PHYSICAL REVIEW A VOLUME 57, NUMBER 5 MAY 1998

Negative ions of carbon, nitrogen, and phosphorus

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(Received 22 December 1997)

Negative ions of the nitrogen atom have yet to be observed. We estimate the electron affinity of the N^- system to be approximately -0.181 eV using the multiconfiguration Dirac-Fock method. Similar calculations for the neighboring (same row) C^- and (same column) P^- system yield, respectively, 1.210 eV and 0.702 eV, in good agreement with measurements: respectively, 1.263 eV and 0.746 eV. The discrepancies that remain are primarily due to core-core and core-valence correlation effects that have been neglected. The improbability of the existence of a stable N^- system is already evident from a comparison of much simpler calculations with measurements for systems in the same row and neighboring row of the Periodic Table.
[S1050-2947(98)10805-3]

PACS number(s): 31.25.−v, 31.30.Jv

I. INTRODUCTION

The Periodic Table of the negative ions is still only begining to be understood. Mysteries abound in the attempt to describe the negative ions of the elements in a systematic manner. For example, the group-IIB negative ions are all unstable in contrast to those of group-IIA [1,2]. Another example is the negative ions of group-IIA elements where, Be^- is a metastable ion [3,4], Mg^- is unstable [1,2,5,6] and the ions such as Ca^- and beyond are stable with progressively increasing binding energies [7]. Similarly, nitrogen, the lightest of the group VB elements, does not form a stable negative ion but the subsequent group-VB elements do, and with increasing electron affinities [1,2].

In this paper the instability of the negative ion of nitrogen will be addressed and contrasted to the stability of the phosphorus negative ion. Nitrogen, which has a half-filled outer shell $(1s^2 2s^2 2p^3)$, is known to form negative ions with difficulty or not at all as might be expected from elementary arguments based on the Pauli exclusion principle [8]. But it is interesting to note that phosphorus, which also has a half-filled outer shell $(1s^2 2s^2 2p^6 3s^2 3p^3)$, does form stable negative ions, unlike nitrogen.

As seen from Table I, the Dirac-Fock (DF) electron affinities of B, C, N, O, F, Al, Si, P, S, and Cl reproduce the observed trend in electron affinities, though the magnitudes are underestimated. This clearly shows that an analysis of the contributions from the Coulomb and exchange interactions to the DF ground-state energies of N and N^- and P and P^- may explain the instability and stability of the respective anions. We report such studies in this paper. For comparison, similar studies were carried out for C and C^-. To support the results

TABLE I. Ground-state (GS) symmetries of neutral B, C, N, O, F, Al, Si, P, S, and Cl and their anions, and corresponding DF electron affinities (EA's). Observed electron affinities taken from Hotop and Lineberger [1,2] are also presented for comparison. Electron affinities are measured in eV.

Element	B $(Z=5)$	C $(Z=6)$	N $(Z=7)$	O $(Z=8)$	F $(Z=9)$
GS of neutral	$2p(^2\mathrm{P}^o_{1/2})$	$2p^2(^3\mathrm{P}^e_0)$	$2p^3(^4\mathrm{S}^o_{3/2})$	$2p^4(^3\mathrm{P}^e_2)$	$2p^5(^2\mathrm{P}^o_{3/2})$
GS of anion	$2p^2(^3\mathrm{P}^e_0)$	$2p^3(^4\mathrm{S}^o_{3/2})$	$2p^4(^3\mathrm{P}^e_2)$	$2p^5(^2\mathrm{P}^o_{3/2})$	$2p^6(^1\mathrm{S}^e_0)$
EA (DF)	-0.270	0.542	-2.141	-0.548	1.332
EA (Experiment)	0.277	1.2629	<0	1.4611	3.399
Element	Al $(Z=13)$	Si $(Z=14)$	P $(Z=15)$	S $(Z=16)$	Cl $(Z=17)$
GS of neutral	$3p\ (^2\mathrm{P}^o_{1/2})$	$3p^2(^3\mathrm{P}^e_0)$	$3p^3(^4\mathrm{S}^o_{3/2})$	$3p^4(^3\mathrm{P}^e_2)$	$3p^5(^2\mathrm{P}^o_{3/2})$
GS of anion	$3p^2(^3\mathrm{P}^e_0)$	$3p^3(^4\mathrm{S}^o_{3/2})$	$3p^4(^3\mathrm{P}^e_2)$	$3p^5(^2\mathrm{P}^o_{3/2})$	$3p^6(^1\mathrm{S}^e_0)$
EA (DF)	0.033	0.930	-0.536	0.891	2.524
EA (Experiment)	0.441	1.385	0.7465	2.0771	3.617

