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CHOICE OF THE WAVE FUNCTION FOR THE HELIUM GROUND STATE FOR PRECISION CALCULATIONS OF QUASISTATIONARY STATE PARAMETERS

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In the problems of ionization of atoms by photons and electrons, the necessity of choosing the multiparametric wave functions for the description of an atom in the ground state has been substantiated. The helium atom is taken as an example. The energies, widths, and partial widths of the lowest ^1P *autoionizing state of helium, located above the excited ions formation threshold, are calculated. The results obtained with the use of different ground state wave functions are compared. It is shown that, contrary to the total widths of autoionizing states, the partial widths are substantially different for different ground-state wave functions.*

K e y w o r d s: autoionizing states, quasistationary states, overlapping configurations, multiparametric wave functions.

1. Introduction

In modern calculations of the cross-sections of atomic ionization by photons, electrons, or other particles, the wave function of the initial state is selected, as a rule, in the same approximation as the wave function of the final state, as was shown in Burke's [1] and Luke's [2] articles. In paper [3], Fano plausibly proved that, when analyzing the processes of excitation of two-particle states for a considerable number of atoms of chemical elements in the ground state, it is necessary, first of all, to consider multielectron correlations of the type $n\ell^2$. This circumstance is related to the fact that if there are only two electrons in a single atomic shell, the correlations in the ground state become important.

In the case where the ionization cross-sections are calculated for two-electron systems (e.g., for a helium atom above the excited ions formation threshold, namely, He^+ $(N = 2)$) this problem has a principal meaning. It is so because, in this problem, together with the one-particle channel $1s\varepsilon\ell$, the interaction with double-excited channels $2s\varepsilon L$, $2p\varepsilon(L-1)$, and $2p\varepsilon(L+1)$ has to be taken into consideration. The excitation amplitudes for those channels are determined by both their coupling with channel $1s\varepsilon\ell$ in the final state and the multielectron correlations in the ground state.

The problem of the ground-state wave function calculation for the model system considered here, which is described by the projection of the Hamiltonian onto the subspace of the $1s$, $2s$, and $2p$ states of He^+ ion, corresponds to the solution of the problem of the coupling of three closed channels. In this case, the sys-

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tem of equations of the coordinate representation of closed coupled channels method transforms into the Hartree–Fock equations in the multiconfiguration approach [4]. The solution of this system of equations within the method of interacting configurations corresponds to the problem of finding the eigenvalues for the matrix of an infinite rank real symmetric operator. In the case of two-electron systems, this task corresponds to the solving of the multiconfiguration problem with regard for account the $n\ell^2$ configurations for the corresponding atom.

2. Role of the Wave Function Choice for the Ground State of an Atom in the Atomic Ionization Problem. Choice of a Wave Function for the Ground State of He Atom

In the problems of atomic ionization, the choice of a function for the ground state of an atom is very important. A criterion for the choice of that or another wave function for the ground state is the energy value for the atom in the ground state, which is obtained, by using the corresponding wave function. The coincidence between the calculated value of the ground state energy and its experimental value is not a permanent occasion. In the case of precision calculations of autoionizing state parameters, this factor will have a principal importance. Therefore, while carrying out such calculations, a wave function such that exactly reproduces the experimental value of the ground-state energy should be selected.

The most known class of functions used for the ground states of helium-like systems contains the wave functions presented in Hylleraas' papers [5, 6],

$$\Psi_0 = \sum_{n,\ell,m} C_{n\ell m}\psi_{n\ell m}, \quad \psi_{n\ell m} = \frac{e^{-s/2}s^n t^\ell u^m}{(n+\ell+m+2)!}. \quad (1)$$

Here, $\ell = 0, 2, 4, \ldots$. A detailed description of the parameters and their choice can be found in works [5, 6]. These functions describe well the energy of He atom in the ground state. However, their application in ionization problems is complicated, to a great extent, owing to the amplitude calculation procedure. For the most part, the relevant difficulties are associated with finding the integrals containing a multiplier of the type $|\mathbf{r}_1 - \mathbf{r}_2|^m$ in the integrand. In the case where the coordinate representation is used in the framework of closed coupled channels method, the amplitudes are calculated once at every energy point.

