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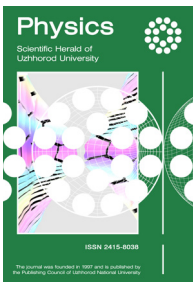

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Calculations of the Energy Structure of *P*, *S* Atoms by the *R*-Matrix Method with *B*-Splines

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Abstract

Purpose. Over the past decades, the physics of electron-atomic (EA) collisions has been intensively developed. This is due both to the fundamental nature of the studied processes and applied needs. This is primarily about understanding at a deep level the behavior of submicroscopic, often strongly correlated, quantum mechanical many-particle systems. The result of this understanding is obtaining a large amount of data necessary for modeling the behavior of various types of plasma and discharges, as well as to diagnose their properties.

Methods. We have presented the general principles and idea, underlying in the *B*-spline *R*-matrix method (BSR) with a non-orthogonal orbitals. The use of non-orthogonal single-electron orbitals eliminates orthogonal restrictions applied in many other theoretical approaches. These restrictions are introduced purely for the convenience of calculation, rather than for reasons of physical necessity. Rejecting the orthogonality conditions, BSR method significantly improves the accuracy of the target description. Accordingly, it becomes possible to further accurate calculation of the collision processes.

Results. We considered the application of the BSR method to the calculation of the energy structure of a phosphorus and sulfur atoms, that is of considerable practical interest. The calculation results demonstrate good agreement with the available experimental data.

Conclusions. In this paper, the energy structure of the phosphorus atom was calculated. The calculation results demonstrate good agreement with the available experimental data. In the future, our data will be used in the study of electron scattering on phosphorus and sulfur atoms.

Keywords: phosphorus atom, sulfur atom, structure calculation of atomic systems, *B*-spline *R*-matrix method, Hartree-Fock method, multi-electronic bases, correlation interaction, single- and multi-configuration approximation

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Introduction

In recent decades, there has been an intensive development in the study of electron-atom (EA) collision processes. The importance of the results of systematic calculations of the structural properties of phosphorus and sulphur atoms for various applications in atomic physics, electron-atom collision theory, and plasma modeling cannot be overemphasized. Thus, elementary processes involving atoms and ions play an important role in plasma injection and diagnostics in modern thermonuclear installations and affect the processes occurring in the plasma itself, determine the operating conditions of X-ray and gas lasers, and are important in the design and use of heavy ion accelerators.

In this research, the energy structure of phosphorus and sulphur atoms is calculated using the method proposed in [3-11] *R*-matrix with non-orthogonal orbitals and *B*-splines as basic functions (BSR) [1]. In the calculations of the energy structure of P, S atoms, the multiconfiguration Hartree-Fock method (MCHF) [2] with non-orthogonal orbitals optimized in independent calculations for individual terms was also used. The results obtained will be used in the future to study the processes of scattering slow electrons on phosphorus and sulphur atoms.

Calculation Methods

In this section, we will briefly look at the main aspects of the new version of the *B*-spline *R*-matrix method (BSR Method) [1]. This method is successfully applied both in calculations of the atomic structure and in the study of the processes of elastic and inelastic scattering of slow electrons on complex atoms and ions. A special feature of the BSR method is the use of basic splines B_i to represent both the bound orbitals of the target atom and the orbitals of the scattered electron. The problem of low-energy electron scattering on N-electron atom is reduced to solving the Schrödinger equation (1):

$$(H_{N+1} - E)\psi_\alpha^G(X, x_{N+1}) = 0,$$
$$H_{N+1} = \sum_{i=1}^{N+1}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i>j=1}^{N+1}\frac{1}{r_{ij}} \quad (1)$$

with appropriate boundary conditions. Here E and H_{N+1} – full energy and Hamiltonian $(N+1)$-electronic system "atom + incident electron", Z – nuclear charge. Hamiltonian H_{N+1}(1) diagonal to the total orbital momentum L, full spin S, their projections M_L, M_S on a given axis and π parity. Function $\Psi_\alpha^G(X,x_{N+1})$ commonly referred to as the wave function collapse is a completely antisymmetric wave function of $(N+1)$-electron system, $X\equiv(x_1, \ldots, x_N)$, $G\equiv(\gamma LSM_L M_{S\pi})$, a $x_i\equiv(\vec{r_i}, \sigma_i)$ denotes a set of spatial $\vec{r_i}$ and spin σ_i coordinates of i electron. The index α characterizes the initial conditions and usually denotes the input channel $e+A$ – scattering. Excluding ionization decomposition of the total wave function collapse $\Psi_\alpha^G(X,x_{N+1})$ can be represented as (2):

$$\Psi_\alpha^G(X, x_{N+1}) = A\sum_{i=1}^{n}\bar{F}_i^G(X;\ \hat{r}_{N+1}, \sigma_{N+1}) \times \frac{F_{i\alpha}^G(r_{N+1})}{r_{N+1}} + \sum_{j=1}^{m} c_j\chi_j^G(X, x_{N+1}) \quad (2)$$