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1050-2947/98/57(5)/3462(7)/$15.00

of these calculations further, a series of multiconfiguration DF (MCDF) calculations were also performed to study the effects of the interactions among valence electrons in the electron affinities of C, N, and P. The multiconfiguration models presented account for most valence shell correlation effects; MCDF models account for all of the dominant relativistic corrections to electronic structure.

A brief overview of the theory underlying our method is given in Sec. II. Some important details of our calculation are described in Sec. III. Our results are presented and compared with previous calculations and with measurements in Sec. IV. A summary and conclusion follow in Sec. V.

II. THEORY

A detailed presentation of the multiconfiguration Dirac-Fock (MCDF) theory may be found in Grant's review paper [9]. Our overview is intended only to establish notation and conventions. A relativistic many-body Hamiltonian H^R may be constructed from one-body Dirac operators, $H^D(i)$, and two-body operators — here taken to be those due to the Coulomb interaction — $H^C(ij)=\mathrm{e}^2/r_{ij}$,

$$H^R=\sum_i H^D(i)+\sum_{i<j} H^C(ij). \tag{1}$$

The operator H^R commutes with the atomic total angular momentum operator $\mathbf{J}^2$, the z component of this operator J_z, and the atomic parity operator Π. Configuration state functions (CSF's) are eigenfunctions of these three operators with eigenvalues $J(J+1)$, M, and P, respectively (Hartree atomic units are used here and throughout unless specifically mentioned otherwise). CSF's are linear combinations of Slater determinants of relativistic orbitals,

$$\phi_{n\kappa}(\mathbf{r})=\frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\,\chi_{+\kappa m}(\hat{\mathbf{r}}) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{2}$$

Here $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are, respectively, the large- and small-component radial wave functions; n is the principal quantum number; κ is the relativistic angular quantum number: $\kappa=\pm(j+\frac{1}{2})$ for $l=j\pm\frac{1}{2}$; the spherical spinors $\chi_{\kappa m}(\hat{\mathbf{r}})$ are eigenfunctions of the one-electron angular momentum operators $\mathbf{j}^2$, $\mathbf{l}^2$, $\mathbf{s}^2$, and j_z, and of the parity operator π. Approximate atomic state functions (ASF's) may be constructed as linear combinations of CSF's with given J^P. The orbitals and the ASF's and their energies are calculated using the self-consistent-field (SCF) procedure appropriate to the variational extremum of the optimal level (OL) energy functional.

We have used GRASP92 package [10] in all calculations. GRASP92 is designed for MCDF calculations involving a large number of CSF's. The package is based on the Hamiltonian (1) and thus provides a nonperturbative treatment of relativistic effects.

III. METHOD

The GRASP92 MCDF program [10] was used to perform series of OL [9] calculations to estimate the total energies and wave functions of the lowest-lying states of neutral C, N, and P, and their anions. The results of these calculations are summarized in Tables II, III, and IV.

A ''minimal'' CSF basis set was used in the calculations labeled ''Step 1'' in these tables: all ''relativistic'' CSFs with the appropriate total angular momentum and parity that arise from the equivalent ''nonrelativistic'' configuration are included in the calculation. For instance, consider the ground state of N: the nonrelativistic configuration is $2s^22p^3$, from which we obtain the three relativistic configurations $2s^22\overline{p^2}2p$, $2s^22\overline{p}2p^2$, and $2s^22p^3$. (We have used Swirles' notation in which a bar is placed above a symmetry label when the symmetry with $j=l-1/2$ is implied; the symmetry with $j=l+1/2$ is otherwise intended.) From these configurations, we obtain the three CSFs with $J^P=\frac{3}{2}^o$, which provide the relativistic equivalent of the LS-coupled representation $2s^22p^3(^4\mathrm{S}^o_{3/2})$. All radial functions were allowed to vary in step 1.

