The fine structure levels for ground states of negative ions of nitrogen and phosphorus

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ABSTRACT

The fine structure levels for negative ions (anions) of nitrogen and phosphorus have been investigated using multiconfiguration Hartree-Fock method within the framework of Breit-Pauli Hamiltonian (MCHF+BP). Nitrogen and phosphorus have half-filled outer shell in ground state 1s\(^2\)2s\(^2\)2p\(^3\) 4S and 1s\(^2\)2s\(^2\)2p\(^3\)3s\(^2\)3p\(^3\) 4S, respectively. It has been stated in most works that the negative ion of nitrogen is instable whereas the negative ion of phosphorus is stable. The results obtained have been compared with other works.

Key words: MCHF method, Breit-Pauli Hamiltonian, electron affinity, fine structure levels

Azot ve fosfor’un negatif iyonlarının temel hallerinin ince yapı seviyeleri

ÖZET

Azot ve Fosfor’un negatif iyonları için ince yapı seviyeleri, Breit-Pauli Hamiltonyeni içeren çok konfigürasyonlu Hartree-Fock yöntemi (MCHF+BP) kullanarak incelemiştir. Azot ve fosfor temel halde (azot için 1s\(^2\)2s\(^2\)2p\(^3\) 4S ve fosfor için 1s\(^2\)2s\(^2\)2p\(^3\)3s\(^2\)3p\(^3\) 4S) yarı dolu dış tabakaya sahiptirler. Çoğu çalışmalarında azotun negatif iyonunun kararsız fosforun ise kararlı olduğu belirtilmektedir. Elde edilen sonuçlar diğer çalışmalarla karşılaştırılmaktadır.

Anahtar Kelimeler: MCHF yöntemi, Breit-Pauli Hamiltonyeni, elektron ilgisi, ince yapış seviyeleri

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1. INTRODUCTION

Investigations for the level structures of negative ions provide valuable insight into the fundamental problem of many-body. Negative ions are ideal systems for studies of electron correlation effects. Structural differences between a negative ion and an atom or positive ion originate from the nature of the force binding extra electron due to the polarization and exchange [1]. The electron affinity (EA) is often the difference in the correlation energies of the atom and its negative ion,

\[ EA = E(\text{neutral}) - E(\text{anion}) \]  

Electron affinity has been regarded as one of the hardest atomic or molecular property to produce an ab initio quantum mechanical calculation.

The electron affinity of an atom is a measure of the stability of the corresponding negative ion [1].

The data for half-filled subshell negative ions can be found in NIST website [2]. Some of these works for the negative nitrogen and negative phosphorus are given. Binding energy and fine-structure splitting in atomic negative nitrogen ion was reported by Hotop and Lineberger [3]. Davidson et al [4] presented ground-state correlation energy of nitrogen. A theoretical study of N ion of interest to accelerator mass spectrometry was reported by Wijesundera and Litherland [5]. Atomic ionization potential and electron affinity with relativistic and mass corrections of N ion was calculated by Koga et al [6]. Cowan et al [7] calculated energy levels and lifetimes of negative nitrogen ion. Gutsev et al [8] calculated electron affinity of nitrogen with coupled-cluster method. The electron affinity of nitrogen was reported with the density function theory (DFT) by Chen et al [9]. Wijesundera and Papia [10] estimated the electron affinity of negative nitrogen using the multi-configuration Dirac-Fock method. Piangos and Nicolaides [11] presented very highly excited bound states of N⁻ ion. Biémont et al [12] calculated ionization energy of N with the relativistic multi-configuration Hartree-Fock method. Binding energy and electron affinity of negative nitrogen was presented by Andersen et al [13]. Klopper et al [14] computed the ionization potentials and electron affinities of the atoms H through Ne including N using coupled-cluster method. The electron affinity of phosphorus was performed with multireference single and double excitation configuration interaction calculations (MRSD-Cl) by Woon and Dunning [15]. Wang and Smith [16] reported the electron affinity of phosphorus. Atomic ionization potential and electron affinity with relativistic and mass corrections of P⁻ ion were calculated by Koga et al [6]. Gutsev et al [8] computed the electron affinity of phosphorus using coupled-cluster method. The electron affinity results of phosphorus were reported using density function theory (DFT) by Chen et al [9]. The electron affinity of negative phosphorus ion was calculated using multi-configuration Dirac-Fock method by Wijesundera and Papia [10]. Biémont et al [12] calculated the ionization energy of phosphorus using relativistic multi-configuration Hartree-Fock method. Binding energy and electron affinity of negative phosphorus ion were presented by Andersen et al [13]. Andersson et al [1] measured the energies of fine structure components of negative phosphorus ion using laser photodetachment threshold spectroscopy. Peláez et al [17] studied the electron affinity and an excited spectral term of phosphorus with the photodetachment microscope.