Here A is the antisymeterization operator; $\bar{F}_i^G$ – wave function of i- channel built by vector relation of the wave function N-electron target $F_i(X)$ with the angular and spin parts of the wave function of the scattered electron; $\chi_i^G(X,x_{N+1})$ – a set of quadratically integrated antisymmetric correlation functions that provide completeness of decomposition (2). The problem is to find radial wave functions of $F_{i\alpha}^G(r_{N+1})$ scattered electron and coefficients cj of decomposition (2). Atomic wave functions $F_i(X)$ are plotted as a multi-configuration schedule (3):

$$F_i(x_1, \ldots, x_N) = \sum_j c_{ij}\varphi_j(x_1, \ldots, x_N) \quad (3)$$

where φ_j – single-configuration wave functions of the target atom. Coefficients c_{ij} obtained by diagonalization of N- electronic Hamiltonian of HN target atom (4):

$$\langle F_i | H_N | \Phi_j \rangle = E_i(Z, N)\delta_{ij} \quad (4)$$

Usually, the first sum on the right side of decomposition (2) includes only those target states that, at a given energy $E = E_i + \frac{k_i^2}{2}$ correspond to the so-called open channels. In the first sum can also be included some pseudostates which approximately represent states of a continuous spectrum. The selection of pseudostates is carried out on the basis of accurate account of the polarizability of the main and several excited states of the target. In addition to using pseudostates, the contribution of closed channels can be partially accounted for using a finite number of correlation functions $\chi_i^G(X,x_{N+1})$ included in the second sum of the decomposition (2).

Basic functions φ_j and χ_j in decompositions (2), (3) are constructed from single-electron atomic orbitals $\varphi_{\alpha i}$, which in the approximation of the central field have the form (5):

$$\varphi_{\alpha_i}(x) = 1/r \cdot P_{n_i l_i}(r) Y_{l_i m_i}(\hat{r}) \chi(m_s|\sigma), x \equiv (\vec{r_i}, \sigma) \quad (5)$$

where α_i – abbreviated designation of a set of quantum numbers n_i, l_i, m_i and mS. In the standard version *R*-matrix approach for easy calculation of radial wave functions of a scattered electron $F_{i\alpha}^G$ are selected orthogonal to all atomic orbitals of the target $P_{nj\,lj}$ of the same symmetry (6):

$$\int_0^\infty P_{n_j l_j}(r) F_{i\alpha}^{\mathrm{G}}(r) dr = 0 \quad (6)$$

when $l_j = l_i$.

Condition (6) actually means that an incident electron cannot be virtually trapped in one of the unfilled sub-shells taken into account in decomposition (3) of the target states. Substituting decomposition (2) into equation (1), multiplying it alternately by the functions $\bar{F}_i^G$ and $\bar{\chi}_j^G$ after integration over all variables except r_{N+1}, can be obtained a system of integrodifferential equations for functions $F_i \equiv F_{i\alpha}$ (7):

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r} + k_i^2\right) F_i(r) = 2\sum_j (V_{ij} + W_{ij} + X_{ij}) F_j(r) \quad (7)$$

where $k_i^2 = 2[E - E_i(Z,N)]$, a V_{ij}, W_{ij}, X_{ij} – local direct, non-local exchange, and non-local correlation potentials, respectively. For electron scattering on complex atoms, an explicit form of these potentials is generated automatically by the BSR program [1], depending on the type of input data.