A detailed analysis of the parameter calculation procedure following Hylleraas' technique was carried out in work [7], where Fock's modification [8] was taken into account. In work [7], it was shown that, already in the sixth approximation, we have

$$\Psi^6 = \Psi^4 + \left[c_5 u^5 r^{-2} + c_6(5s + t^2/s)r^3\right] e^{-zS}, \quad (2)$$

where

$$\Psi^4 = e^{-zS}\left\{1 + u/2 + A + c_4 u^2 R_1 r^{-3}\right\}, \quad (3)$$

and

$$A \equiv (1 + u/2)R_1\left[c_1 r^{-1} + c_2 + c_3 r\right].$$

This ground-state function gives the energy value that is close to the experimental one, namely, $E = -2.903557$ a.u.

As a rule, these are the Hylleraas multiparameter wave functions that are used in calculations (in particular, 6-, 8-, or even 56-parameter functions). Unlike this type of variational functions, the wave functions obtained in the Hartree–Fock multiconfiguration approximation do not reproduce ground-state energies that would be close to the experimental value for He (see, e.g., works [4, 9] and references therein). We consider the works by Pekeris (see, e.g., work [10] and references therein) as the most exact analysis of multiparameter variational wave functions for He atom. However, the application of those functions in large-scale calculations is extremely difficult and cumbersome.

In another approach, the wave functions of the ground state for two-electron systems are analyzed in the framework of the Monte Carlo method. For example, in work [11], this was done for a function that looks like

$$\Psi_{49} = (1 + P_{12}) \exp\left(\frac{\sum_{k=0} a_k r_1^n r_2^\ell r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^\ell r_{12}^m} + B\right), \quad (4)$$

where

$$B \equiv c(r_1^2 + r_2^2 - r_{12}^2)\ln[r_1^2 + r_2^2] - \alpha r_1 - \beta r_2.$$

In this approximation, the exact value of energy for the ground state of helium was obtained. However, let us return to the approaches that are closer to ours.

It is more convenient to seek a solution of the Schrödinger equation for the ground state of He in the class of functions with separable variables. Among

them, the most known functions describing the He ground state are the analytic Hartree–Fock wave function in the one-configuration approximation,

$$\chi(r) = N_r \left(e^{-\xi r} + 0,6e^{-\zeta r}\right), \tag{5}$$

where the meaning of the parameters ξ and ζ are explained in works [12,13], and the Eckart correlation function

$$\chi(\alpha r) = N_\alpha e^{-\alpha r}, \quad \alpha = 2/a_0, \tag{6}$$

where a_0 is the Bohr radius. The coefficients N_r and N_α in these functions are determined by normalizing the wave function $\Psi_0(\mathbf{r}_1, \mathbf{r}_2)$ to 1. However, the functions of this type are used only for rough estimations.

According to work [14], the wave function of the ground state has the form

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \sum_\ell B_\ell Y_\ell^{00}(\mathbf{r}_{12}) F_\ell(r_1, r_2), \tag{7}$$

where Y_ℓ^{00} can be presented as follows:

$$Y_\ell^{00} = \sum_\mu Y_{\ell\mu}(\theta_1, \varphi_1) C^{00}_{\ell\mu\ell-\mu} Y_{\ell\mu}(\theta_2, \varphi_2). \tag{8}$$

In formulas (7) and (8), the following notations are used: B_ℓ is the expansion coefficient, $\mathbf{r}_i$ is the radius vector of the i-th electron, r_i is its magnitude, $C^{LM}_{\ell\mu\ell-\mu} \equiv \langle \ell\mu\ell - \mu | LM \rangle$ are the coefficients of vector summation, and $F_\ell(r_1, r_2)$ are radial functions that describe the contributions of $n\ell^2$ configurations to the ground state. In the general case, the trial functions $F_\ell(r_1, r_2)$ can be chosen arbitrarily. The only requirements consist in the linear independence of the functions in the chosen set and in a correct asymptotics of the solution. In this case, the functions $F_\ell(r_1, r_2)$ can be written as follows:

$$F_\ell(r_1, r_2) =$$

$$= \sum_{m,n} A^\ell_{mn} \left[\chi^\alpha_m(r_1)\chi^\beta_n(r_2) + \chi^\alpha_n(r_2)\chi^\beta_m(r_1)\right], \tag{9}$$

where χ^α_n are arbitrary continuous functions of one variable, and α and β are parameters that are determined on the basis of the variational principle. Generally speaking, when calculating the functions $F_\ell(r_1, r_2)$, the variational principle can be omitted, and the functions χ^α_n can be taken in the form of a Coulomb basis. But, in this case, a series expansion of types (7) and (9) converges very slowly, so that a large number of terms should be involved in order to achieve the required accuracy.

At the same time, the application of the variational principle for the choice of parameters α and β considerably accelerates the convergence of expansion (9). In work [14], Tweed formulated a one-parameter variational problem for the expansion of type (7). He suggested to seek the functions $\chi^\alpha_n(r)$ in the form

$$\chi^\alpha_n(r) = r^n \exp\left(-\frac{\alpha}{2} r\right), \quad \alpha = \beta, \tag{10}$$

where α is determined from the condition that the ground-state energy has to be minimum. The coefficients A^ℓ_{mn} are calculated by diagonalizing the matrix of the corresponding Hamiltonian. Depending on the number of multipoles that are taken into account in expansion (7), the class of Tweed wave functions includes 21-, 31-, and 41-parameter functions. They contain $(np)^2$, $(nd)^2$, and $(nf)^2$ configurations, respectively. For the calculation procedure, we used the formula

$$F_\ell(r_1, r_2) =$$

$$= \sum_{m,n} A_{\ell mn} (r_1^m r_2^n + r_1^n r_2^m) \exp\left[-\frac{1}{2} k(r_1 + r_2)\right], \tag{11}$$

which was proposed in Tweed's work [14].

3. Calculation Technique

The diagonalization approximation makes it possible to trace how, i.e., into which channels and with which ratios, the autoionizing states with the energy exceeding the threshold for the formation of excited He^+ ions decay. This possibility is especially actual, because it allows one to reveal the resonances that practically decay into a single (arbitrary) channel, so that the coupling of channels can be neglected in this case. The method can also reveal the resonances that decay into several channels, so that the account for the channel coupling for them is mandatory. Generally speaking, the relevant information can be obtained from the data analysis, by comparing the positions and the widths of resonances obtained in various approximations. However, the absence of the data for partial decay widths makes this information incomplete.

In order to calculate the oscillator strength of the transition (or the ionization cross-sections), it is necessary to determine the ionization amplitude, which can be written, in the general case, in the form

$$T_{|0\rangle\to|\lambda E\rangle} = \sqrt{C(E)}\left\langle \Psi_\lambda^{E(-)} \left|\hat{t}\right| 0\right\rangle, \tag{12}$$

where $|0\rangle = |n_0 L_0 S_0\rangle$ means the wave function of the initial atomic state, and $C(E)$ is a kinematic multiplier. Let the wave functions $|\lambda E\rangle$ satisfy the corresponding asymptotic conditions [15]. Then the wave function $\Psi_\lambda^{E(-)}(\mathbf{r}_1, \mathbf{r}_2)$ can be written as follows:

$$\left|\Psi_\lambda^{E(-)}(\mathbf{r}_1, \mathbf{r}_2)\right\rangle = |\lambda E\rangle + \\ + \sum_m \frac{\tilde{V}_{m\lambda}(E)}{E - E_m(E) + i\Gamma_m(E)/2}\left(\left|\tilde{\Phi}_m^E\right\rangle - i\left|\chi_m^E\right\rangle\right), \tag{13}$$

where

$$\left|\tilde{\Phi}_m^E\right\rangle = |\varphi_m^c\rangle + \frac{1}{\pi}\int\limits_0^\infty \frac{\left|\chi_m^{E'}\right\rangle}{E - E'}dE', \\ \left|\chi_m^E\right\rangle = \pi\textstyle\sum_\lambda \tilde{V}_{m\lambda}(E)\left|\chi_m^E\right\rangle, \tag{14}$$

and the subscript λ stands for a set of quantum numbers that is determined by a relation for the asymptotics (see work [16]).