In this work we have investigated the electron affinities of nitrogen and phosphorus, and the fine structure of negative ions of these atoms. It is known that the negative ion of nitrogen is unstable while the negative ion of phosphorus is stable. Nitrogen and phosphorus have half-filled outer shell in ground state (1s²2s²2p³ and 1s²2s²2p³3s²3p³, respectively). An extra electron is bound to 2p and 3p subshell of nitrogen and phosphorus, respectively, in their anions. The calculations on electron affinities and fine structure of ground state of negative ions of nitrogen and phosphorus have been performed using multiconfiguration Hartree-Fock (MCHF) method developed by Fischer [18]. We have previously investigated the electron affinities for nitrogen and phosphorus. We have also considered correlation and relativistic effects within the framework of the Breit-Pauli approximation. For considering correlation effects we have taken various configuration sets. A set of orbitals (or active set) determines the set of all possible configuration state functions (CSFs). The CSFs grow rapidly with the number of electrons and with the size of active set. For these reasons most MCHF expansions are limited to restricted active space (RAS). In this work we have taken the configurations according to single and double excitations together (sd replacements).

2. CALCULATION METHOD

In the multiconfiguration Hartree-Fock (MCHF) approximation [18], Hamiltonian is used for obtaining the best radial functions for the set of non-relativistic energies of the interacting terms. The wave function is expressed as a linear combination of orthonormal configuration state functions (CSFs) so that

\[ \Psi(\gamma LS) = \sum_{i=1}^{M} c_i \Phi(\gamma LS), \quad \sum_{i=1}^{M} c_i^2 = 1 \.]  

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In this expansion \( \Phi(\gamma_i LS) \), \( \gamma_i \), and \( c_i \) represent configuration state function in LS coupling, configurations, and mixing coefficients of configurations, respectively. Then the non-relativistic energy expression becomes

\[
e(\gamma LS) = \sum_{i=1}^{M} \sum_{j=1}^{M} c_i c_j \langle \Phi(\gamma_i LS) | H | \Phi(\gamma_j LS) \rangle
= \sum_{i=1}^{M} \sum_{j=1}^{M} c_i c_j H_{ij} = \sum_{i=1}^{M} c_i^2 H_a + 2 \sum_{i<j} c_i c_j H_{ij}.
\]

(3)

If the interaction matrix \( H = (H_{ij}) \) and a column vector of the expansion coefficients (or mixing coefficients) \( c = (c_1, ..., c_M)^T \), the energy of system is

\[
E = c^T H c
\]

(4)

The energy functional will depend on both \( P \) (the column vector of radial functions) and \( c \), since \( H_{ij} \) depends on the radial functions. A solution of the MCHF problem requires simultaneously the solution of the secular equation and variational radial equations. Only if the secular problem is solved, it is called a configuration interaction (CI) calculation. If any radial function is optimized, it is called a multiconfiguration Hartree-Fock calculation. Therefore it is taken into account in the correlation effects.

The Breit-Pauli Hamiltonian includes relativistic effects. This Hamiltonian can be written as

\[
H_{BP} = H_{NR} + H_{RS} + H_{FS}.
\]

(5)

where \( H_{NR} \) is the non-relativistic many-electron Hamiltonian, and \( H_{RS} \) is the relativistic shift operator including mass correction, one-and two-body Darwin terms, spin-spin contact term and orbit-orbit term and is given by

\[
H_{RS} = H_{MC} + H_{D1} + H_{D2} + H_{OO} + H_{SS}.
\]

(6)

Fine structure Hamiltonian \( H_{FS} \) consists of the spin-orbit, spin-other-orbit, and spin-spin terms,

\[
H_{FS} = H_{SO} + H_{SOO} + H_{SS}.
\]

(7)