To solve the CC equation system (7), can be applied a variant of the method *R*-matrix based on the use of non-orthogonal orbitals and *B*-splines as basic functions. This method makes it possible to describe various types of reactions within a single formalism, such as elastic scattering, excitation, and ionization of an atom by electron shock. Main idea *R*-matrix method consists in dividing the configuration space of the "atom + electron" system into two regions: internal $r<A$ and external $r>a$. The radius of the inner region $r=A$ is chosen so that the exchange and correlation effects are sufficiently small at $r \geq a$. The full wave function $(N+1)$ of an electronic system in the inner region can be represented at a given energy E as a decomposition:

$$\Psi_{\mathrm{E}}^{\mathrm{G}} = \sum_k A_{Ek}^{\mathrm{G}} \Psi_k^{\mathrm{G}} \quad (8)$$

by an energy independent discrete base set Ψ_k^G

$$\Psi_k^G(X, x_{N+1}) = A \sum_{ij} \overline{F}_i^G(X; \hat{r}_{N+1}, \sigma_{N+1}) \times \frac{u_j(r_{N+1})}{r_{N+1}} c_{ijk}^G + \sum \chi_i^G(X, x_{N+1}) d_{ik}^G \quad (9)$$

where $\bar{F}_i^G$ and $\bar{\chi}_i^G$ are defined in the same way as in formula (2). Functions $F_{i\alpha}^G$, describing the radial motion of a scattered electron in i-channel, are presented as a linear combination of a finite number of basis functions uj, which satisfy the boundary conditions $u_j = 0, (a/u_j) du_j/dr|_{r=a} = b$, where b – an arbitrary valid constant. For such basic functions, the Hamiltonian (1) in the inner domain is not Hermitian due to nonzero (at $r=a$) surface terms arising from the kinetic energy operator. However, these terms can be removed using the Bloch operator L_{N+1}. The formal solution of Schrödinger's Equation (1) takes the following form (10):

$$|\Psi\rangle = \frac{1}{2}\sum_{kj}|\Psi_k^{\mathrm{G}}\rangle\langle\Psi_k^{\mathrm{G}}|\overline{\mathrm{F}_j^{\mathrm{G}}}\rangle(E_k - E)^{-1} \times (\frac{d}{dr_{N+1}} - \frac{b_j}{r_{N+1}})\langle\overline{\mathrm{F}_j^{\mathrm{G}}}\,|\Psi\rangle \quad (10)$$

Projecting this equation onto channel functions $\bar{F}_i^G$ and performing calculations on the border of the inner region, the following results are obtained (11):

$$F_i^{\mathrm{G}}(a) = \sum_{j=1}^{n} R_{ij}^{\mathrm{G}}(E)(\frac{adF_i^{\mathrm{G}}}{dr_{N+1}} - b_j F_j^{\mathrm{G}})_{r_{N+1}=a} \quad (11)$$

where entered R- a matrix is introduced with elements (12):

$$R_{ij}^{\mathrm{G}}(E) = \frac{1}{2a}\sum_k \frac{w_{ik}^{\mathrm{G}}(a)w_{jk}^{\mathrm{G}}(a)}{(E_k^{\mathrm{G}} - E)} \quad (12)$$

radial functions F_i^G and surface amplitudes w_{ik}^G are given. Diagonalizing the matrix $\langle\psi_k^{\mathrm{G}}|H_{N+1} + + L_{N+1}|\psi_k^{\mathrm{G}}\rangle_{int}$ for each set of quantum numbers G, the energies E_k^G and coefficients c_{ijk}^G, d_{ik}^G in decomposition can determined (9), i.e. wave functions ψ_k for the corresponding base states. However, it only needs to be done once to determine R-matrix over the entire range of collision energies.

As noted above, the inclusion in the output decomposition (9) of additional correlation functions χ_j^G allows to partially take into account the effects associated with the conditions of orthogonality (6) of the functions $F_{i\alpha}^G$ and the limitation of the first sum in (9) finite number of terms. However, this leads in most cases to the appearance of a pseudo-resonant structure in the scattering cross-sections and to an excessively large number of additional integro-differential equations, which must be left out in (9) for realistic calculations of complex atoms and the processes of their interaction with electrons. In this respect, it is worth mentioning that condition (6) is not mandatory and does not follow from general quantum mechanical principles. Therefore, in studies [3-11], the authors abandoned the requirement (6) of orthogonality of functions $F_{i\alpha}^G(r_{N+1})$ to bound orbitals P_{njlj} of targets of the same symmetry. Worth noting that in BSR version of the R-Matrix method proposed by us, correlation functions χ_j can be left out, or used only to compensate for defects in the collapse function associated with limiting the first sum in decomposition (9) by a finite number of terms $\psi_{E^*}^G$.

