions for negative ions and to compare these with experimental data, when available.

An excellent review of data and problems related to negative ions has been published recently by Branscomb.<sup>1</sup> The comprehensive list of references offered there can be used to supplement those given in this paper.

### II. HARTREE-FOCK FUNCTIONS

In Roothaan's formulation of the Hartree-Fock method<sup>9</sup> each set of electrons of a given azimuthal quantum number occupies orbitals which are expanded in terms of exponential basis functions (Slater-type orbitals) of the type

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

where  $N$  is a normalizing factor;  $n$ ,  $l$ ,  $m$  are integer quantum numbers,  $\zeta$  is an orbital exponent; and  $r$ ,  $\theta$ ,  $\phi$  are the spherical polar coordinates based on the nucleus. The electrons are under the constraint that all electrons in atomic orbitals with the same principal and azimuthal quantum numbers have the same radial distribution. This happens to be an important constraint in calculations on negative ions where we should distinguish between two cases:

(a) The electron or electrons added to the neutral atom are assigned to an orbital with the same principal

<sup>7</sup> E. Clementi, *J. Chem. Phys.* **38**, 2248 (1963); *J. Chem. Phys.* **39**, 175 (1963).

<sup>8</sup> H. Hartmann and E. Clementi (to be published); E. Clementi, *J. Mol. Spectry.* (to be published).

<sup>9</sup> C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960); C. C. J. Roothaan and P. Bagus, *Methods in Computational Physics* (Pergamon Press, Inc., New York, 1963), Vol. II.

TABLE I. Orbital exponents of the basis functions.<sup>a</sup>

	Li <sup>-</sup> ( <sup>2</sup> S)	B <sup>-</sup> ( <sup>3</sup> P)	B <sup>-</sup> ( <sup>1</sup> D)	B <sup>-</sup> ( <sup>1</sup> S)	C <sup>-</sup> ( <sup>1</sup> S)	C <sup>-</sup> ( <sup>2</sup> D)	C <sup>-</sup> ( <sup>2</sup> P)
1s	2.4739	4.5640	4.5391	4.5688	5.4195	5.3913	5.4416
1s	4.6925	8.0511	8.2048	8.0187	9.1839	9.1515	9.0528
2s	0.2675	1.6148	1.6205	1.6221	2.1527	2.1319	2.0017
2s	0.5352	4.0979	3.9275	4.1555	4.7820	4.8765	5.2357
2s	1.0287	0.8981	0.9138	0.9066	1.1782	1.1950	1.1305
2p	1.6350 <sup>b</sup>	1.2949	1.1970	0.6671	1.4569	1.4808	1.4019
2p		2.0385	2.3454	1.9123	2.4600	2.5569	2.5430
2p		0.8615	0.7965	5.5469	0.8755	0.8959	1.0175
2p		0.4208	0.3450	3.5000	0.5308	0.5050	0.5129
2p		5.3082	7.9566		5.6874	6.0238	6.3854
	N <sup>-</sup> ( <sup>3</sup> P)	N <sup>-</sup> ( <sup>1</sup> D)	N <sup>-</sup> ( <sup>1</sup> S)	N <sup>-</sup> ( <sup>2</sup> P)	O <sup>-</sup> ( <sup>2</sup> P)	O <sup>-</sup> ( <sup>1</sup> S)	F <sup>-</sup> ( <sup>1</sup> S)
1s	6.5155	6.5287	6.5044	6.5007	7.6126	7.6169	8.9165
1s	10.9756	11.1375	11.1168	11.0638	13.3654	12.2200	14.7007
2s	2.5696	2.5660	2.5559	2.5802	3.2045	2.7615	3.2762
2s	5.7021	5.5984	5.5431	5.6431	6.2896	7.0898	8.0477
2s	1.4260	1.4275	1.4353	1.4031	1.7637	1.4861	1.8485
2p	1.6109	1.6000	1.5950	1.6093	1.7424	1.5566	2.0519
2p	3.0338	3.0279	3.0118	2.9317	3.4363	3.4300	3.9288
2p	0.8693	0.8837	0.9696	0.7000	0.8565	0.4302	1.4496
2p	0.5696	0.5683	0.5791	0.4000	0.4700	0.5501	0.9763
2p	7.1175	7.1499	7.2644	3.6175	7.8070	8.1268	8.2943

<sup>a</sup> In this table the notation 1s, 2s, 2p refers to Slater-type basis functions. In Table II notation 1s, 2s, 2p refers to Hartree-Fock atomic orbitals.