In step 2 and all subsequent steps, correlation among the electrons outside the largest possible ''rare gas core'' was estimated by a procedure in which the CSF ''basis'' was systematically expanded. In each successive step of the expansion, at least two, but in many cases three, four, or even five, such ''valence'' electrons were permitted the additional degrees of freedom represented by one-electron states with principal quantum number, n, in the range $n_{\min}\leqslant n\leqslant n_{\max}$, where $n_{\min}$ was 2 for C and N, but 3 for P. In Steps 2, 3, 4, ... , respectively, $n_{\max}=n_{\min}$, $n_{\min}+1$, $n_{\min}+2$, ... All radial wave functions were allowed to vary in the MCDF-OL1 calculations in step 2. In the MCDF-OL1 calculations of step 3 and all subsequent MCDF-OL1 calculations, all radial wave functions from the preceding calculations were held fixed so that only those radial wave functions with $n=n_{\max}$ were allowed to vary. Only single and double replacements were permitted in the generation of the CSF bases used in the MCDF-OL1 calculations. In our recent study of the electron affinity of Al [11], we found that inclusion of three- and four-electron excitations reduces the differences between the observed and calculated results. This is our motivation in including triple, quadruple, and even quintuple excitations in CI calculations for C, N, and P. Similar procedures were adopted to estimate the ground-state energies of the anions.

Electron correlation calculations are known to converge rather slowly as the CSF basis is expanded. A procedure for the acceleration of this convergence, based on the observed variation of the MCDF-OL1 energy with $n_{\max}$, was described by Parpia and Grant [12], and used to estimate Dirac-Coulomb ground-state energies of heliumlike systems with very high accuracy. In the present work we make use of Aitken's δ-squared process [13]

$$S'_n=S_{n+1}-\frac{(S_{n+1}-S_n)^2}{S_{n+1}-2S_n+S_{n-1}}, \tag{3}$$

which was found to yield essentially the same results and can be applied to the present case which also exhibits approximately geometric convergence.

Aitken's δ-squared process was applied to triplets of MCDF-OL1 calculations, to CI1 calculations, and to triplets of estimates from the δ-squared process itself. In Tables II–IV, extrapolations based on Eq. (3) for a triplet of successive

TABLE II. MCDF and relativistic CI total energies E of the $2s^2 2p^2(^3\mathrm{P}_0^e)$ ground (1, or first lowest) state of the C atom and the $2s^2 2p^3(^4\mathrm{S}_{3/2}^o)$ ground (1, or first lowest) state of the C^- anion; these are, respectively, the ''reference'' states from which CSF bases are generated by single (S), double (D), triple (T), quadruple (Qa), and quintuple (Qi) ''replacements'' of electronic states OL energy functionals have been used in the MCDF calculations; in steps 1 and 2 all radial functions are allowed to vary; in steps 3 and beyond, only radial functions with principal quantum number $n=$step are allowed to vary. The number of CSF's in a calculation is denoted n_{CSF}. Certain extremely large CI calculations were not attempted. All extrapolations were carried out using Aitken's δ-squared process. The details of the calculations labeled ''Best estimate'' are given in the text. The electron affinity (EA) obtained from each step of the calculation appears in the last column. The observed electron affinity is taken from Ref. [2].