Calculation Results

A) Energy Structure of the P Atom

Structural calculations in the case of the *P* atom were performed using both the MCHF package [2] and the BSR package [1]. By the BSR Method [1] in LS- approximation calculated single-electron orbitals of 36 lower states of the *P* atom with configurations $1s^22s^22p^63s^23p^3(^4S^o, ^2D^o, ^2P^o)$, $3s^23p^2$ (^3P) nl (n=3, 4, 5, 6; l=0, 1, 2), $3s^23p^2$ (^1D) nl (n=4; l=0, 1), $3s^23p^2$ (^1P) 4s and $3s3p^4(^4P, ^2D, ^2S)$. The spectrum of the phosphorus atom according to NIST data [12] is quite complex. The energy values of the spectroscopic states of the *P* atom are obtained by weight averaging of the fine structure levels during the transition from *LSJ-NIST* representation of the approximation *LS*-coupling used. The next few levels of the *P* spectrum are formed mainly by the excitation of one 3*p*-electron from the valence shell at one of the spectroscopic levels of configuration $3s^23p^2$ (^3P) nl (n=3, 4, 5, 6, 7; l=0, 1, 2, 3, 4). However, it is already the 6th in order LS-Level $3s3p^4$ ^4P formed by excitation 3*s*-electron, as a result, it is necessary to consider configurations with vacancies in the internal 3*s*-shell. The 8th in order also causes difficulties LS-Level $3s^23p^2$ (1D) $4s$ ^2D formed with an intermediate ^1D-, not ^3P-therm, as in other cases. All this requires significant adjustments to the scheme for calculating the configuration states of the phosphorus atom. Presence in the lower part of the spectrum of states with thawed 3*s*-shell indicates the need to take into account not only the valence, but also the core-valence correlation in calculations. A relatively small core charge and no strong splitting of levels on *LSJ*-sublevels indicates a relatively insignificant role of relativistic effects in calculating the lower energy levels of the *P* atom.

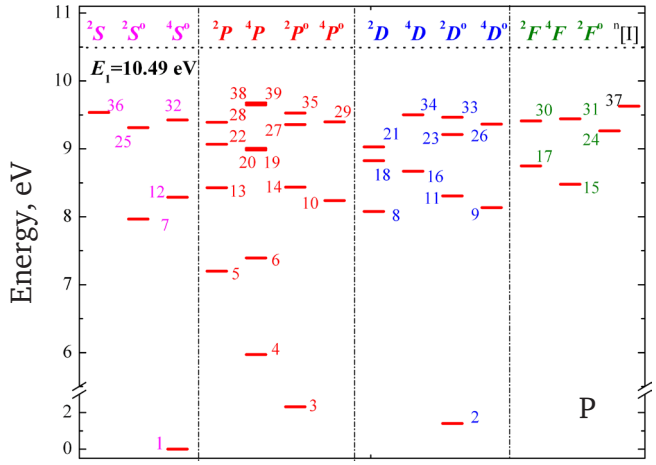

Figure 1. Layout of the 39 lower energy levels (in the LS representation) of the phosphorus atom (P I) and their distribution by terms according to NIST data

Table 1 shows the results of calculating the energies of 36 lower levels of the *P* atom. The main attention is paid to obtaining the exact excitation energies of spectroscopic states under the first ionization threshold and taking into account the interelectronic correlation when calculating the corresponding wave functions. To control the accuracy of calculating the wave functions of the *P* atom, the oscillator forces between the main one – and two-electron junctions are also calculated. A comparison of multi-configuration Hartree-Fock (MCHF) excitation energies previously calculated by us with the NIST reference data [12].

Table 1. Excitation energies (в eB) of the phosphorus atom: our MCHF calculations of excitation energies are compared with the NIST data [12]

No.	Configuration	Term	Eex NIST	Eex MCHF	ΔEex
1	$3s^23p^3$	$^4S^o$	0.0	0.0	0.0
2	$3s^23p^3$	$^2D^o$	1.410	1.426	-0.016
3	$3s^23p^3$	$^2P^o$	2.323	2.294	0.030
4	$3s^23p^2(^3P)4s$	^4P	5.971	6.249	-0.278
5	$3s^23p^2(^3P)4s$	^2P	7.200	7.178	0.023
6	$3s^23p^4$	^4P	7.395	6.540	0.855
7	$3s^23p^2(^3P)4p$	$^2S^o$	7.965	8.008	-0.043
8	$3s^23p^2(^1D)4s$	^2D	8.078	8.337	0.259
9	$3s^23p^2(^3P)4p$	$^4D^o$	8.136	8.146	-0.011
10	$3s^23p^2(^3P)4p$	$^4P^o$	8.239	8.198	0.041
11	$3s^23p^2(^3P)4p$	$^2D^o$	8.306	8.801	-0.495
12	$3s^23p^2(^3P)4p$	$^4S^o$	8.286	8.383	-0.096
13	$3s^23p^2(^3P)3d$	^2P	8.429	8.727	-0.298
14	$3s^23p^2(^3P)4p$	$^2P^o$	8.437	8.338	0.099
15	$3s23p2(^3P)3d$	^4F	8.478	8.557	-0.079
16	$3s^23p^2(^3P)3d$	^4D	8.671	8.669	0.002
17	$3s^23p^2(^3P)3d$	^2F	8.749	8.763	-0.015
18	$3s^3p^4$	^2D	8.825	9.68	-0.858
19	$3s^23p^2(^3P)5s$	^4P	9.008	9.015	-0.006
20	$s^23p^2(^3P)3d$	^4P	8.984	8.057	0.927