<sup>b</sup> This basis function for Li<sup>-</sup> is of 2s type.

and azimuthal quantum numbers as the orbital of some other electron in the neutral atom.

(b) The electron or electrons added to the neutral atom are assigned to an orbital having either principal or azimuthal quantum numbers or both, different from the orbitals of all the other electrons.

In case (a) one can without difficulty for the ground-state electronic configurations of the negative ions obtain stable Hartree-Fock solutions in which the added electrons are bound, even though in some cases the energy of this state is above the energy of the photodetached state (i.e., the energy of the neutral atom). In these cases if the constraint were not present, during the optimization of the wave function, the added electron would probably become more and more radially diffuse in order to minimize the energy of the system; but with the constraint, enough electrons to leave a positive ion would have to be detached from the atom, and is energetically unfavorable. Examples of case (a) are Li<sup>-</sup>, B<sup>-</sup>, C<sup>-</sup>, N<sup>-</sup>, N<sup>-</sup>, O<sup>-</sup>, O<sup>-</sup>, and F<sup>-</sup> in their lowest electronic configurations, and the results of Roothaan-Hartree-Fock calculations on the states of these configurations are given in Tables I-III. Case (a) examples where an excited electronic configuration is involved and where one can probably, in the Hartree-Fock approximation, obtain stable negative ion solutions are Li<sup>-</sup>:1s<sup>2</sup>2p<sup>2</sup> and F<sup>-</sup>:1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>3s<sup>2</sup>.

In case (b), since the added electrons are not under the constraint of having the same radial dependence as some other electrons in the atom, during the optimization of the wave function for the negative-ion system, it is our experience that one of the orbital exponents in the basis set will approach zero, and the corresponding basis function will become the dominant component in an occupied atomic orbital. In the limit this corresponds

to the photodetached state. Examples are He<sup>-</sup>, Be<sup>-</sup>, and Ne<sup>-</sup> in their lowest configurations. If one could find a case (b) example where, in the Hartree-Fock approximation, the negative ion had a lower energy than the neutral atom, then the procedure involved in optimizing the wave function would converge on a state corresponding to a stable ion.

Table I lists for the lowest electronic configurations of some first-row ions, the optimized orbital exponents along with the symmetry types and principal quantum numbers of the Slater-type orbital basis functions used to construct Hartree-Fock atomic orbitals. Table II lists the coefficients of the basis functions in the Hartree-Fock orbitals. Table III lists total energies and orbital energies computed from the wave functions of Tables I and II. For comparison it also lists similar data for previously published wave functions<sup>6</sup> for the ground state of the corresponding neutral atoms.

The ratio of  $V/E$  (where  $V$  and  $E$  are the Hartree-Fock potential and total energies, respectively) for the calculations reported here is in the range  $2 \pm 10^{-5}$ , with the exception of the calculations for B<sup>-</sup>(<sup>1</sup>S), N<sup>-</sup>(<sup>2</sup>P), O<sup>-</sup>(<sup>1</sup>S). Because of difficulties with convergence of the self-consistent field procedure for these cases, and the added difficulty that these wave functions that did converge in many instances were excited-state wave functions, the calculations for these three states are suspect. For B<sup>-</sup>, the Lande interval rule for the multiplets of the lowest configuration should be satisfied better than our calculations show, which is another indication that the B<sup>-</sup>(<sup>1</sup>S) calculation needs improving. Also, these three states, in our calculations, have a positive orbital energy, again signifying that there is something wrong.

If the quantum mechanical virial theorem is satisfied,

then the ratio  $V/E$  should be precisely 2. The calculated ratio  $V/E$  gives an indication of how well the wave function has been optimized with respect to both orbital exponents and expansion coefficients, since if complete optimization is carried out, the virial theorem is automatically satisfied. However, it should be added, one can chance on wave functions that have ratios  $V/E$  very close to 2, even though they are not well optimized, and also that the ratio gives no indication whatsoever of how close the computed wave function is to the Hartree-Fock solution. Indeed, very simple wave functions can exactly satisfy the virial theorem, even though the basis set used is quite inadequate to reach the Hartree-Fock limit.

In comparing the results for neutral atoms and negative ions the fact that the energy of the orbital containing the added electrons is higher in the negative ion than in the neutral atom should be noted. Correspondingly, the maximum in the radial distribution for this orbital is farther away from the nucleus in the ion than in the neutral atom.