			C		C^-	
Step	Calculation	n_{CSF}	E (hartree)	n_{CSF}	E (hartree)	EA (eV)
1	MCDF-OL1	2	−37.705 130 96	3	−37.725 053 63	0.5421
2	SD-MCDF-OL1	4	−37.722 779 67	4	−37.725 053 65	0.0619
3	SD-MCDF-OL1	67	−37.789 998 95	252	−37.821 731 98	0.8635
	SDT-CI1	115	−37.790 672 26	700	−37.823 818 98	0.9020
	SDTQa-CI1	144	−37.790 765 29	1 127	−37.824 831 34	0.9270
	SDTQaQi-CI1			1 272	−37.824 851 09	0.9275
4	SD-MCDF-OL1	267	−37.800 657 66	1 288	−37.838 046 90	1.0174
	Extrap (3,4,5)		−37.804 038 22		−37.843 561 35	1.0755
	SDT-CI1	938	−37.801 819 12	8 264	−37.842 015 04	1.0938
	Extrap (3,4,5)		−37.805 382 55		−37.848 371 75	1.1698
	SDTQa-CI1	1 776	−37.801 930 21	27 076	−37.843 158 38	1.1219
	ΔE(Qa)		−0.000 111 10		−0.001 143 34	
	SDTQaQi-CI1			45 545	−37.843 195 52	
	ΔE(Qi)				−0.000 037 14	
5	SD-MCDF-OL1	658	−37.803 224 20	3 640	−37.842 168 31	1.0597
	Extrap (4,5,6)		−37.804 554 92		−37.844 304 05	1.0816
	Extrap (4,5,6)		−37.804 901 00		−37.844 841 31	1.0868
	SDT-CI1	4 155	−37.804 519 34	42 593	−37.846 726 00	1.1485
	Extrap (4,5,6)		−37.805 899 29		−37.849 168 78	1.1774
	ΔE(Extrap (4,5,6))		−0.001 344 37		−0.004 864 74	
	SDTQa-CI1	12 212	−37.804 637 43	247 165		
6	SD-MCDF-OL1	1 306	−37.804 100 55	7 794	−37.843 575 06	1.0742
	Extrap (5,6,7)		−37.804 762 18		−37.844 615 79	1.0845
	Extrap (5,6,7)		−37.804 989 01		−37.844 857 76	1.0849
	SDT-CI1	13 210	−37.805 432 58	147 371	−37.848 334 65	1.1674
	SDTQa-CI1	58 652	−37.805 553 21	1 377 113		
7	SD-MCDF-OL1	2 264	−37.804 477 55	14 208	−37.844 173 25	1.0802
	Extrap (6,7,8)		−37.804 870 48		−37.844 752 02	1.0852
8	SD-MCDF-OL1	3 588	−37.804 669 95	23 332	−37.844 467 41	1.0829
	Best estimate	SD	−37.804 989 01		−37.844 857 76	
		T	−0.001 344 37		−0.004 864 74	
		Qa	−0.000 111 10		−0.001 143 34	
		Qi			−0.000 037 14	
			−37.806 444 48		−37.850 902 97	1.2098
Experiment						1.2629

GRASP92 estimates of a particular kind (SD-MCDF-OL1 or SDTQa-CI1, for instance) are denoted ''Extrap'' followed by the three steps involved listed in parentheses. Succesive estimates are successively indented.

The best estimate based on the systematically extended SD-MCDF-OL1 calculations are collected at the bottom of each of Tables II, III, and IV, together with the best estimates of the incremental changes to the energy due to the inclusion of triple, quadruple, and in some cases, quintuple, replacements. The differences in the final best estimate pair of energies for the neutral atom and its anion yield our best estimate of the electron affinity of the neutral system.

IV. RESULTS AND DISCUSSIONS

A. Dirac-Fock calculations

The DF method is a relativistic generalization of the usual (nonrelativistic) Hartree-Fock (HF) method. In the HF approach, an atomic state function is approximated by a single

TABLE III. MCDF and relativistic CI total energies E of the $2s^22p^3(^4S^o_{3/2})$ ground (1, or first lowest) state of the N atom and the $2s^22p^4(^3P^e_2)$ ground (1, or first lowest) state of the N^- anion; these are, respectively, the ''reference'' states from which CSF bases are generated by single (S), double (D), triple (T), quadruple (Qa), and quintuple (Qi) ''replacements'' of electronic states. Optimal level (OL) energy functionals have been used in the MCDF calculations; in steps 1 and 2 all radial functions are allowed to vary; in steps 3 and beyond, only radial functions with principal quantum number n = step are allowed to vary. The number of CSF's in a calculation is denoted n_{CSF}. Certain large CI calculations were not attempted. All extrapolations were carried out using Aitken's δ-squared process. The details of the calculation labeled ''Best estimate'' are given in the text. The electron affinity (EA) obtained from each step of the calculation appears in the last column. A stable negative ion of nitrogen has not yet been observed.