The Breit-Pauli wavefunctions are obtained as a linear combination of the form

\[
\Psi(\gamma JM) = \sum_{i=1}^{M} c_i \Phi(\gamma_i L_i S_i, JM)
\]

(8)

where \( \Phi(\gamma LSJM) \) are LSJ coupled configuration state functions (CSFs), that is,

\[
\Phi(\gamma LSJM) = \sum_{M_i M_s} \langle LM_i SM_s | LSJM \rangle \Phi(\gamma LM_i SM_s),
\]

(9)

and \( \gamma_i \) denotes configurations; the orbital \( L_i \) and the spin \( S_i \) angular momenta are coupled to give the total angular momentum \( J \). The mixing (or expansion) coefficients \( c_i \) are obtained by diagonalizing the Breit-Pauli Hamiltonian. The radial functions building the CSFs are taken from a previous non-relativistic MCHF calculation and only the expansion coefficients are optimized. The matrix eigenvalue problem becomes

\[
H c = E c,
\]

(10)

where \( H \) is the Hamiltonian matrix with elements

\[
H_{ij} = \langle \gamma_i L_i S_i JM | H_{BP} | \gamma_j L_j S_j JM \rangle.
\]

(11)

and \( c = (c_1, ..., c_M)^T \) is the column vector of the expansion coefficients. The Breit-Pauli Hamiltonian is a first-order perturbation correction to the non-relativistic Hamiltonian.

3. RESULTS AND DISCUSSION

We have here studied the fine structure levels of ground state of nitrogen and phosphorus anions (N\(^-\) and P\(^-\)) using the MCHF atomic structure code [19] based on multiconfiguration Hartree-Fock method within the framework of Breit-Pauli Hamiltonian for relativistic effects in addition to the correlation effects. It is noted in [5] that the relativity must be included in theoretical calculations, especially for negative ions. The electron affinity of a neutral atom is the difference between the binding energy of the neutral atom and the negative ion. We have here reported the fine structure levels including both correlation and relativistic effects. Different calculations according to various configuration sets have been presented in tables. The excited states of negative nitrogen ion were studied by Cowan et al [7] with different configuration set using MCHF method. They also applied to the study of the electron affinities of the 2p\(^3\) 1D and 1S states of N relative to the 2p\(^3\) 2D neutral nitrogen parent state. We have here considered the state 2p\(^3\) 1P for N\(^-\) and 2p\(^3\) 3S for N; in similar 3p\(^3\) 3P for P and 3p\(^3\) 4S for P.
In Table 1, the ground state energies (in au) for the neutral nitrogen (N) and negative ion of nitrogen (N^-), and electron affinity (in eV) are reported. Energies have been presented as nonrelativistic, $E_{\text{MCHF}}$, and in addition to Breit-Pauli relativistic effects, $E_{\text{MCHF+BP}}$. The superscripts A, B, C and D, and 1, 2, 3, 4 and 5 represent the calculations performed according to four different configuration set for N and N^-, respectively. All of the configuration sets have been selected as single (s) and double (d) excitations from subshells. We have taken 2s, 2p, 3s, 3p, 3d in calculation A, +4s, 4p, 4d, 4f in calculation B, +5s, 5p, 5d, 5f in calculation C as virtual orbitals. In calculation D the configurations have been produced as active set approach. In this calculation 2s, 2p, 3s, 3p, 3d virtual orbitals have been selected. In the calculations on N, 1s^2 have been fixed. In same way 2s, 2p, 2d, 3s, 3p, 4f, 4p, 4f, 4f, 5f active set orbitals in calculation 1; 2s, 2p, 3s, 3p, 4f, 4f, 5f active set orbitals in calculation 4; 2s, 2p, 2d, 3s, 3p, 3d, 4s, 4p, 4d, 4f virtual set orbitals in calculation 5 have been selected for nitrogen anion. In calculation 2 we have only taken the excitations from 1s core. There are no more differences between $E_{\text{MCHF}}$ and $E_{\text{MCHF+BP}}$. For the atoms with lower Z, it is known that the relativistic effects are not essentially important. Although so, the electron affinity values have been given according to different configuration sets in last column include the correlation and in addition to the relativistic corrections. In literature the electron affinity values for nitrogen are very scarce and generally negative. For this reason negative ion of nitrogen has been determined as instable. As seen Table 1, we also obtained some negative values besides the positive ones in some calculations. Good agreement has been obtained when compared to the other works [3, 9, 20, 21].