### III. CORRELATION ENERGY AND ELECTRON AFFINITY

Inspection of the differences in the Hartree-Fock energies of the negative ions and the neutral atoms given in Table IV shows that in the Hartree-Fock approximation, of all the first-row negative ions only  $C^-(4S)$  and  $F^-(1S)$  are energetically stable in comparison with the lowest detached state, or in other words only these two atoms have positive electron affinities. This is not the case in reality, and one has to correct the Hartree-Fock model by taking into account the correlation energies in these systems and to a much smaller extent making relativistic corrections. We can write an expression for the total energy  $E_{tot}$  of a system, in terms of a Hartree-Fock energy  $E_{H.F.}$ , a correlation energy  $E_C$ , and a relativistic energy  $E_R$ ,<sup>10</sup> namely

$$E_{tot} = E_{H.F.} + E_C + E_R. \quad (1)$$

In Eq. (1), if  $E_{H.F.}$  has been calculated for infinite mass nuclei, then to yield the true experimental energy it should be mass corrected,<sup>11</sup> but since in our further discussion we will be using only differences of energies of systems with the same nuclei, it will be satisfactory to disregard this particular correction. Using Eq. (1), we can simply write an expression for the electron affinity E.A.(A) of a species A, namely,

$$\begin{aligned} \text{E.A.}(A) &= E_{tot}(A) - E_{tot}(A^-) \\ &= [E_{H.F.}(A) - E_{H.F.}(A^-)] + [E_C(A) - E_C(A^-)] \\ &\quad + [E_R(A) - E_R(A^-)]. \quad (2) \end{aligned}$$

Correlation energy and relativistic energy data is presented in Table III. The relativistic correction is

<sup>10</sup> A. Fröman, Phys. Rev. 112, 870 (1958).

<sup>11</sup> H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, Part I, p. 253.

TABLE II. Expansion coefficients.<sup>a</sup>

Li <sup>-(1S)</sup>	B <sup>-(3P)</sup>	B <sup>-(1D)</sup>	B <sup>-(1S)</sup>	C <sup>-(4S)</sup>	C <sup>-(2D)</sup>	C <sup>-(2P)</sup>	N <sup>-(3P)</sup>	N <sup>-(1D)</sup>	N <sup>-(1S)</sup>	N <sup>-(2P)</sup>	O <sup>-(2P)</sup>	O <sup>-(1S)</sup>	F <sup>-(1S)</sup>
1s	0.90851	0.92265	0.90478	0.91905	0.92119	0.90450	0.92193	0.92668	0.92905	0.92721	0.93738	0.89703	0.89485
0.89781	0.06844	0.06396	0.06986	0.08065	0.08346	0.08659	0.06151	0.05684	0.05833	0.05998	0.03883	0.06383	0.03607
0.11220	0.00145	0.00141	0.00147	0.00365	0.00413	0.00338	0.00320	0.00274	0.00298	0.00320	0.00177	0.00417	0.00398
-0.00001	0.03697	0.02578	0.03953	0.00806	0.00199	0.01822	0.02643	0.02664	0.02199	0.02193	0.03521	0.05143	0.08584
0.00012	-0.00008	-0.00015	-0.00009	-0.00049	-0.00073	-0.00062	-0.00020	-0.00008	-0.00020	-0.00020	0.00049	-0.00059	-0.00053
-0.00111													
0.00722													
2s	0.16997	0.18094	0.16746	0.18726	0.18862	0.17870	0.20046	0.20540	0.20983	0.20101	0.21372	0.20153	0.20209
0.10060	-0.01482	-0.01198	-0.01675	-0.01610	-0.01745	0.02193	-0.01158	-0.00926	-0.00850	-0.01267	-0.00567	0.01235	0.00806
0.01091	0.60870	0.63364	0.61199	0.54530	0.55640	-0.65181	0.56948	0.58165	0.59439	0.60300	0.50515	-0.70969	0.62940
-0.39777	0.07949	0.08084	0.08306	0.08783	-0.08448	0.07960	-0.09245	-0.09331	-0.09194	-0.10047	-0.11256	0.08239	-0.09702
-0.56499	0.49398	0.47204	0.49053	0.57448	0.55756	-0.45023	0.55196	0.54189	0.52883	0.52787	0.63373	-0.40236	0.48231
-0.20472													
0.08563	2p	2p	2p	2p	2p	2p	2p	2p	2p	2p	2p	2p	2p
	0.19089	-0.33010	0.82821	0.37911	0.37353	0.34219	0.49201	0.48071	0.44663	0.61028	0.53263	0.59510	0.49534
	0.15130	-0.11623	0.28246	0.21400	0.19624	0.21672	0.25176	0.25542	0.26146	-0.01751	0.30422	0.29159	0.30959
	0.43894	0.32479	0.00974	0.37520	0.33978	0.25896	0.29931	0.27317	0.22239	0.02922	0.28544	0.51530	0.05259
	0.36354	-0.42197	-0.01377	0.14926	0.23326	0.34134	0.08896	0.13205	0.22481	0.48426	0.00840	-0.13422	0.26664
	0.00825	-0.00229		0.01400	0.01072	0.00874	0.01108	0.01081	0.01042	0.16623	0.01370	0.01046	0.01709

