ELASTIC SCATTERING OF ELECTRONS BY HELIUM ATOMS

R. K. PETERKOP

Physics Institute, Latvian Academy of Sciences

Submitted December 23, 1967

Zh. Eksp. Teor. Fiz. 54, 1581–1589 (May, 1968)

A system of equations for elastic scattering of electrons by helium atoms is derived and the phase shift of the s-wave is calculated with allowance for exchange and correlations. A method is used which yields the lower bound of the phase shift if the exact wave function of the atom is employed. Thirty-two (and in one case 36) correlation terms are taken into account in the calculations. It is found that the results should be appreciably altered if terms that vanish when the exact atomic wave function is used are retained. When such terms are not taken into account, the scattering phase shift is in good agreement with the most exact results of other methods. A less accurate value has been obtained for the scattering length. The behavior of the phase shift as a function of the number of correlation terms when $k = 1.25$ (k is the momentum of the incident electron in atomic units) indicates that resonance should occur at $k < 1.25$. No signs of resonance have been observed for $k \leq 1$.

1. INTRODUCTION

IN a number of recent papers, attempts were made to calculate more accurately the phase shifts of elastic scattering of electrons by helium atoms. Different variants of the polarization potential were used in the adiabatic approximation in [1-4]. Pu and Chang[5] calculated, with the aid of a modified perturbation theory, the second-order correction to the exchange-static approximation. Herzenburg and Lau[6] discussed the possibility of resonance at low energies. The approximations used in these papers have a somewhat arbitrary character. The calculated scattering phase shift may turn out to be either larger or smaller than the real phase shift. At the same time, it was shown recently[7, 8] that there exist calculation methods that have extremal properties. These are the methods that follow from the Kohn variational principle and in which the space of the trial functions for the open channels is not limited. The calculated scattering phase shift (or K matrix) must then be smaller than the real phase shift, and increases monotonically with increasing space of the trial functions for the closed channels. In other words, when the number of variational parameters increases, the scattering phase shifts changes in analogy with the change of the absolute value of the energy in variational calculations of the discrete spectrum.

Among the extremal methods, the simplest are those in which the closed channels are described by finite algebraic expressions, i.e., by linear combinations of known functions. In this case, if only elastic scattering is open, then there follows from the variational principle a system of a single integral-differential and several algebraic equations.

This method was used to calculate the phase shifts (more accurately, the lower bounds of the phase shifts) of elastic scattering of positrons[9, 10] and electrons[11, 12] by hydrogen atoms.[1)]

In the present paper we use a similar calculation method for the elastic scattering of electrons by helium atoms. Unfortunately, owing to the inaccuracy of the wave function of the atom, an additional error is produced in this case. The error can have an arbitrary sign, so that the extremality of the result may be violated.

2. SYSTEM OF EQUATIONS

In the absence of spin-orbit interaction, the problem reduces the solution of the Schrödinger equation in coordinate space. The wave function with the required symmetry properties can be constructed with the aid of the Slater determinants, Fock's rules,[14] or Young patterns. In the present article we use symmetrization operators corresponding to a certain combination of Young patterns. For a system of three electrons with total spin equal to ½, the most convenient operators are

$$Q_1 = (1/2\sqrt{3})(1 - P_{23})(1 + P_{12})(1 + P_{13}), \tag{1}$$

$$Q_2 = {}^1\!/_6(1 - P_{23})(1 + P_{12})(1 - P_{13}), \tag{2}$$

$$Q_3 = {}^1\!/_6(1 + P_{23})(1 - P_{12})(1 + P_{13}), \tag{3}$$

$$Q_4 = (-1/2\sqrt{3})(1 + P_{23})(1 - P_{12})(1 - P_{13}), \tag{4}$$

where P_{ij} is the operator of permutation of the i-th and j-th electrons.

These operators differ insignificantly from those given in the book by Slater.[15] They constitute a complete set of basis operators for the space containing all the operators of permutation of three arguments orthogonal both to the symmetrization operator S and to the anti-symmetrization operator A, where

$$S = {}^1\!/_6(1 + P_{23})(1 + P_{12})(1 + P_{13}), \qquad A = {}^1\!/_6(1 - P_{23})(1 - P_{12})(1 - P_{13}). \tag{5}$$

The properties of the operators Q_i are discussed in greater detail in [16]. We note here that the pairs $Q_1 - Q_2$ and $Q_3 - Q_4$ generate an irreducible unitary representation of the permutation group when multiplied by P_{ij} from the right (i.e., QP_{ij}), while the pairs $Q_1 - Q_3$ and $Q_2 - Q_4$ do the same when multiplied from the left.