Table 2 exhibits the ground state energy levels and electron affinity values for phosphorus. Same systematic calculations have been made for this atom and its anion. The configurations have been performed by the virtual sets 3s, 3p, 3d, 4s, 4p in calculation A; +4d in calculation B; 2p, 3s, 3p, 3d in calculation C; 3s, 3p, 4s, 4p, 5s, 5p, 6s in calculation D for neutral phosphorus. The 1s^22s^2p^6 have been taken core in all calculations except calculation C because of the investigation core correlation. In same way, considering 1s^22s^2p^6 as core (except calculation 3 and calculation 4), the virtual sets 3s, 3p, 3d, 4s, 4p in calculation 1, +4f, 5s, 5p in calculation 2, 2p, 3s, 3p, 3d, 4s in calculation 3, and +2p, 4p in calculation 4 have been selected for phosphorus anion. In calculations 3 and 4 core is 1s^22s^2. The electron affinity values obtained from different configuration sets for phosphorus show good agreement according to nitrogen. In neutral phosphorus and its anion the relativistic energies are somewhat different according to the nitrogen and its anion.

Table 3 shows the transition energies from fine structure levels for negative ions of nitrogen and phosphorus. We have only compared the fine structure levels of negative ion of phosphorus. As stressed before, there are no data on fine structure levels on negative ion of nitrogen. For phosphorus, transition energies in the levels of ground state show good agreement with other work [1, 13, 17, 24].
Table 1. Ground state energies, $E_{\text{MCHF}}$ and $E_{\text{MCHF+BP}}$ (in au) of N and N' and electron affinity, EA (in eV). The total energies of the $1s^22s^22p^3\text{^1}S_{\text{1/2}}$ ground (first lowest) state for N and the $1s^22s^22p^1\text{^3}P_{\text{1/2}}$ ground (first lowest) state for N' are taken.

| N     | $E_{\text{MCHF}}$ | $E_{\text{MCHF+BP}}$ | $E_{\text{MCHF}}$ | $E_{\text{MCHF+BP}}$ | MCHF | MCHF+BP |
|-------|-------------------|----------------------|-------------------|----------------------|-------|---------|
| -54.496357$^A$ | -54.4496373$^A$ | -54.3564275$^I$  | -54.3565514$^I$  | -2.535$^A$  | 2.532$^A$  |
|       |                   | -54.3958049$^2$  | -54.3959147$^2$  | -1.464$^A$  | -1.461$^A$  |
|       |                   | -54.3941060$^3$  | -54.3942300$^3$  | -1.510$^A$  | -1.507$^A$  |
|       |                   | -54.3940641$^4$  | -54.3941882$^4$  | -1.512$^A$  | -1.508$^A$  |
|       |                   | -54.5212759$^5$  | -54.5212759$^5$  | 1.949$^A$  | 1.949$^A$  |
|       | -54.520074$^6$  | -54.520074$^6$  | 1.916$^A$  | 1.916$^A$  |
|       | -54.4856334$^B$ | -54.4856343$^B$ | -54.3564275$^I$  | -54.3565514$^I$  | -3.514$^B$  | -3.511$^B$  |
|       |                   | -54.3958049$^2$  | -54.3959147$^2$  | -2.443$^B$  | -2.440$^B$  |
|       |                   | -54.3941060$^3$  | -54.3942300$^3$  | -2.490$^B$  | -2.486$^B$  |
|       |                   | -54.3940641$^4$  | -54.3941882$^4$  | -2.491$^B$  | -2.487$^B$  |
|       |                   | -54.5212759$^5$  | -54.5212759$^5$  | 0.969$^B$  | 0.969$^B$  |
|       | -54.520074$^6$  | -54.520074$^6$  | 0.937$^B$  | 0.938$^B$  |
|       | -54.4851636$^C$ | -54.4851647$^C$ | -54.3564275$^I$  | -54.3565514$^I$  | -3.502$^C$  | -3.498$^C$  |
|       |                   | -54.3958049$^2$  | -54.3959147$^2$  | -2.431$^C$  | -2.428$^C$  |
|       |                   | -54.3941060$^3$  | -54.3942300$^3$  | -2.477$^C$  | -2.473$^C$  |
|       |                   | -54.3940641$^4$  | -54.3941882$^4$  | -2.478$^C$  | -2.475$^C$  |
|       |                   | -54.5212759$^5$  | -54.5212759$^5$  | 0.982$^C$  | 0.982$^C$  |
|       | -54.520074$^6$  | -54.520074$^6$  | 0.950$^C$  | 0.950$^C$  |
|       | -54.4248177$^D$ | -54.4248186$^D$ | -54.3564275$^I$  | -54.3565514$^I$  | -1.860$^D$  | -1.857$^D$  |
|       |                   | -54.3958049$^2$  | -54.3959147$^2$  | -0.789$^D$  | -0.786$^D$  |
|       |                   | -54.3941060$^3$  | -54.3942300$^3$  | -0.835$^D$  | -0.832$^D$  |
|       |                   | -54.3940641$^4$  | -54.3941882$^4$  | -0.836$^D$  | -0.833$^D$  |
|       |                   | -54.5212759$^5$  | -54.5212759$^5$  | 2.624$^D$  | 2.624$^D$  |