<sup>a</sup> See footnote a of Table I. These expansion coefficients correspond to the basis functions of Table I.

TABLE III. Hartree-Fock, correlation, relativistic, and orbital energies for first-row atoms and ions in lowest electronic configuration.<sup>a</sup>

	$E_{H.F.}^b$	$E_C^c$	$E_R^d$	$\epsilon(1s)$	$\epsilon(2s)$	$\epsilon(2p)$
Li( <sup>2</sup> S)	-7.432726	-0.0453	-0.00055	-2.4777	-0.1963	
Li-( <sup>1</sup> S)	-7.428230	-0.071±0.002	-0.00055	-2.3228	-0.0145	
B( <sup>2</sup> P)	-24.52905	-0.125	-0.00610	-7.6953	-0.4947	-0.3099
B-( <sup>3</sup> P)	-24.51919	-0.146±0.002	-0.00605	-7.4247	-0.2423	-0.0263
B-( <sup>1</sup> D)	-24.49048	-0.156±0.002	-0.00608	-7.4710	-0.2752	-0.0077
B-( <sup>1</sup> S)	-24.43950 <sup>d</sup>	-0.177±0.003	-0.00605	-7.4434	-0.2494	+0.0509
C( <sup>2</sup> P)	-37.68861	-0.158	-0.01379	-11.3255	-0.7056	-0.4333
C-( <sup>4</sup> S)	-37.70878	-0.181±0.002	-0.01369	-10.9560	-0.3727	-0.0769
C-( <sup>2</sup> D)	-37.64252	-0.201±0.002	-0.01372	-11.0044	-0.4023	-0.0473
C-( <sup>2</sup> P)	-37.60084	-0.221±0.002	-0.01371	-11.0384	-0.4238	-0.0311
N( <sup>4</sup> S)	-54.40091	-0.188	-0.02740	-15.6289	-0.9452	-0.5675
N-( <sup>3</sup> P)	-54.32189	-0.257±0.004	-0.02720	-15.2421	-0.5805	-0.0935
N-( <sup>1</sup> D)	-54.26687	-0.267±0.004	-0.02723	-15.2718	-0.5981	-0.0774
N-( <sup>1</sup> S)	-54.18682	-0.297±0.005	-0.02727	-15.3174	-0.6257	-0.0554
N-( <sup>2</sup> P)	-54.02902 <sup>d</sup>	-0.323±0.010	-0.02723	-15.1583	-0.4521	+0.1265
O( <sup>3</sup> P)	-74.80936	-0.258	-0.04943	-20.6686	-1.2442	-0.6319
O-( <sup>2</sup> P)	-74.78948	-0.323±0.005	-0.04917	-20.1978	-0.8132	-0.1289
O-( <sup>1</sup> S)	-74.48442 <sup>d</sup>	-0.406±0.006	-0.04899	-20.0476	-0.6286	+0.1255
F( <sup>2</sup> P)	-99.40929	-0.324	-0.08288	-26.3829	-1.5726	-0.7300
F-( <sup>1</sup> S)	-99.45936 <sup>f</sup>	-0.398±0.003	-0.08242	-25.8294	-1.0744	-0.1808

<sup>a</sup> Energies in atomic units.<sup>b</sup> Calculated energies not mass corrected. For ions, wave functions are in Tables I and II, for atoms, see Ref. 6.<sup>c</sup> For atoms, correlation energies from Ref. 7; for ions, by extrapolation from tables in Ref. 7.<sup>d</sup> Calculations on this state were difficult, due to a combination of nonconvergence in the self-consistent field procedure, and wave functions for excited states being produced. These values are, therefore, suspect.<sup>e</sup> Spin-orbit correction not included.<sup>f</sup> Hartree-Fock calculations on F<sup>-</sup> have been previously made by L. C. Allen, J. Chem. Phys. **34**, 1156 (1961); L. M. Sachs, Phys. Rev. **134**, 1283 (1961).