[1)] Some of the closed channels were described in [13], for the same problem, with the aid of functions that were not specified beforehand, thus increasing the number of integro-differential equations.

The wave function of the system of three electrons is chosen in the form

$$\Phi = \sqrt{3/2}\left[Q_1\Phi_0 + \sum_{i=1}^{N} (a_iQ_1 + b_iQ_2)\Phi_i \right], \tag{7}$$

where

$$\Phi_0 = (4\pi)^{-1/2}r_1^{-1}f(r_1)\psi_0(\mathbf{r}_2,\ \mathbf{r}_3), \tag{8}$$

ψ_0 is the wave function of the ground state of the helium atom. The function f describes the scattered electron:

$$f(\infty) \sim \sin(kr + \eta), \tag{9}$$

where η—phase shift of the scattering (we are considering an s-wave), $k = \sqrt{2(E - E_0)}$—momentum of the incident (and scattered) electron, and E_0—energy of the ground state of the atom (we used an atomic system of units).

The sought function f and the parameters a_i and v_i are determined from the variational principle:

$$\delta I / \delta f = 0,\quad \partial I / \partial a_i = 0,\quad \partial I / \partial b_i = 0,\quad i = 1, \ldots, N, \tag{10}$$

where

$$I = \langle \Phi | H - E | \Phi \rangle - {}^1\!/_2 k\eta. \tag{11}$$

Substituting (7) in (10) and (11), and choosing ψ_0 in the self-consistent field approximation

$$\psi_0 = (4\pi r_1r_2)^{-1}u(r_1)u(r_2), \tag{12}$$

where u satisfies the Hartree equation, we obtain a system containing one integro-differential equation and several ($\leq 2N$) algebraic equations:

$$Lf(r) + 3\sum_j [a_j\varphi_j^{(3)}(r) + b_j\varphi_j^{(4)}(r)] = 0, \tag{13}$$

$$\int_0^\infty \varphi_i^{(3)}(r)f(r)\,dr + \sum_j (M_{ij}^{(3)}a_j + M_{ij}^{(4)}b_j) = 0, \tag{14}$$

$$\int_0^\infty \varphi_i^{(4)}(r)f(r)\,dr + \sum_j (M_{ij}^{(1)}a_j + M_{ij}^{(2)}b_j) = 0,\quad i = 1, 2, \ldots, N. \tag{15}$$

Here

$$Lf(r_1) = \left(-\frac{d^2}{dr_1^2} + 2V(r_1) - k^2 \right) f(r_1) - 2u(r_1)\int_0^\infty u(r_2)r_>^{-1}f(r_2)\,dr_2, \tag{16}$$

$$V(r_1) = -2r_1^{-1} + 2\int_0^\infty u^2(r_2)r_>^{-1}\,dr_2, \tag{17}$$

$$\varphi_i^{(n)}(r_1) = (4\pi)^{-1/2}\langle \psi_0(\mathbf{r}_2, \mathbf{r}_3) | H - E | Q_n\Phi_i(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rangle, \tag{18}$$

$$M_{ij}^{(n)} = \langle \Phi_i | H - E | Q_n\Phi_j \rangle; \tag{19}$$

$r_>$ denotes the larger of r_1 or r_2. The integration in the angle brackets of (11) and (19) is over all the coordinates of the electrons, while the integration in (18) is over the angles of the first electron and all the coordinates of the remaining electrons. In the derivation of (16) it was assumed that

$$\int_0^\infty f(r)u(r)\,dr = 0. \tag{20}$$

The total wave function of the system of three electrons, containing also the spin variables, is of the form

$$\Psi = P^+(\beta(1)\alpha(2)\alpha(3)\Phi(1, 2, 3)], \tag{21}$$

where P^+ is the sum of the cyclic-permutation operators:

$$P^+F(1, 2, 3) = F(1, 2, 3) + F(2, 3, 1) + F(3, 1, 2), \tag{22}$$

α and β are the spin functions of the states with definite spin-projection directions.