Table 1, Continued

No.	Configuration	Term	Eex NIST	Eex MCHF	ΔEex
21	$3s^23p^2(^3P)3d$	^2D	9.029	8.933	0.096
22	$3s^23p^2(^3P)5s$	^2P	9.069	8.980	0.089
23	$3s^23p^2(^1D)4p$	$^2D^o$	9.211	9.349	-0.138
24	$3s^23p^2(^1D)4p$	$^2F^o$	9.265	9.265	0.000
25	$3s^23p^2(^3P)5p$	$^2S^o$	9.312	9.242	0.069
26	$3s^23p^2(^3P)5p$	$^4D^o$	9.364	9.286	0.078
27	$3s^23p^2(^1D)4p$	$^2P^o$	9.358	9.547	-0.189
28	$3s^23p^2(^3P)4d$	^2P	9.393	9.439	0.046
29	$3s^23p^2(^3P)5p$	$^4P^o$	9.398	9.298	0.10
30	$3s^23p^2(^3P)4d$	^2F	9.411	9.464	-0.053
31	$3s^23p^2(^3P)4d$	^4F	9.443	9.404	0.040
32	$3s^23p^2(^3P)5p$	$^4S^o$	9.425	9.370	0.055
33	$3s^23p^2(^3P)5p$	$^2D^o$	9.464	9.378	0.086
34	$3s^23p^2(^3P)4d$	^4D	9.503	9.418	0.085
35	$3s^23p^2(^3P)5p$	$^2P^o$	9.527	9.273	0.253
36	$3s^23p^2(^1S)4s$	^2S	9.536	9.664	0.128

Table 1 shows that in the case of a phosphorus atom, the standard procedure for calculating the energies of spectroscopic states using orbitals that are orthogonalized in independent calculations for individual terms is very complicated. So, for example, for terms ^{4}P it is necessary to calculate single electron orbitals of configurations $3s^23p^2(^3P)4s$; $3s3p^4$; $3s^23p^2(^3P)5s$, $3d$, $4d$, $6s$ with two different atomic residues $3s^23p^2(^3P)$ and $3s3p^4$. This necessitates the consideration in further calculations of two different $3p$-orbitals of the atomic phosphorus residue for this term.

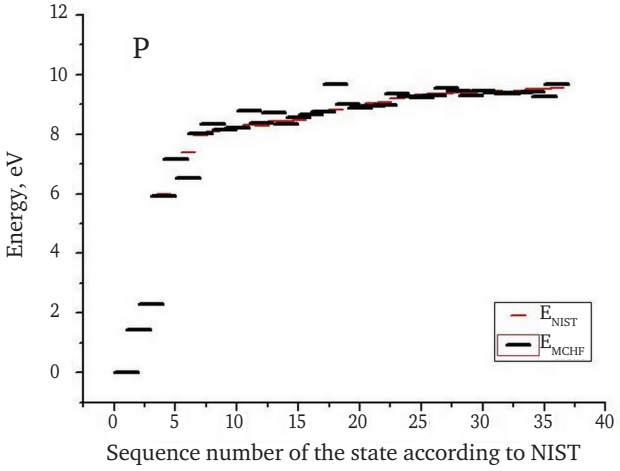

Figure 2. The layout of the energy thresholds of the excitation of the phosphorus atom. Date from our MCHF calculations (E_{MCHF}) compared with the NIST data (E_{NIST})

Figure 2 compares calculated by us MCHF-excitation energies of EMCHF with the NIST reference data (E_{NIST}). The accuracy of MCHF energies obtained in this case is mostly in the range of ~ 0.05-0.2 eV, which makes it possible to use them to calculate the processes of electron scattering on the *P* atom. As can be seen from Figure 2, the phosphorus atom is characterized by a fairly high ionization threshold E_{ion}=10.49 EV. However, there is too narrow an energy gap between the main $3p^3\,^4S^o$-state and lower excited states of the same configuration $3p^3\,^2D^o$ and $3p^3\,^2P^o$. In this case, the excitation energies of the above states are 0.0; 1.4097 and 2.3234 eV, respectively.