Diğer Çalışmalar EA (eV)  
-0.067$^e$; -0.27$^b$; -0.07$^c$; 0.05$^d$

$^a$Chen et al [9]; $^b$Pekers[20]; $^c$ Hotop and Lineberger [3]; $^d$Edlén[21]
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Table 2. Ground state energies, $E_{\text{MCHF}}$ and $E_{\text{MCHF+BP}}$ (in au) of P and $P^-$ and electron affinity, EA (in eV). The total energies of the $1s^22s^22p^33s^23p^3$ $^3S_{1/2}$ ground (first lowest) state for P and the $1s^22s^22p^33s^23p^4$ $^3P^-$ ground (first lowest) state for $P^-$ are taken.

|        | $P$       | $P^-$    |        |        |
|--------|-----------|----------|--------|--------|
|        | $E_{\text{MCHF}}$ | $E_{\text{MCHF+BP}}$ | $E_{\text{MCHF}}$ | $E_{\text{MCHF+BP}}$ | EA (eV) |
| -341.5953742$^A$ | -341.5953742$^A$ | -341.6162729$^1$ | -341.6166351$^1$ | 0.568$^{A1}$ | 0.578$^{A1}$ |
|        |           | -341.6208966$^2$ | -341.6212691$^2$ | 0.694$^{A2}$ | 0.704$^{A2}$ |
|        |           | -341.5917156$^3$ | -341.5921254$^3$ | -0.099$^{A3}$ | -0.088$^{A3}$ |
|        |           | -341.5606668$^4$ | -341.5611449$^4$ | -0.944$^{A4}$ | -0.931$^{A4}$ |
| -341.5947962$^B$ | -341.5947962$^B$ | -341.6162729$^1$ | -341.6166351$^1$ | 0.584$^{B1}$ | 0.94$^{B1}$ |
|        |           | -341.6208966$^2$ | -341.6212691$^2$ | 0.710$^{B2}$ | 0.720$^{B2}$ |
|        |           | -341.5917156$^3$ | -341.5921254$^3$ | -0.084$^{B3}$ | -0.073$^{B3}$ |
|        |           | -341.5606668$^4$ | -341.5611449$^4$ | -0.928$^{B4}$ | -0.915$^{B4}$ |
| -341.6052196$^C$ | -341.6052196$^C$ | -341.6162729$^1$ | -341.6166351$^1$ | 0.301$^{C1}$ | 0.311$^{C1}$ |
|        |           | -341.6208966$^2$ | -341.6212691$^2$ | 0.426$^{C2}$ | 0.437$^{C2}$ |
|        |           | -341.5917156$^3$ | -341.5921254$^3$ | -0.367$^{C3}$ | -0.356$^{C3}$ |
|        |           | -341.5606668$^4$ | -341.5611449$^4$ | -1.121$^{C4}$ | -1.199$^{C4}$ |
| -341.5729046$^D$ | -341.5729229$^D$ | -341.6162729$^1$ | -341.6166351$^1$ | 1.180$^{D1}$ | 1.180$^{D1}$ |
|        |           | -341.6208966$^2$ | -341.6212691$^2$ | 1.305$^{D2}$ | 1.315$^{D2}$ |
|        |           | -341.5917156$^3$ | -341.5921254$^3$ | 0.512$^{D3}$ | 0.522$^{D3}$ |
|        |           | -341.5606668$^4$ | -341.5611449$^4$ | -0.333$^{D4}$ | -0.320$^{D4}$ |