Substituting (7) in (21), we can reduce the obtained expression with the aid of (1)–(4) to the form

$$\begin{aligned} \Psi = P^+\Big\{ & \Phi_0(1, 2, 3)\chi_1(1; 2, 3) \\ & + {}^1\!/_2 \sum_i a_i[\Phi_i(1, 2, 3) + \Phi_i(1, 3, 2)]\chi_1(1; 2, 3) \\ & + {}^1\!/_2 \sum_i b_i[\Phi_i(1, 2, 3) - \Phi_i(1, 3, 2)]\chi_2(1; 2, 3) \Big\}, \end{aligned} \tag{23}$$

where χ_1 and χ_2 are the spin functions of the states in which the total spin of all three electrons is equal to $1/2$ and the total spin of the second and third electrons is equal to zero or unity:

$$\chi_1 = \sqrt{3/2}Q_1\beta(1)\alpha(2)\alpha(3), \tag{24}$$

$$\chi_2 = \sqrt{3/2}Q_3\beta(1)\alpha(2)\alpha(3). \tag{25}$$

It is clear therefore that the coefficients a_i and b_i characterize the virtual excitation of singlet and triplet atomic states.

If the operators Q_1 and Q_2 in the expression for the coordinate wave function (7) are replaced by Q_3 and Q_4, then formulas (13)–(19), which determine the system of equations, remain unchanged. Consequently, the phase shift of the scattering remains unchanged also (or else the energy level in the discrete-spectrum problem). This is a manifestation of the fact that the two-dimensional representation has two realizations. From this point of view, Fock's conditions separate one of the two equivalent possibilities. We note that Q_1 and Q_2 satisfy Fock's conditions, which for three electrons are of the form[17]

$$(1 + P_{23})Q = (1 - P_{12} - P_{13})Q = 0. \tag{26}$$

The operators Q_3 and Q_4 satisfy the modified conditions

$$(1 - P_{23})Q = (1 + P_{12} + P_{13})Q = 0. \tag{27}$$

However, when we replace Q_1 and Q_2 in (7) by Q_3 and Q_4, the total wave function defined by (21) will be different. Instead of an anti-symmetrical function we then obtain a function that is symmetrical with respect to electron permutation.[16] Thus, in the absence of interactions that depend on the spins, the Hartree-Fock equations do not depend on the type of symmetry of the total wave function.

We denote by Φ^+ the function which we obtain by replacing Q_1 by Q_3 and Q_2 by Q_4 in (7). The following relations hold:

$$\Phi^+ = \Pi\Phi,\quad \Phi = \Pi\Phi^+, \tag{28}$$

where

$$\Pi = \frac{1}{\sqrt{3}}(P_{12} - P_{13}) = Q_1 + Q_4, \tag{29}$$

$$\Pi^2 = Q_2 + Q_3 = 1 - S - A. \tag{30}$$

The functions Φ and Φ^+ are expressed in terms of each other for all permutations of the arguments—they constitute a basis of an irreducible two-dimensional representation.

Phase (in radians) of s-wave of elastic scattering of electrons by helium atoms (the scattering length is given for k = 0).

	k, at. un.					
	0	0,25	0,5	0.75	1,0	1,25
$\varkappa$ γ	1,6 3,6	2 3,6	2,4 4	2,6 4	2,8 4	2 4
Exchange-static approximation	1,483	2,7756	2.4356	2,1386	1,8899	1,6866
Allowance for 32 correlation terms and using (34)	1,282	2,8127	2.4845	2,1910	1,9479	1,7359
Allowance for 32 correlation terms without using (34)	—14,9		2,6386		1,9896	

The fact that the use of Q_3 and Q_4 leads to a symmetrical total wave function can be understood by taking into account the definition of the determinant and noting that these operators, expressed in the form of a sum of permutations, differ from Q_1 and Q_2 only in the sign of the even or the odd permutations.

3. CALCULATION RESULTS

The functions Φ_i in (7) describe the correlation of the electrons. They were chosen in the form

$$\Phi_i = (4\pi)^{-3/2} r_1^{m-1} r_2^{n-1} e^{-\varkappa(r_1+r_2)/2} P_l(\cos\theta_{12}) r_3^{p-1} e^{-\gamma r_3/2}. \qquad (31)$$

The part that depends on r_1 and r_2 is analogous to that previously employed in the papers of Gaĭlitis[11] and Aronson et al.[12], who investigated e^-–H scattering. The third electron can be regarded as being in the ground state of the helium ion ($\gamma \approx 4$). The index i denotes here the aggregate of the integers l, m, n, p. The quantities κ and γ are regarded as nonlinear variational parameters. The system of equations was solved by a non-iterative method,[11, 13] in which the problem is reduced to the solution of a series of inhomogeneous integro-differential equations, the calculation of matrix elements, and the solution of a system of algebraic equations.