discussed in the next section of this paper. For elements in the first row of the periodic table, the difference between neutral atom and negative-ion relativistic corrections is negligible, as can be seen from the data in Table III. This difference is not tabulated in Table IV, while the other two differences on the right of Eq. (2) are. The correlation energy data is obtained either directly or by extrapolation from tables previously published by one of us.<sup>7</sup> If we accept the previously published correlation energies for the neutral atoms and positive ions as correct, then the range of uncertainty quoted in Table III for the correlation energies of the negative ions has been given rather conservatively, and we therefore feel that our table of electron affinities is fairly reliable.

Previously, the electron affinity of boron has been known only on the basis of empirical extrapolation procedures, and we note that our determination here of  $0.3 \pm 0.05$  eV agrees well with that predicted by Edlen,<sup>12</sup> but is in disagreement with that predicted by Johnson and Rohrlich.<sup>13</sup>

According to our determination here, the electron affinity of nitrogen is definitely negative and in the range  $-0.16$  to  $-0.38$  eV. This is in disagreement with both extrapolation procedures,<sup>12,13</sup> but certainly indicates that, of the two, Edlen's is the more reliable.

The discrepancy between our result and the accurate experimental determination for oxygen<sup>14</sup> should be

<sup>12</sup> B. Edlen, J. Chem. Phys. **33**, 98 (1960).<sup>13</sup> H. R. Johnson and F. Rohrlich, J. Chem. Phys. **30**, 1608 (1959).<sup>14</sup> L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. **111**, 504 (1958).

noted. This possibly points up errors in our correlation energy data, but not sufficient to invalidate our conclusion on the sign of the nitrogen electron affinity, and the magnitude of the electron affinity of boron.

#### IV. RELATIVISTIC ENERGIES

The relativistic correction can be approximated by the use of first-order perturbation theory on the Hartree-Fock functions. The method and the program used in obtaining the results shown in Table III is described at length by Hartmann and Clementi.<sup>8</sup> Here, we wish to point out that the Hartree-Fock functions are not sufficiently accurate representations of the system to yield quantitative results, and the computed relativistic energy is systematically too large in absolute magnitude by a few percent. However, considerable numerical improvement can be obtained by correcting the relativistic energy computed for the 1s electrons, by using values obtained from Pekeris' correlated functions. This is equivalent to subtracting a constant amount from ions and atoms with the same atomic number. Since we are interested in differences of relativistic energies for ions with the same atomic number, we can use the less accurate data presented in Table III without making the above mentioned correction. A spin-orbit correction should be added to the data in Table III. However, the spin-orbit splitting for the first-row elements is at most of the order  $400 \text{ cm}^{-1}$ . In addition, keeping in mind the Landé rules, only a fraction of this value should be taken as the spin-orbit correction, i.e., the difference between the lowest multiplet and the center of gravity of the term. Thus,

TABLE IV. Stability of states of the lowest configuration of negative ions relative to the neutral atom.<sup>a</sup>