B) Energy Structure of the S Atom

Using the MCHF program code [2], we calculated 35 lower states of the *S* atom with configurations $1s^22s^22p^63s^23p^4$ (^3P,^1D, ^1S), $3s^23p^3$ ($^4S^o$) *nl* (n=3, 4, 5, 6; l = 0, 1, 2), $3s^23p^3$ ($^2D^o$) *nl* (n= 4; l= 0, 1), $3s^23p^3$ ($^2P^o$) 4*s* and $3s3p^5$($^{3,1}P^o$). As in the case of the phosphorus atom, the spectrum of the sulphur atom, according to NIST data [13], cannot be attributed to simple ones. As can be seen from Figure 2, the phosphorus atom is characterized by a fairly high ionization threshold E_{ion}=10.49 eV. The bottom three (^3P, ^1D, ^1S) levels correspond to the ground state configuration $3s^23p^4$ with energies of 0,02427, 1,1454 and 2,7500 EV, respectively. The value of the ground state energy is obtained by weight averaging the levels of the fine structure of the triplet $3s^23p^4$ $^3P_{0,1,2}$ when switching from *LSJ-NIST* image [13] to the approximation we used *LS*-coupling. The next few levels of the *P* spectrum are formed mainly by the excitation of one 3*p*-electron from the valence shell at one of the spectroscopic levels of configuration $3s^23p^3$ ($^4S^o$) *nl* (n= 3, 4, 5, 6, 7; l=0, 1, 2, 3, 4). However, already the 9th and 11th *LS*-levels $3s^23p^3$ (^2D) 4*s* ^{3,1}D formed with an intermediate ^{2}D-, not $^4S^o$ term. Even more difficult to calculate is the 15th *LS*-level $3s3p^5\,^3P^o$ with thawed 3*s*-shell. The presence in the lower part of the spectrum of the *S* atom of states with a thawed 3*s* shell indicates the need to consider not only valence but also core-valence correlation in the calculations. In addition, the presence of a stable negative sulphur ion S^- with configuration $3p^5$ $P_{3/2}$ and the affinity energy of 2,0771 eV indicates the need to take into account the valence and core-valence correlations in the calculations of processes of e+S-scattering.

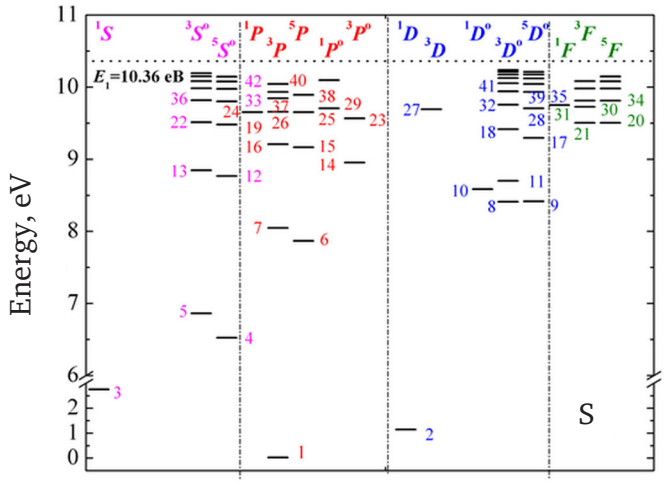

Figure 3. Layout of the 42 lower energy levels (in the LS representation) of the sulphur atom and their distribution by temperature according to NIST data [13]

Figure 4 shows a comparison of multiconfiguration Hartree-Fock (MCHF) excitation energies E_{MCHF} with NIST reference data [13] E_{NIST}. The accuracy of the obtained MCHF-excitation energies of the states of the *S* atom is ~ 0.04-0.2 eV. When calculating wave functions and excitation energies, the main attention is paid to taking into account the effects of valence and core-valence correlation. To control the accuracy of the calculated wave functions of an atom *S* the oscillator forces for single- and two-electron junctions are also calculated.