In the first part of the calculations we determined the optimum values of the parameters κ and γ. To this end, we solved equations with a small number (≤ 8) variational parameters for different κ and γ. In accordance with the extremality principle, the optimal values are those for which the scattering phase shift is maximal. Then, using the optimal values of κ and γ, we solved equations with 32 variational parameters. These values of κ and γ are listed in the table. The used values of the numbers l, m, n, and p are seen in Fig. 1. If $m \neq n$, then two terms in the sum (7) or (23) correspond to the set of numbers l, m, n, and p. In Fig. 1 we show first the singlet term. When m = n there are no triplet terms. This is connected with the fact that $Q_2\Phi = \sqrt{3}\,Q_1\Phi$ if $\Phi(1, 2, 3) = \Phi(2, 1, 3)$. Therefore we can put $b_i = 0$ when m = n.

As the radial wave function of the atom we use the three-parameter function[18]

$$u(r) = Cr(e^{-Zr} + 0{,}6^{-2Zr}), \qquad (32)$$

$$C = 2{,}968466, \quad Z = 1{,}455799, \qquad (33)$$

which differs little from the exact numerical solution of the self-consistent-field equation.

In calculating the functions $\varphi_i^{(n)}$ defined by (18), we used a simplification which is valid if ψ_0 is an exact eigenfunction of the helium atom. Then we have in (18)

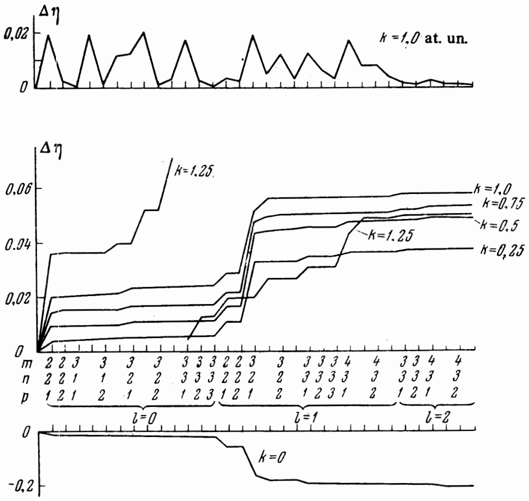

FIG. 1. Change of phase with increasing number of correlation terms. We plotted $\Delta\eta = \eta - \eta_{\text{stat}}$, where η_{stat} – phase of the exchange-static approximation; the corresponding difference in the scattering length was determined at k = 0. The upper $\Delta\eta$ curve was obtained with allowance for only one correlation term.

$$H - E = -\tfrac{1}{2}\Delta_1 - 2/r_1 + 1/r_{12} + 1/r_{13} - \tfrac{1}{2}k^2. \qquad (34)$$

Generally speaking, the wave function of the self-consistent field (12) is not an exact eigenfunction. In order to determine how this affects the results, the calculations were also performed at certain energies of the incident electron without using the simplification (34), i.e., retaining all the terms in (18). At low energies, the scattering phase shift turned out to be much larger, and the scattering length much smaller (see the table). The scattering length has in this case a value which is definitely improbable. Thus, at low energies, the inaccuracy of the atomic function comes strongly into play.[2)] The use of (34) decreases its influence. We note in this connection that in the derivation of (16) we did not take into account the fact that the function (32) employed by us is not an exact solution of the self-consistent-field equation. In analogy with the foregoing, we can expect allowance for the corresponding additional terms in (16) not to improve the result. The question of the two variants of the exchange part of the static approximation was considered in the monograph

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[2)] A similar circumstance was observed in an investigation of the dispersion relations for the scattering of electrons by helium atoms[19].

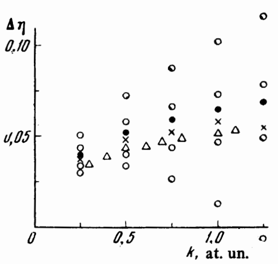

FIG. 2. Change of phase in comparison with the results of other investigations (we plotted $\Delta\eta = \eta - \eta_{\text{stat}}$): X – results of present work (with $k \leqslant 1$ and with allowance for 32 correlation terms, and with k = 1.25 with allowance for 36 terms), O – different variants of the adiabatic polarization potential [1]; ● – expanded polarization potential [4]; Δ – optical potential with allowance for second-order term [5].

by Drukarev,[17] where it was shown that the exchange particle responding to expression (16) comes closer to the exact exchange operator, since it does not contain terms of the type 2/r.