<i>A</i>	<i>A</i> <sup>-</sup>	$E_{H.F.}(A) - E_{H.F.}(A^-)^b$	$E_C(A) - E_C(A^-)^b$	$E_{tot}(A) - E_{tot}(A^-)^c$	Electron affinity <sup>d</sup>
Li( <sup>2</sup> S)	Li <sup>-</sup> ( <sup>1</sup> S)	-0.004496	0.026±0.002	+0.0215±0.002	0.023 (0.616 eV) <sup>e</sup>
B( <sup>2</sup> P)	B <sup>-</sup> ( <sup>3</sup> P)	-0.00986	0.021±0.002	+0.011 ±0.002	
B( <sup>2</sup> P)	B <sup>-</sup> ( <sup>1</sup> D)	-0.03857	0.031±0.002	-0.008 ±0.002	
B( <sup>2</sup> P)	B <sup>-</sup> ( <sup>1</sup> S) <sup>i</sup>	-0.08950	0.052±0.003	-0.037 ±0.003 <sup>i</sup>	
C( <sup>2</sup> P)	C <sup>-</sup> ( <sup>4</sup> S)	+0.02017	0.023±0.002	+0.043 ±0.002	0.046 (1.25 eV) <sup>f</sup>
C( <sup>2</sup> P)	C <sup>-</sup> ( <sup>2</sup> D)	-0.04609	0.043±0.002	-0.003 ±0.002	
C( <sup>2</sup> P)	C <sup>-</sup> ( <sup>2</sup> P)	-0.08777	0.063±0.002	-0.025 ±0.002	
N( <sup>4</sup> S)	N <sup>-</sup> ( <sup>3</sup> P)	-0.07902	0.069±0.004	-0.010 ±0.004	
N( <sup>4</sup> S)	N <sup>-</sup> ( <sup>1</sup> D)	-0.13404	0.079±0.004	-0.055 ±0.004	
N( <sup>4</sup> S)	N <sup>-</sup> ( <sup>1</sup> S)	-0.21409	0.109±0.005	-0.105 ±0.005	
N <sup>-</sup> ( <sup>3</sup> P)	N <sup>-</sup> ( <sup>2</sup> P) <sup>†</sup>	-0.29287	0.066±0.014	-0.227 ±0.014 <sup>†</sup>	
O( <sup>2</sup> P)	O <sup>-</sup> ( <sup>2</sup> P)	-0.01988	0.065±0.005	+0.045 ±0.005	0.054 (1.465 eV) <sup>g</sup>
O <sup>-</sup> ( <sup>2</sup> P)	O <sup>-</sup> ( <sup>1</sup> S) <sup>†</sup>	-0.30506	0.083±0.011	-0.222 ±0.011 <sup>†</sup>	
F( <sup>2</sup> P)	F <sup>-</sup> ( <sup>1</sup> S)	+0.05007	0.074±0.003	+0.124 ±0.003	0.127 (3.448 eV) <sup>h</sup>

<sup>a</sup> Energies in atomic units unless specifically designated otherwise.

<sup>b</sup> Calculated from Table III.

<sup>c</sup> Calculated from Eq. (2).

<sup>d</sup> The values listed in this column are selected from available literature as probably being the most reliable. If other values are available they are listed for completeness in the succeeding footnotes. This compilation is largely taken from Table III in Ref. 1.

<sup>e</sup> A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

<sup>f</sup> M. Seman and L. M. Branscomb, Phys. Rev. **125**, 1602 (1962).

<sup>g</sup> L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. **111**, 504 (1958).

<sup>h</sup> R. S. Berry and C. W. Reimann, J. Chem. Phys. **38**, 1540 (1963). Other values are 3.62±0.09 eV [T. L. Bailey, J. Chem. Phys. **28**, 792 (1958)], 3.48 eV [D. Cubicciotti, J. Chem. Phys. **31**, 1646 (1959)], 3.47 eV [I. N. Bakulina and N. I. Ionov, Dokl. Akad. Nauk. SSSR **105**, 680 (1955)].

<sup>†</sup> See footnote d to Table III.

we can safely conclude that neglecting the spin-orbit correction is entirely reasonable for our purposes.

#### V. STABILITY OF EXCITED STATES OF THE LOWEST CONFIGURATION OF NEGATIVE IONS

Little is known experimentally about the stability of excited states of negative ions. Theoretical indications<sup>4</sup> have been that while there is little likelihood of excited electronic configurations of light atoms being bound, excited states of the ground configuration might be, in certain cases. Our results presented in Table IV indicate that, for the first row of the periodic table, no excited states of the ions have a lower energy than the ground state of the atom, although the C<sup>-</sup>(<sup>2</sup>D) state is very close in energy to that of C(<sup>3</sup>P), our estimate being 0.03 to 0.15 eV above. The C<sup>-</sup>(<sup>2</sup>D) state has recently

been observed by Seman and Branscomb.<sup>15</sup> These authors conclude that this state lies very near the continuum corresponding to the photodetached state, and they tentatively predict that this <sup>2</sup>D state is -0.05-eV bound, on the basis of the extrapolation procedures of Edlen,<sup>12</sup> and Johnson and Rohrlach.<sup>13</sup> This value lies within our predicted range.

For the second row of the periodic table<sup>6</sup> the situation is different because of the smaller multiplet splittings between the state of a given electronic configuration, and in this case there are excited states more stable than the neutral atom. In agreement with earlier predictions<sup>4</sup> the most favorable case is that of Si<sup>-</sup>(<sup>2</sup>D).

<sup>15</sup> M. Seman and L. M. Branscomb, Phys. Rev. **125**, 1602 (1962).

<sup>16</sup> E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine (to be published).