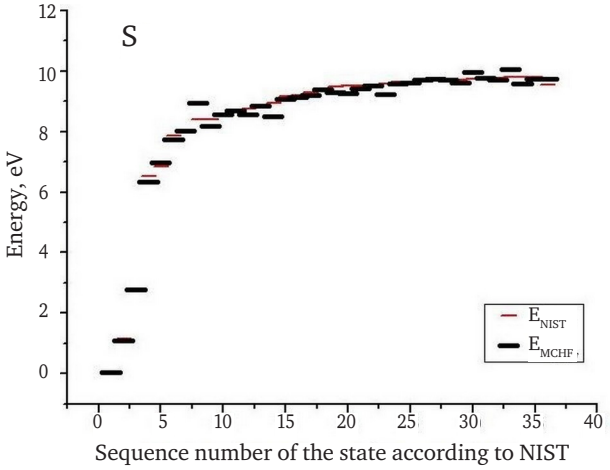

Figure 4. Layout of excitation energy thresholds Eexitof the sulphur atom. The results of our MCHF calculations are compared with NIST data [13]

The numerical values of the excitation energies obtained in MCHF calculations are presented in the Table 2. The results of our calculations are in good agreement with the data of the NIST database [13].

Table 1. Excitation energies (in EV) of the sulfur atom [12]

No.	Configuration	Term	Eex NIST	Eex MCHF	ΔEex
1	$3s^23p^4$	^3P	0,024	0,024	0,000
2	$3s^23p^4$	^1D	1,145	1,089	0,057
3	$3s^23p^4$	^1S	2,750	2,765	-0,015
4	$3s^23p^3(^4S^o)4s$	$^5S^o$	6,524	6,337	0,187
5	$3s^23p^3(^4S^o)4s$	$^3S^o$	6,860	6,974	-0,114
6	$3s^23p^3(^4S^o)4p$	^5P	7,868	7,744	0,124
7	$3s^23p^3(^4S^o)4p$	^3P	8,045	8,020	0,026
8	$3s^23p^3(^2D^o)4s$	$^3D^o$	8,410	8,940	-0,530
9	$3s^23p^3(^4S^o)3d$	$^5D^o$	8,417	8,171	0,246
10	$3s^23p^3(^2D^o)4s$	$^1D^o$	8,584	8,575	0,010
11	$3s^23p^3(^4S^o)3d$	$^3D^o$	8,700	8,705	-0,005
12	$3s^23p^3(^4S^o)5s$	$^5S^o$	8,766	8,569	0,197
13	$3s^23p^3(^4S^o)5s$	$^3S^o$	8,846	8,839	0,008
14	$3s3p^5$	$^3P^o$	8,952	8,508	0,444
15	$3s^23p^3(^4S^o)5p$	^5P	9,165	9,059	0,106
16	$3s^23p^3(^4S^o)5p$	^3P	9,208	9,131	0,077
17	$3s^23p^3(^4S^o)4d$	$^5D^o$	9,296	9,188	0,108
18	$3s^23p^3(^4S^o)4d$	$^3D^o$	9,417	9,393	0,024
19	$3s^23p^3(^4S^o)6s$	$^5S^o$	9,480	9,298	0,183
20	$3s^23p^3(^4S^o)4f$	^5F	9,504	9,276	0,228
21	$3s^23p^3(^4S^o)4f$	^3F	9,504	9,421	0,083
22	$3s^23p^3(^4S^o)6s$	$^3S^o$	9,512	9,514	-0,002
23	$3s^23p^3(^2P^o)4s$	$^3P^o$	9,567	9,222	0,345
24	$3s^23p^3(^4S^o)6p$	^5P	9,653	9,583	0,069
25	$3s^23p^3(^2D^o)4p$	^1P	9,653	9,627	0,026
26	$3s^23p^3(^4S^o)6p$	^3P	9,658	9,708	-0,049
27	$3s^23p^3(^2D^o)4p$	^3D	9,693	9,727	-0,034
28	$3s^23p^3(^4S^o)5d$	$^5D^o$	9,704	9,714	-0,010
29	$3s^23p^3(^2P^o)4s$	$^1P^o$	9,707	9,611	0,096
30	$3s^23p^3(^2D^o)4p$	^3F	9,725	9,970	-0,245
31	$3s^23p^3(^2D^o)4p$	^1F	9,750	9,770	-0,020
32	$3s^23p^3(^4S^o)5d$	$^3D^o$	9,757	9,704	0,052
33	$3s^23p^3(^4S^o)7s$	$^5S^o$	9,802	10,073	-0,271
34	$3s^23p^3(^4S^o)5f$	^5F	9,812	9,583	0,230
35	$3s23p3(^4S^o)5f$	^3F	9,813	9,726	0,086