		N		N^-		
Step	Calculation	n_{CSF}	E (Hartree)	n_{CSF}	E (Hartree)	EA (eV)
1	MCDF-OL1	3	−54.432 463 52	2	−54.353 766 84	−2.1414
2	SD-MCDF-OL1	4	−54.432 463 70	2	−54.353 766 84	
3	SD-MCDF-OL1	252	−54.531 019 72	298	−54.492 220 78	−1.0558
	SDT-CI1	700	−54.532 363 32	1 183	−54.495 122 70	−1.0134
	SDTQa-CI1	1 127	−54.532 782 01	2 676	−54.498 276 45	−0.9389
	SDTQaQi-CI1	1 272	−54.532 786 16	3 788	−54.498 352 05	−0.9370
	ΔE(Qi)		−0.000 004 15		−0.000 075 60	
4	SD-MCDF-OL1	1 288	−54.550 177 28	1 658	−54.524 531 91	−0.6978
	Extrap (3,4,5)		−54.556 269 30		−54.537 944 92	−0.4986
	SDT-CI1	8 264	−54.552 548 76	16 364	−54.531 865 66	−0.5628
	Extrap (3,4,5)		−54.559 088 38		−54.548 295 98	−0.2937
	ΔE(Extrap (4,5,6))		−0.002 819 08		−0.010 351 06	
	SDTQa-CI1	27 076	−54.553 041 13	86 051	−54.535 613 06	−0.4742
	ΔE(Qa)		−0.000 492 36		−0.003 747 39	
5	SD-MCDF-OL1	3 640	−54.554 799 47	4 901	−54.534 010 26	−0.5657
	Extrap (4,5,6)		−54.557 209 48		−54.539 739 39	−0.4754
	Extrap (4,5,6)		−54.557 818 49		−54.541 404 83	−0.4466
	SDT-CI1	42 593	−54.557 488 14	90 404	−54.543 219 08	−0.3883
	SDTQ-CI1	247 165		880 702		
6	SD-MCDF-OL1	7 794	−54.556 383 54	10 817	−54.537 581 05	−0.5116
	Extrap (5,6,7)		−54.557 579 08		−54.540 603 16	−0.4619
	Extrap (5,6,7)		−54.557 997 27		−54.540 490 88	−0.4764
	SDT-CI1	147 371		326 090		
7	SD-MCDF-OL1	14 208	−54.557 064 87	20 133	−54.539 217 86	−0.4856
	Extrap (6,7,8)		−54.557 775 28		−54.540 474 10	−0.4708
8	SD-MCDF-OL1	23 332	−54.557 412 65	33 557	−54.539 928 61	−0.4758
	Best estimate	SD	−54.557 997 27		−54.540 490 88	
		T	−0.002 819 08		−0.010 351 06	
		Qa	−0.000 492 36		−0.003 747 39	
		Qi	−0.000 004 15		−0.000 075 60	
			−54.561 312 86		−54.554 664 93	−0.1809
	Experiment					<0

CSF that is a single determinant. In the DF approach, an atomic state function is approximated by a set of jj-coupled CSF's that reduce to a single nonrelativistic (LS-coupled) CSF in the formal limit $c \rightarrow \infty$, where c is the velocity of light in the vacuum [14]. A DF wavefunction may be viewed as the probability wavefunction for a single electron moving in the electromagnetic field produced by the nucleus and the average electromagnetic field produced by the remaining electrons. In this approach, the average field of the remaining electrons is represented by the direct (Coulomb) and exchange interactions [15].