The scattering phase shift in the variant in which relation (34) was not used is undoubtedly larger than the real scattering phase shift. Consequently, the error in the atomic function leads to a violation of the extremality principle. We cannot state that the use of (34) restores the correctness of this principle, but comparison with the results of other calculations (see Fig. 2) allows us to think that this is possible. Our results lie between the results of the two papers [4, 5] which can be regarded as the most accurate. In [4] a most complete account was taken of all the possible terms of the polarization potential in the adiabatic approximation, while in [5] the optical potential was constructed with allowance for terms of second order in the modified perturbation theory.

For k = 1.25, a calculation was also performed with 36 variational parameters. In addition to those shown in Fig. 1, we used for l, m, n, p the values 0421 and 1321. We then obtained $\eta = 1.7432$. It should be noted that at k = 1.25 the validity of the employed approximation is less reliable, since no account is taken of inelastic processes that are possible at this value of k.

In order to obtain a solution with a smaller number of correlation terms, it is necessary to repeat only the last stage of the solution process—to solve the decreased algebraic system of equations. Therefore in each case we calculated also the phase shifts corresponding to allowance for 1, 2, ... correlation terms. The change of the phase shift with increasing number of the correlation terms is shown in Fig. 1. We see that, in accordance with the extremality principle, the phase shift increases everywhere. An exception is the case k = 1.25. This quantity lies above the e^-–He resonance,[20] and therefore the strict extremality principle no longer holds for it. The jump in the phase shift indicates a resonance at k < 1.25. The absence of phase-shift jumps at $k \leq 1$ indicates that there is no resonance in this region.

It should be noted that the fact that the phase shift increases with increasing number of variational parameters is in general insufficient to cause it to represent the lowest limit. Owing to the inaccuracy of the atomic wave function, the phase shift may turn out to be larger than the exact value. For example, in the case without the use of (34), the phase shift also increases throughout (when $k \leq 1$), but it reaches values that are clearly too high.

Figure 1 shows also the change of the phase at k = 1, which we obtain by adding to the static approximation only one correlation term. We see that in this case the effect produced by it can greatly differ from that when other terms are also taken into account. The influence of the different correlation terms has a non-additive character.

The sign of the scattering length is the opposite of the sign of the tangent of the phase. Therefore, with increasing number of variational parameters, the scattering length decreases (see Fig. 1). Allowance for 32 correlation terms decreases it from 1.483 to 1.282. But this is certainly insufficient. With the aid of the dispersion relations,[19] and also by the method of the expanded polarization potential,[4] we obtained a value 1.15. Thus, allowance for the polarization with the aid of functions of the type (31) has slow convergence if k = 0. A similar result was observed by Schwartz[21] in a calculation of the scattering length of electrons by hydrogen atoms.

In the present paper, within the framework of the statistical approximation, we also calculated the dependence of the phase shift of the s-wave on the choice of the wave function of the atom. Besides the functions (12) and (32), we used 1-, 3-, and 6-parameter Hylleras functions.[22] The results are shown in Fig. 3. In the case when no exchange is taken into account, the phase shift changes monotonically with increasing number of parameters of the atomic function—it increases throughout. This is the consequence of the monotonic decrease of the static potential (17), which in turn is apparently connected with the monotonic increase of the scale factor in the wave function. The phase changes in this case in analogy with the energy: the difference between the results of the 3- and 6-parameter functions is much smaller than for the 1- and 3-parameter functions. The results for the 3-parameter Hylleras function and the functions (12) and (32) are practically equal, this being a certain justification for the use of the latter in the calculation with allowance for the correlation. Calculations with allowance for exchange were made only with the 1-parameter Hylleras function and with the functions (12) and (32). In this case, the change of the phase is much smaller (≤ 0.01) and is non-monotonic—negative at small k.