Diğer Çalışmalar EA (eV)

|        |
|--------|
| 0.748$^e$; 0.7465$^f$; 0.7468$^e$; 0.7464$^e$; 0.7465$^e$; 0.7467$^f$ |

$^A$Chen et al [9]; $^B$Hopat and Lineberger [3]; $^C$Feldman [22]; $^D$Slater ve Lineberger [23]; $^E$Andersen et al [13]; $^F$Andersson et al [1]

Table 3. The transition energies, $\Delta E$ (meV), in fine structure levels for ground state of nitrogen anion (N$^-$) and phosphorus anion ($P^-$).

| Term     | $N^-$        | $P^-$        |
|----------|--------------|--------------|
|          | $\Delta E$ This work | $\Delta E$ Other works | $\Delta E$ This work | $\Delta E$ Other works |
| $^3P_0 - ^3P_1$ | 2.93$^1$ | - | 9.71$^1$ | 12.29$^a$ |
|          | 2.56$^2$ | | 10.06$^2$ | 10.25$^b$ |
|          | 2.93$^3$ | | 11.02$^3$ | 10.29$^c$ |
|          | 2.92$^4$ | | 10.96$^4$ | - |
| $^3P_1 - ^3P_2$ | 6.82$^1$ | | 19.69$^1$ | 24.57$^a$ |
|          | 6.03$^2$ | | 20.24$^2$ | 22.48$^b$ |
|          | 6.80$^3$ | | 22.30$^3$ | 22.43$^c$ |
|          | 6.81$^4$ | | 25.05$^4$ | 22.40$^d$ |
| $^3P_0 - ^3P_2$ | 9.75$^1$ | - | 29.40$^1$ | 36.86$^a$ |
|          | 8.59$^2$ | | 30.30$^2$ | 32.73$^b$ |
|          | 9.73$^3$ | | 33.32$^3$ | 32.72$^c$ |
|          | 9.73$^4$ | | 36.01$^4$ | 32.60$^d$ |

$^a$Oliveria et al[24]; $^b$Andersson et al[1]; $^c$Pelaez et al[17]; $^d$Anderssen et al[13]
4. CONCLUSION

In this work it is aimed to investigate the correlation and relativistic effects on the behavior of electron affinities of nitrogen and phosphorus. We also worked the ground state fine structure levels of the nitrogen and phosphorus anions. The ground state configuration of neutral nitrogen is $2p^3$ half-filled shell and highest multiplicity from this configuration is $^8S^o$. The ground state of nitrogen anion is $2p^4$ and highest multiplicity from this configuration is $^3P^o$. Generally the ground state energy of $N^-$ ion in our calculations is larger than that in $N$. The reason for this case can be explained as larger the Coulomb repulsion between four outer electrons in nitrogen anion (for example, in [5]). This case is different in phosphorus which also occupies the same column of Periodic Table. The electron affinity of phosphorus is higher than that of nitrogen. The neutral phosphorus has eight more electrons relative to the nitrogen. It is supposed that three outer electrons ($3p^3$) reduced the screening effect due to the inner electrons. And the effective additional attraction of electrons in different orbits is well explained in [25]. The $2p$ shell in neutral nitrogen unlike $3p$ shell in neutral phosphorus is compact. In addition the transition energies in ground state fine structure levels of $N^-$ ion are very small than those in $P$.