The DF method provides a qualitative understanding of some of the general features of atoms and negative ions. For example, the DF electron affinities of B, C, N, O, F, Al, Si, P, S, and Cl are presented in Table I. Observed electron affinities were taken from Hotop and Lineberger [1,2]. It is interesting to note that the calculated DF electron affinities given in Table I reproduce the observed trend in electron affinities while generally underestimating the magnitudes.

In general, the observed electron affinities [1,2] of the above elements (except N and P) increase as the nuclear charge Z increases. As one goes from one element to another in a given row of Table I, both the nuclear charge and the electronic charge increase by one unit. The extra electron is first of all added to the $2p$ shell and then to the $3p$ shell. The screening effect due to the other electrons on this extra elec-

TABLE IV. MCDF and relativistic CI total energies E of the $3s^23p^3(^4\mathrm{S}^o_{3/2})$ ground (1, or first lowest) state of the P atom and the $3s^23p^4(^3\mathrm{P}^e_2)$ ground (1, or first lowest) state of the P^- anion; these are, respectively, the reference states from which CSF bases are generated by single (S), double (D), triple (T), quadruple (Qa), and quintuple (Qi) ''replacements'' of electronic states. OL energy functionals have been used in the MCDF calculations; in steps 1 and 2, all radial functions are allowed to vary; in steps 3 and beyond, only radial functions with principal quantum number $n=\mathrm{step}+1$ are allowed to vary. The number of CSFs in a calculations is denoted n_{CSF}. Certain large CI calculations were not attempted. All extrapolations were carried out using Aitken's δ-squared process. The details of the calculation labeled ''Best estimate'' are given in the text. The electron affinity (EA) obtained from each step of the calculation appears in the last column. The observed electron affinity is taken from Refs. [1] and [2].

		P		P^-		
Step	Calculation	n_{CSF}	E (Hartree)	n_{CSF}	E (Hartree)	EA (eV)
1	MCDF-OL1	3	−341.564 5679	2	−341.544 8517	−0.5365
2	SD-MCDF-OL1	66	−341.633 5327	76	−341.614 1257	−0.5281
3	SD-MCDF-OL1	802	−341.666 1726	1054	−341.676 1180	0.2706
	SDT-CI1	4 320	−341.669 5480	8630	−341.682 9256	0.3640
	SDTQa-CI1	12 148	−341.670 0827	38260	−341.685 8443	0.4289
	ΔE(Qa)		−0.000 5347		−0.002 9187	
	SDTQaQi	18 469	−341.670 0934	92607	−341.685 9882	
	ΔE(Qi)		−0.000 0107		−0.000 1438	
4	SD-MCDF-OL1	2 816	−341.671 0025	3841	−341.686 7035	0.4272
	Extrap (3,4,5)		−341.672 8311		−341.690 6323	0.4844
	SDT-CI1	30 305	−341.674 9521	64848	−341.695 3236	0.5543
	ΔE(T)		−0.003 9496		−0.008 6201	
5	SD-MCDF-OL1	6 622	−341.672 3289	9276	−341.689 5688	0.4691
	Extrap (4,5,6)		−341.673 2664		−341.691 5596	0.4978
	Extrap (4,5,6)		−341.673 4159		−341.692 0206	0.5063
	SDT-CI1	119 751		266432		
6	SD-MCDF-OL1	12 686	−341.672 8782	18103	−341.690 7435	0.4861
	Extrap(5,6,7)		−341.673 3777		−341.691 8675	0.5031
7	SD-MCDF-OL1	21 460	−341.673 1398	31038	−341.691 3179	0.4947
	Best estimate:	SD	−341.673 4159		−341.692 0206	
		T	−0.003 9496		−0.008 6201	
		Qa	−0.000 5347		−0.002 9187	
		Qi	−0.000 0107		−0.000 1438	
			−341.677 9109		−341.703 7033	0.7018
	Experiment					0.7465

tron is expected to become smaller as the shell is filled. This reduction of screening of outer electrons is the reason for the above observed trend in electron affinities.