Substituting expressions (13) and (14) into Eq. (12), we determine the partial amplitudes of the resonant ionization in the form:

$$T_{|0\rangle\to|\lambda E\rangle} = t_\lambda^{\rm dir}(E) + \sum_m \frac{H_{m\lambda}(E)}{\varepsilon_m(E) + 1}, \tag{15}$$

where

$$\varepsilon_m(E) = \frac{2[E - E_m(\tilde{E}_m)]}{\Gamma_m(\tilde{E}_m)},$$

and $\Gamma_m(\tilde{E}_m)$ are the widths of autoionizing states. Expression (15) divides the amplitude into two terms. They describe the contributions made by the direct and resonant processes, respectively. The quantities in formula (15) are defined by the following relations:

$$t_\lambda^{\rm dir}(E) = \sqrt{C(E)}\left\langle \lambda E\left|\hat{t}\right| 0\right\rangle, \\ H_{m\lambda}(E) = 2\tilde{V}_{m\lambda}(E)\left[t_m(E) - i\tau_m(E)\right]\Gamma_m^{-1}(E), \\ t_m(E) = \sqrt{C(E)}\left\langle \tilde{\Phi}_m^E\left|\hat{t}\right| 0\right\rangle, \\ \tau_m(E) = \sqrt{C(E)}\left\langle \chi_m^E\left|\hat{t}\right| 0\right\rangle. \tag{16}$$

The partial differential oscillator strength for the transition into the ionization channel λ is proportional to the squared absolute value of expression (15). The total ionization cross-section is calculated, by summing all partial contributions over the superscript λ.

The states of helium in the continuous spectral interval, where autoionizing states converging to the third threshold are located, were described by a wave function [15] that involves all interactions between a finite number of basic configurations corresponding to two-electron excitations in the region between the second and third thresholds (closed channels) and an electron with the positive energies in the ground and first excited states of He^+ ion (open channels). In calculations, the states with the total momentum $L \le 3$ of He atom were taken into account.

For each momentum L, the subspace of closed channels was filled with 20 configurations. The Coulomb wave functions with the charge $z = 2$ were used as basis functions for their description. Then the subspace of those states was preliminarily diagonalized. The subspace of open channels included three configurations for $L = 0$ and four configurations for other momenta L, which corresponds to the inclusion of channels corresponding to the ground and first excited states of He^+ ion: $1s\varepsilon L$, $2s\varepsilon L$, $2p\varepsilon(L-1)$, and $2p\varepsilon(L+1)$.

When calculating the differential characteristics of the autoionizing state excitation, it is often required to determine the partial widths of the decay of a quasistationary state into several channels. Let us introduce the partial width similarly to how this is done in the diagonalization approximation, i.e., in terms of the decay matrix element:

$$\tilde{\Gamma}_m(E) = 2\pi\sum_\lambda \left|\left\langle m\left|\hat{V}\right|\lambda\varepsilon\right\rangle\right|^2, \quad \lambda \in \alpha. \tag{17}$$

The total width corresponds to $\alpha = \Delta(\tilde{\Gamma}_m(E)) = \\ = \Gamma_{\Delta m}(E)$. Note that the total width of a quasistationary state and the ionization cross-section are calculated by summing all partial contributions over the subscript λ. In this case, α determines a selected group of channels from all the channels that were taken into account in the given problem.

In the case of interacting quasistationary states, the partial widths are introduced analogously:

$$\tilde{\Gamma}_j(E) = 2\pi\sum_\lambda \tilde{V}_{m\alpha}(E)\tilde{V}^*_{m\lambda}(E), \tag{18}$$

Parameters of the lowest ^1P autoionizing state of He in the energy interval above the threshold for the formation of excited ions

	E, eV	Γ, eV	$1ses$, eV	$2sep$, eV	$2pep$, eV	$2ped$, eV
Work [17], 6-parameter Hylleraas function	69.89	0.150	0.893(−3)	0.918(−1)	0.313(−1)	0.257(−1)
41-parameter Tweed function	69.92	0.165	0.312(−3)	0.945(−1)	0.320(−1)	0.389(−1)
6-parameter Hylleraas function	69.90	0.154	0.871(−3)	0.814(−1)	0.315(−1)	0.407(−1)
8-parameter Hylleraas function	69.81	0.158	0.852(−3)	0.836(−1)	0.310(−1)	0.425(−1)
Work [11], Monte Carlo function	69.91	0.159	0.476(−3)	0.991(−1)	0.235(−1)	0.359(−1)

where j is the index of partial channel. However, the total width $\Gamma_m(E)$ determined from the diagonalization of the complex matrix does not coincide with the sum of partial widths, as was in case (17).