Conclusions

Comparison of the excitation energies of *P* and *S* atoms calculated in the approximate LS-coupling with the available experimental data indicates the high efficiency and accuracy proposed in

BSR-versions of the method *R*-matrix based on the use of non-orthogonal orbitals and *B*-splines as basic functions. The accuracy achieved is ~ 0.05-0.2 eV for lower energy levels. The oscillator forces for the main one- and two-electron junctions in phosphorus and sulphur atoms are also calculated. The electronic wave functions calculated in the MCHF approximation fully take into account the effects of electronic correlations. The values of the excitation energies and wave functions of the 36 lowest states of the *P* atom and the 35 lowest states of the *S* atom calculated by us will be used in the future to calculate the complete and differential cross-sections of slow electron scattering on phosphorus and sulphur atoms.

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Розрахунки енергетичної структури атомів *P*, *S* методом *R*-матриці з *B*-сплайнами

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Анотація

Мета. Протягом останніх десятиліть фізика електронно-атомних (ЕА) зіткнень інтенсивно розвивалася. Це пояснюється як фундаментальною природою досліджуваних процесів, так і прикладними потребами. Це насамперед про розуміння на глибокому рівні поведінки субмікроскопічних, часто сильно корельованих, квантово-механічних багаточастинкових систем. Результатом цього розуміння є отримання великої кількості даних, необхідних для моделювання поведінки різних типів плазми та розрядів, а також для діагностики їх властивостей.

Методи. У статті представлено загальні принципи та ідею, що лежать в основі методу *B*-сплайнової *R*-матриці (БСР) з неортогональними орбіталями. Використання неортогональних одноелектронних орбіталей усуває ортогональні обмеження, що застосовуються у багатьох інших теоретичних підходах. Ці обмеження було запроваджено виключно для зручності розрахунків, а не з міркувань фізичної необхідності. Відхиляючи умови ортогональності, метод БСР значно покращує точність опису цілі. Відповідно, стає можливим подальший точний розрахунок процесів зіткнення.

Результати. Було розглянуто застосування методу БСР для розрахунку енергетичної структури атомів фосфору та сірки, що представляє значний практичний інтерес. Результати розрахунків демонструють хорошу згоду з наявними експериментальними даними.

Висновки. У роботі розраховано енергетичну структуру атома фосфору. Результати розрахунків демонструють хорошу згоду з наявними експериментальними даними. Надалі наші дані буде використано при вивченні розсіювання електронів на атомах фосфору та сірки

Ключові слова: атом фосфору, атом сірки, обчислення структури атомних систем, метод *R*-матриці з *B*-сплайнами, метод Хартрі-Фока, багатоелектронні бази, кореляційна взаємодія, одно- і багатоконфігураційне наближення

Расчеты энергетической структуры атомов *P, S* методом *R*-матрицы с *B*-сплайнами

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Аннотация

Цель. В течение последних десятилетий физика электронно-атомных (ЕА) столкновений интенсивно развивалась. Это объясняется как фундаментальной природой исследуемых процессов, так и прикладными потребностями. Это прежде всего о понимании на глубоком уровне поведения субмикроскопических, часто сильно коррелированных, квантово-механических многочастичных систем. Результатом этого понимания является получение большого количества данных, необходимых для моделирования поведения различных типов плазмы и разрядов, а также для диагностики их свойств.

Методы. В статье представлены общие принципы и идею, которые лежат в основе метода *B*-сплайновой *R*-матрицы (БСР) с неортогональными орбиталями. Использование неортогональных одноэлектронных орбиталей устраняет ортогональные ограничения, применяемые во многих других теоретических подходах. Эти ограничения были введены исключительно для удобства расчетов, а не из соображений физической необходимости. Отклоняя условия ортогональности, метод БСР значительно улучшает точность описания цели. Соответственно, становится возможным дальнейший точный расчет процессов столкновения.

Результаты. Было рассмотрено применение метода БСР для расчета энергетической структуры атомов фосфора и серы, что представляет значительный практический интерес. Результаты расчетов показывают хорошее согласие с имеющимися экспериментальными данными.

Выводы. В работе рассчитано энергетическую структуру атома фосфора. Результаты расчетов показывают хорошее согласие с имеющимися экспериментальными данными. В дальнейшем наши данные будут использованы при изучении рассеяния электронов на атомах фосфора и серы

Ключевые слова: атом фосфора, атом серы, рассчет структуры атомных систем, метод *R*-матрицы с *B*-сплайнами, метод Хартри-Фока, многоелектронные базы, кореляционное взаимодействие, одно- и многоконфигурационное приближение