REFERENCES

[1] ANDERSSON, P., LINDAHL, A.O., ALFREDSSON, C., ROGSTRÖM, L., DIEHL, C., PEGG, D.J., HANSTORP, D., The electron affinity of phosphorus, J. Phys. B: At. Mol. Opt. Phys., 40, 4097–4107, 2007
[2] NIST(https://physics.nist.gov/PhysRefData/ASD/index.html)
[3] HOTOP, H., LINEBERGER, W.C., Binding energies in atomic negative ions, J. Phys. Chem. Ref. Data, 4, 539–576, 1975
[4] DAVIDSON, E.R., HAGSTROM, S.A., CHAKRAVORTY, S.J., UMAR, V.M., FISCHER, C.F., Ground-state correlation energies for two- to ten-electron atomic ions, Phys. Rev. A, 44, 7071–7083, 1991
[5] WIJESUNDERA, W.P., LITHERLAND, A.E., A theoretical study of some negative ions of interest to accelerator mass spectrometry, Nuclear Instruments and Methods in Physics Research B, 123, 527-531,1997
[6] KOGA, T., AOKI, H., DE LA VEGA, G., J.M., TATEWAKI, H., Atomic ionization potentials and electron affinities with relativistic and mass corrections, Theor. Chem. Acc., 96, 248-255, 1997
[7] COWAN, R.D., FISCHER, C.F., HANSEN, J.E., KEMPTER V., Excited states of the negative nitrogen ion: energies and lifetimes, J. Phys. B: At. Mol. Opt. Phys. 30, 1457–1466, 1997
[8] GUTSEV, G.L., JENA, P., BARLETT, R.J., Electric quadrupole moments and electron affinities of atoms from H to Cl: a coupled-cluster study, Chemical Physics Letters, 291, 547–552, 1998
[9] CHEN, G., ONG, P.P., TING, L., DFT approach for electron affinity of negative atomic ions, Chemical Physics Letters, 290, 211–215,1998
[10] WIJESUNDERA, W. P., PARPIA, F. A., Negative ions of carbon, nitrogen, and phosphorus, Phys. Rev. A, 57, 3462–3468, 1998
[11] PIANGOS, N.A., NICOLAIDESY, C.A., Very highly excited bound states of atomic negative ions having all their electrons with unpaired spins, J. Phys. B: At. Mol. Opt. Phys., 31, L147–L154, 1998
[12] BIEMONT, E., FREMAT, Y., QUINET, P., Ionization potentials of atoms and ions from lithium to tin (Z=50), Atomic Data and Nuclear Data Tables, 71, 117–146,1999
[13] ANDERSEN, T., HAUGEN, H.K., HOTOP, H., Binding Energies in Atomic Negative Ions: III, J. Phys. Chem. Ref. Data. 28, 1511-1533, 1999
[14] KLOPPER, W., BACHORZ, R.A., Sub-meV accuracy in first-principles computations of the ionization potentials and electron affinities of the atoms H to Ne, Physical Review A, 81, 022503, 2010
[15] WOON, D.E., DUNNING JR, T.H., Calculation of the Electron Affinities of the Second Row Atoms: Al–Cl, J. Chem. Phys. 99, 3730–3737, 1993
[16] WANG, J., SMITH, JR.V.H., 1/Z Expansions for isoelectronic systems from He through Ar, Phys. Rev. A, 52, 1060–1066, 1995
[17] PELÁEZ, R.J., BLONDEL, C., VANDEVRAYE, M., DRAG, C., DELSART, C., Photodetachment microscopy to an excited spectral term and the electron affinity of phosphorus, J. Phys. B: At. Mol. Opt. Phys., 44, 195009, 2011
[18] FISCHER, C.F., BRAGE, T., JÖNSSON, P., Computational atomic structure—an MCHF approach, (Bristol and Philadelphia), 1997
[19] FISCHER, C.F., The atomic structure package, Comp.Phys. Commun., 128,635-636, 2000
[20] PEKERIS C.L., Ground state of two-electron atoms, Phys. Rev., 112, 1649-1658, 1958
[21] EDLEN, B., Isoelectronic extrapolation of electron affinities, J. Chem. Phys. 33, 98-105, 1960
[22] FELDMAN, D., Infrared photodetachment threshold measurements: Li and P, Z. Phys. A: Hadrons and Nuclei, 277, 19-25, 1976
[23] SLATER , J., LINEBERGER, W.C., High-resolution photodetachment studies of P and Te, Phys. Rev. A, 15, 22772282, 1977
[24] OLIVERIA, DE G., MARTIN, J.M.L., PRAFT, D.E., GEERLINGS, P., Electron affinities of the first
and second-row atoms: benchmark ab initio and density-functional calculations, Phys., Rev. A, 60, 1034-1045, 1999

[25] LINDGREN, L., MORRISON, J., Atomic Many-body Theory. (Springer-Verlag, Berlin), 1982