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Electron Affinity of Boron, Carbon, Nitrogen, and Oxygen Atoms

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The electron affinity of boron, carbon, nitrogen, and oxygen atoms has been calculated by the method of Bacher and Goudsmit which enables the energy of a state in an n-electron configuration to be calculated in terms of the spectroscopic values of the energies of states of the $(n-1)$-, $(n-2)$-, ..., 1-electron ions. The negative ions of boron and nitrogen are found to be unstable, the electron affinity being *ca* -0.14 and -0.72 ev, respectively. The electron affinities of carbon and oxygen atoms are 1.75 and 1.13 ev, respectively. The last value is in fair agreement with the recently observed values, 1.48 ev found by Branscomb and Smith, and 1.05 found by Schüler and Bingel.

VARIOUS theoretical calculations have been suggested for the estimation of the electron affinity of various atoms.[1] For the simplest of atomic systems, namely the negative ion of the hydrogen atom, accurate calculations have been carried out by the variational method. For ions involving more than two electrons, calculations of similar accuracy (i.e., with the use of Hylleraas wave functions) would be excessively lengthy. Calculations with the Hartree-Fock method would be simpler, but that method is not suitable for the accurate determination of the rather small difference between the rather large total energies of the n- and $(n-1)$-electron systems. Extrapolation methods based on some polynomial expressions for the ionization potentials of an isoelectronic sequence in powers of the nuclear charge Z have also been used; but the disadvantage with this method is that the coefficients of terms like $1/Z$, $1/Z^2$ determined from the higher positive ions in the sequence may not be accurate for the extrapolation to the negative ion.

It was first suggested by Bacher and Goudsmit[2] and by the writer[3] that the method of Bacher and Goudsmit,[2] which expresses the energy of a state in an n-electron atom in terms of the energies of various states of the preceding ions, may be useful for the estimation of electron affinity of atoms. The method is the more accurate the further one can go back in the series of $(n-1)$-, $(n-2)$-, $(n-3)$-, $\cdots$, 1-electron ions. The method has been applied to the case of the fluorine atom.[3,4] The limitation of the method is, apart from the approximate nature of the method itself, that in most cases not all the states of the higher ions have been found spectroscopically. In the case of the fluorine atom, this method seems more satisfactory than other calculations of comparable simplicity. In the present note, the Bacher-Goudsmit method has been applied to boron, carbon, nitrogen, and oxygen atoms.

In each case, the energy difference between the ground state of the negative ion and that of the neutral atom is calculated from the spectroscopic term values of the preceding ions.[5] For a multiplet, say ^3P, the "center of gravity" of the components $^3P_{0,1,2}$ is employed. Table I summarizes the spectroscopic data and the result of the calculation. For B$^-$ and C$^-$, the lowest state, namely, $1s^22s^22p^2\,{}^3P$ and $1s^22s^22p^3\,{}^4S$ respectively, can be calculated from the expressions for these states in terms of the ions up to $1s^2\,{}^1S$ given in the paper by Bacher and Goudsmit and the spectroscopic values given in Table I. For N$^-$, the expression for the state $1s^22s^22p^4\,{}^3P$ is also given in that paper. As the states of $1s^22s2p^4\,{}^3P$ of N I and of $1s^22p^4\,{}^3P$ of N II have not yet been observed, these states are in turn expressed in terms of the states of their preceding ions. The final expression is

$$\begin{aligned}
&1s^22s^22p^4\,{}^3P\\
&\quad=\tfrac{1}{3}(s^2p^3)[4\,{}^4S+5\,{}^2D+3\,{}^2P]+(4/3)(sp^4)\,{}^4P\\
&\qquad-\tfrac{1}{3}(s^2p^2)[12\,{}^3P+5\,{}^1D+{}^1S]-(1/9)(sp^3)\\
&\qquad\times[15\,{}^5S+{}^3S+20\,{}^3D+12\,{}^3P]+4(s^2p)\,{}^2P\\
&\qquad+(4/9)(sp^2)[11({}^4P)+{}^2P+5({}^2D)+{}^2S]\\
&\qquad\qquad-(s^2)\,{}^1S-\tfrac{1}{3}(sp)[14\,{}^3P+2\,{}^1P]+(4/3)(s)\,{}^2S.
\end{aligned}$$

From Table I, it is seen that the electron affinity of nitrogen is ~ -5850 cm^{-1} $= -0.72$ ev and no stable N$^-$ exists. This is of considerable interest in connection with the problem of the positive β-decay of the O^{14} nucleus.[6]

For C$^-$, the electron affinity calculated is 14 169 cm^{-1} or 1.75 ev. For B$^-$, it is -1135 cm^{-1} or -0.14 ev so that B$^-$ is unstable.

To obtain an idea of the accuracy of this method of calculation, we have calculated the energy of the $1s^22s^22p^3\,{}^4S$ from the energies of the states of preceding ions by means of the expression for $s^2p^3\,{}^4S$. The calculated value of $E(1s^22s^22p^3\,{}^4S)$ of N I is $-2\,154\,261$ cm^{-1}, referred to the state $1s^2\,{}^1S$ of N VI, compared with the observed value $-2\,153\,201$. The error is -1060 cm^{-1} or 0.13 ev.