The dependence of the phase on the choice of the atomic function in the static approximation with allow-

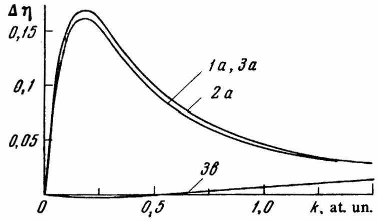

FIG. 3. Dependence of the phase of the static approximation on the choice of the wave function of the atom. We plotted $\Delta\eta = \eta - \eta_1$, where η_1 – phase using the 1-parameter Hylleraas function. 1 and 2 correspond to 3- and 6- parameter Hylleraas functions; 3 – functions (32); a – without allowance for exchange, b – with allowance for exchange. Curves 1a and 3a coincide within the scale of the figure.

ance for exchange was investigated earlier in [23], where it was found that allowance for the term containing r_4^2 in a function of the Hylleras type changes the phase by not more than 0.006, while allowance for the term containing r_1r_2 changes it in the range 0.04–0.1. The latter is an overestimate, since a similar term is contained also by the functions (12) and (32), for which, as already noted, the change of the phase is much smaller (≤ 0.01).

We also used the 1-parameter Hylleras function with $k = 1$ in a calculation with 32 correlation terms. This yielded $\eta = 1.9310$, which is smaller by 0.0170 than the phase obtained with the function (32). The phase difference is somewhat larger than in the exchange-static approximation (0.007), but at the same time smaller than in the static approximation without exchange (0.044).

In conclusion we note that in the present paper we were the first to employ the method determined by formulas (7)–(11) for the collision between an electron and an atom containing more than one electron. This raises a difficulty connected with the inaccuracy of the wave function of the atom. The obtained results indicate that the use of relations of the type (34), i.e., simplifications that are valid for the exact wave function, is one of the possible ways of overcoming this difficulty.

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[1] R. W. LaBahn and J. Callaway, Phys. Rev. **135**, A1539 (1964); **147**, 28 (1966).

[2] J. H. Williamson and M. R. C. McDowell, Proc. Phys. Soc. **85**, 719 (1965).

[3] N. R. Kestner, J. Jortner, M. H. Cohen, and S. A. Rice, Phys. Rev. **140**, A56 (1965).

[4] J. Callaway, W. M. Duxler, R. W. LaBahn, and R. T. Pu, V Intern. Conf. on the Phys. of Electr. and Atomic Collisions (Abstracts of Papers), Leningrad, Nauka, (1967), p. 137.

[5] R. T. Pu and E. S. Chang, Phys. Rev. **151**, 31 (1966).

[6] A. Herzenberg and H. S. M. Lau, V.Intern. Conf. on the Phys. of Electr. and Atomic Collisions (Abstracts of Papers), Leningrad, Nauka, (1967), p. 261.

[7] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962); **130**, 381 (1963); **134**, B397, B911 (1964).

[8] M. Gailitis, Zh. Eksp. Teor. Fiz. **47**, 160 (1964) [Sov. Phys.-JETP **20**, 107 (1965)].

[9] Y. Hahn and L. Spruch, Phys. Rev. **140**, A18 (1965).

[10] C. J. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev. **140**, A413 (1965).

[11] M. Gailitis, in: Éffektivnye secheniya stolknovenii élektronov s atomami [Effective Cross Sections of Electron-atom Collisions], Zinatne, Riga, 1965, p. 155.

[12] I. Aronson, Y. Hahn, P. M. Henry, C. J. Kleinman, and L. Spruch, Phys. Rev. **153**, 73 (1967); **161**, 23 (1967).

[13] P. G. Burke and A. J. Taylor, Proc. Phys. Soc. **88**, 549 (1966).

[14] V. A. Fock, Zh. Eksp. Teor. Fiz. **10**, 961 (1940). Yubileinyi sbornik (Jubilee Collections), part I, AN SSSR, 1947, p. 255.

[15] J. C. Slater, Quantum Theory of Atomic Structure, vol. 2, McGraw-Hill, N. Y. (1960).

[16] R. K. Peterkop, in: Rasseyanie élektronov na atomakh [Scattering of Electrons by Atoms], Zinatne, Riga, 1967, p. 69.

[17] G. F. Drukarev, Teoriya stolknovenii élektronov s atomami [Theory of Electron-atom Collisions], Fizmatgiz, 1963.

[18] L. C. Green, M. M. Mulder, M. N. Lewis, and J. W. Woll, Phys. Rev. **93**, 757 (1954).

[19] J. Lawson, H. Massey, J. Wallace, and D. Wilkinson, Proc. Roy.Soc. **A294**, 149 (1966).

[20] G. J. Schulz, Phys. Rev. Lett. **10**, 104 (1963); Phys. Rev. **136**, A650 (1964).

[21] C. Schwartz, Phys. Rev. **124**, 1468 (1961).

[22] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

[23] R. E. Schenter and R. M. Thaler, Phys. Rev. **146**, 70 (1966).

Translated by J. G. Adashko
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