4. Results of Calculations

To describe the ground state of He atom, one of the coauthors of this paper and our colleagues in works [15, 16] used the 41-parameter Tweed wave function [14]. They obtained exact values for the parameters of those autoionizing states of He atom that are located above the excited ions formation threshold. The analysis of how the choice of the ground state function affects the partial characteristics of autoionizing states is of interest.

The partial widths of autoionizing states were calculated in work [17] in the framework of the problem of helium photoionization. The calculations were carried out with the use of the 6-parameter Hylleraas function in the diagonalization approximation.

The method of interacting configurations in the complex-number representation was used in works [15, 16], besides the diagonalization approximations. The results obtained in all approximations that followed from it were presented. However, the authors used the 41-parameter Tweed function [14] in all calculations as the ground state function for He atom. On the other hand, the concept of partial width has a meaning only in the diagonalization approximation. Therefore, the results of calculations in the diagonalization approximation [15, 16] are also quoted. However, in so doing, we used various wave functions for the ground state of He atom.

The table contains parameters for the lowest ^1P state in the problem of photoionization of He atom above the corresponding excited ions formation threshold. The performed analysis testifies that the parameters of quasistationary states depend on the choice of the wave function of the ground state.

5. Conclusions

1. Theoretical calculations of resonant cross-sections in photoionization problems and the analysis of resonance profiles provide the information concerning a structure of atomic systems and allow theoretical models to be selected more adequately. The choice of the wave function for the ground state affects the values of corresponding resonance parameters.

2. Researches in the excitation energy interval above the second ionization threshold or above the threshold for the formation of excited He^+ ions are similar in many aspects to earlier researches, which were carried out in the energy interval between the first and second ionization thresholds. However, now the research possibilities are more ample. In particular, the spectrum of examined characteristics is richer. This fact is a result of a capability to fill both the ground and excited states of residual ions with photons and electrons in the course of the direct and resonant ionization processes. Later, those ions transit into the ground state, by emitting a photon. Hence, there appears a possibility to study the profiles of resonances that converge to the threshold $N = 3$ of He atom both in the total and partial ionization cross-sections, by considering that the account for the channel coupling in these processes is obligatory. The choice of a wave function for the ground state affects directly the values of corresponding matrix elements in the expression for the ionization cross-section.

3. The results of calculations show that, contrary to the total widths of autoionizing states, the partial widths are substantially different for different wave functions selected for the ground state. From Table 1, one can see that the total widths are also different,

if they are calculated on the basis of different wave functions, although in the framework of the same approach. However, the partial widths turn out to differ even more strongly at that. This fact is explained by the channel coupling, whose account can be different. In order to elucidate the corresponding causes, the further research is required.

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ВИБІР ХВИЛЬОВОЇ ФУНКЦІЇ ОСНОВНОГО СТАНУ He ДЛЯ ПРЕЦИЗІЙНИХ ОБЧИСЛЕНЬ ПАРАМЕТРІВ КВАЗІСТАЦІОНАРНИХ СТАНІВ

Р е з ю м е

На прикладі атома He обґрунтовано необхідність вибору багатопараметричних хвильових функцій для опису основного стану атома в задачах іонізації атомів фотонами та електронами. Обчислюються енергії, ширини і парціальні ширини найнижчого ^1P автоіонізаційного стану He, що знаходиться вище порога утворення збуджених іонів. Порівнюються результати, отримані при використанні різних хвильових функцій основного стану. Показано, що на відміну від повних ширин автоіонізаційних станів, парціальні ширини є суттєво різними для різних хвильових функцій основного стану.