For O$^-$, the expression for the state $1s^22s^22p^5\,{}^2P$ given in Bacher-Goudsmit contain the term $1s^22p^5\,{}^2P$ in O II which has not yet been observed. We shall hence make use of the expression for $1s^22s2p^5\,{}^2P$ of O I in terms of

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[1] See H. S. W. Massey, *Negative Ions* (Cambridge University Press, London, 1950).

[2] R. F. Bacher and S. A. Goudsmit, Phys. Rev. **46**, 948 (1934).

[3] T. Y. Wu, Phil. Mag. **22**, 837 (1936).

[4] J. L. Margrave, J. Chem. Phys. **22**, 636 (1954).

[5] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D. C., 1949).

[6] M. E. Rose, Phys. Rev. **90**, 1123 (1953).

TABLE I. Term values in cm^{-1} referred to the state $1s^2\,{}^1S$.

Atom	B	C	N	O
$1s^2\,{}^1S$	0	0	0	0
$1s^22p\,{}^2P$	257 550	455 622	708 970	
$1s^22s\,{}^2S$	305 931	520 178	789 533	1 114 000
$1s^22p^2\,{}^1D$	406 464			
${}^3P$	409 900	768 911	1 238 786	
$1s^22s2p\,{}^1P$	435 430	803 986	1 283 689	1 873 904
${}^3P$	471 478	853 971	1 347 111	1 950 289
$1s^22s^2\,{}^1S$	508 826	906 338	1 414 384	2 032 702
$1s^22p^3\,{}^4S$		960 972	1 610 207	
$1s^22s2p^2\,{}^2P$	503 213	992 344	1 651 060	2 476 455
${}^2S$			1 666 006	2 492 731
${}^2D$	527 900		1 695 983	2 530 156
${}^4P$	546 946	1 059 964	1 739 727	2 585 719
$1s^22s^22p\,{}^2P$	575 756	1 102 997	1 796 835	2 657 098
$1s^22s2p^3\,{}^1P$				2 889 833
${}^3S$		1 088 074	1 880 726	2 903 205
${}^1D$				2 913 242
${}^3P$			1 926 636	2 957 908
${}^3D$			1 943 606	2 980 250
${}^5S$		1 160 140	1 988 689	3 039 979
$1s^22s^22p^2\,{}^1S$			2 003 169	3 057 108
${}^1D$	569 120 calc.		2 020 540	3 080 021
${}^3P$	B^- 574 621 calc.	1 193 875	2 035 767	3 100 292
$1s^22s2p^4\,{}^2P$				3 171 193
${}^2S$				3 188 132
${}^2D$				3 217 851
${}^4P$			2 065 066	3 263 909
$1s^22s^22p^3\,{}^2P$			2 124 361	3 343 375
${}^2D$			2 133 974	3 357 026
${}^4S$		C^- 1 208 044 calc.	2 153 201	3 383 842
$1s^22s2p^5\,{}^1P$				3 303 842
${}^3P$				3 367 375
$1s^22s^22p^4\,{}^1S$				3 459 887
${}^1D$				3 447 811
${}^3P$			N^- 2 147 351 calc.	3 493 679
$1s^22s^22p^5\,{}^2P$				O^- 3 502 808 calc.

the states of the preceding ions, and obtain

$$\begin{aligned} s^2p^5\,{}^2P={}&\tfrac{1}{3}(s^2p^4)[9\,{}^3P+5\,{}^1D+{}^1S]+\tfrac{1}{2}(sp^5)[3\,{}^3P-{}^1P]\\ &-(s^2p^3)[2\,{}^4S+5\,{}^2D+3\,{}^2P]\\ &-\tfrac{1}{3}(sp^4)[12\,{}^4P-3\,{}^2P+5\,{}^2D+{}^2S]\\ &+\tfrac{1}{3}(s^2p^2)[18\,{}^3P+10\,{}^1D+2\,{}^1P]\\ &+\tfrac{1}{2}(sp^3)[5\,{}^5S-{}^3S+10\,{}^3D+6\,{}^3P]\\ &-5(s^2p)\,{}^2P-\tfrac{1}{3}(sp^2)[18\,{}^4P+10\,{}^2D+2\,{}^2S]\\ &+(s^2)\,{}^1S+\tfrac{1}{2}(sp)[9\,{}^3P+{}^1P]-(s)\,{}^2S. \end{aligned}$$

The calculated energy for $1s^22s^22p^5\,{}^2P$ of O^- is $-3\,502\,808$ cm^{-1} referred to $1s^2\,{}^1S$ of O VI, and this leads to an electron affinity of 9129 cm^{-1} or 1.13 ev which is in fair agreement with the recent observed values, 1.05 ev found by Schüler and Bingel[7] and 1.48 ev found by Branscomb and Smith.[8]

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[7] V. H. Schüler and W. Bingal, Z. Naturforsch. **10A**, 252 (1955).

[8] L. M. Branscomb and S. J. Smith, Phys. Rev. **98**, 1127 (1955), and private communication (to appear in J. Research Natl. Bur. Standards).