The ''non-periodic'' behavior of nitrogen may be explained by analyzing the nonrelativistic (LS-coupled) ground state of the neutral atom. The relativistic effects on the ground state of N are very small and the LS-coupled state is a good approximation to the ground state of the neutral atom. In the LS-coupling scheme, the ground state of a neutral atom is usually the term of highest multiplicity (Hund's rule) [15]. The ground state configuration of neutral nitrogen is $2p^3$ (half-full shell) and the term of highest multiplicity resulting from this configuration is $^4\mathrm{S}^o$. Such a state can only be accomplished according to the Pauli exclusion principle by putting one electron in each spatial orbital and having the spin projections of all electrons parallel to each other. Hence, the three electrons tend to stay away from each other reducing the mutual Coulomb repulsion. The motion of the electrons can then be considered to be correlated. The ground state of the N^- ion is $2p^4\ ^3\mathrm{P}^e$ and in this state, the two electrons whose spin projections are antiparallel, occupy a single spatial orbital. As a result, the mutual Coulomb repulsion between the four outer electrons in N^- is larger than that in neutral nitrogen because of the opposite tendency of antiparallel spin pairs to stay closer together. This is an explanation for the very low ''negative'' DF electron affinity of nitrogen compared to that of other elements. The ground state of C^- ion is $(2p^3\ ^4\mathrm{S}^o)$. As explained above, this state has lower energy than the ground state of neutral carbon, $(2p^2\ ^3\mathrm{P}^e)$.

The observed electron affinity of phosphorus is substantially higher than that of nitrogen, which also occupies the same column of the Periodic Table. As shown from Table I, the additional correlation contribution (>2.141 eV) needed to make N^- almost bound is larger than the additional correlation contribution (1.283 eV) needed to obtain the electron affinity of P. This clearly shows that an explanation of the difference between the DF electron affinities of N and P may also explain why the observed electron affinity of phosphorus is substantially higher than that of nitrogen.

The neutral phosphorus atom has eight more electrons in addition to those in the neutral nitrogen atom. Six of those occupy the $2p$ shell and the exchange interaction between them and the three outer electrons ($3p^3$) helps to reduce the screening effect on the latter due to the inner electrons. This reduction in the screening effect enhances the DF electron affinity of neutral phosphorus. A similar effect was observed in our recent study of the electron affinity of Al [11]. The effective additional attraction (actually a reduction in Coulomb repulsion) of electrons in different orbits is well explained, for example, in Lindgren and Morrison [16]. The $2p$ shell in neutral nitrogen unlike the $3p$ shell in neutral phosphorus is nodeless and compact. This may be another partial explanation for the high Coulomb repulsion in neutral nitrogen.

The DF calculations do not include the correlation contributions to the electron affinity. In the following section we investigate the effects of these correlations on the binding energy of negative ions of C, N, and P.

B. Muticonfiguration Dirac-Fock calculations

The results of our calculations are summarized in Tables II–IV. Our approach, described in Secs. II and III, accounts for the major part of the correlation energy among valence electrons in both ground and excited states; core-valence and core-core correlations have been omitted; also omitted are higher-order relativistic effects such as the transverse photon interaction, the self-interaction, and vacuum polarization, as well as other physical effects such as nuclear motion.

As seen from Tables II–IV, the self-consistent-field (SCF) calculations are reasonably converged. But the electron affinity obtained from step 8 in Table II (1.083 eV) for C is smaller than experiment (1.2629 eV) [2]. This is also true for phosphorus (0.49479 eV as against 0.7465 eV). It is evident that the bulk of the discrepancy that remains between theory and experiment must arise from effects other than correlations between pairs of electrons in the valence shells. Such higher-order effects are taken into account using the configuration interaction (CI) method in the present work. Three-electron replacements are seen to dominate four- and five-electron replacements. Four-electron replacements are significantly more important in anions than in neutral systems. Five-electron replacements contribute to estimated electron affinities at the meV (millielectron volt) level; they are significantly more important in the anions than in the neutral systems. That three- and four-electron replacements represent an important class of correlation effects has also been noted by Froese Fischer, Ynnerman, and Gaigalas [17] in their recent calculations for the electron affinity of boron.

As seen from the above MCDF calculations, the correlation contribution needed to obtain the electron affinity of Al is smaller than that needed to make the ground state of N^- stable. This further supports our previous explanation of the difference between N^- and P^- ions based on the HF calculations.

C. A brief review of previous calculations

Carbon. Many calculations for electron affinity of carbon have been published. Computational methods used in these calculations include CI, perturbation theory, and the quantum Monte Carlo approach. The calculations that are in the best agreement with measurements are the multireference singly and doubly excited configuration interaction calculations of Noro *et al.* [18]. Their calculated electron affinity of carbon (1.264 eV) is in excellent agreement with the observation (1.2629 eV) [2]. A concise review of other previous calculations is given in Noro *et al.* [18] and we will not attempt to paraphrase it here.

Nitrogen. There exist a number of estimates of the electron affinity of nitrogen. These estimates {Glockler [19] (0.04 eV), Bates and Moiseiwitsch [20] (0.1 eV), Edlén [21] (0.05 eV), Crossley [22] (−0.32 eV)} were based on some empirical methods of extrapolation of the ionization potentials of isoelectronic systems. Clementi and McLean [23] used Roothan's formulation of the Hartree-Fock method [24], along with correlation and relativistic corrections, to obtain an electron affinity of (-0.27 ± 0.11) eV for nitrogen. They obtained the correlation correction for the electron affinity from correlation energy data tables previously published [25]. The relativistic correction was approximated by the use of first-order perturbation theory on the Hartree-Fock functions. In a recent paper, Cowan *et al.* [26] used the MCHF procedure to study the binding energies and lifetimes of low-lying excited states of N^-. These levels are identified as $2p^4(^1D)$ and $2p^4(^1S)$. Their results are in good agreement with recent experiment [27].

Phosphorus. A few estimates of the electron affinity of phosphorus are available in the literature. These estimates [Glockler [19] (0.2 eV), Bates and Moiseiwitsch [20] (1.1 eV), Edlén [21] (0.77 eV), and Crossley [22] (0.62 eV)] were based on some empirical methods of extrapolation of the ionization potentials of isoelectronic systems. In a recent calculation, Woon and Dunning [28] used multireference single and double excitation configuration interaction method (MRSD-CI) to obtain an electron affinity of (0.702) eV for phosphorus. Their results are in good agreement with the present calculations and the experiment.

Our calculated electron affinities for carbon, nitrogen and phosphorus are 1.210 eV, −0.181 eV, and 0.702 eV, respectively.

V. CONCLUSIONS

The present study shows that the ''non-periodic'' behavior of the negative ions of nitrogen and phosphorus depends on the exchange interactions among the electrons. In the HF or DF approximation, the increase in the exchange interaction resulting from adding an extra electron to the neutral nitrogen atom is not enough to bind an extra electron in nitrogen unlike in carbon. It is true that this statement is in agreement with the elementary explanation [8], based on Pauli exclusion principle, of the stability of the ground state of the neutral nitrogen atom which has a half-filled outer shell ($1s^22s^22p^3$). But, the present explanation has a wider application. For example, the above elementary argument, which is also valid for neutral phosphorus that occupies the same column of the Periodic Table, fails to explain the stability of its anion. We find that the exchange interaction between $2p$ electrons and the three outer electrons ($3p^3$) in neutral phosphorus helps to reduce the screening effect on the latter due to the inner electrons. This reduction in the screening effect enhances the DF electron affinity of neutral phosphorus. Our MCDF calculations further support the above explanations.

ACKNOWLEDGMENTS

One of us (W.P.W.) is deeply grateful to Ted Litherland for giving the author generously of his perception, knowledge, and friendship. We extend our gratitude to David Rowe, Lynn Trainor, Hua Shi, and John Chevary for many discussions. W.P.W. is also grateful to Harold Haugen for financial support during the period of this work.

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