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RELATIVISTIC EFFECTIVE POTENTIAL IN ELECTRON — Au ATOM AND ELECTRON—SUFACE SCATTERING CALCULATIONS

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We present effective l-dependent potentials $V^{(a)}$ for electron — Au atom interactions. The potential is based on previously developed effective electron — positive atomic ion model interaction $V^{(+)}$; all energies are in good agreement with Dirac—Hartree—Fock calculations and experimental data. We generalized $V^{(+)}$for the electron — atom Au interaction and obtained the effective potential $V^{(a)}$. We applied potential $V^{(a)}$ to electron—Au elastic scattering calculations. Calculated cross sections at impact energies 400 eV—30 keV are in excellent agreement with other model potential calculations at impact energies exceeding 400 eV. We examined the validity of the first and the second Born approximations for electron—gold cross section calculations at nonrelativistic collision energies. We estimated the effect of potential confinement in electron—Gold scattering. Refs 19. Figs 3. Tables 1.

Keywords: effective potential, electron, atom, Gold, scattering, cross sections, integral, differential, calculation, partial wave, semiclassical approximation, relativistic approximation, Dirac equation.

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РЕЛЯТИВИСТСКИЙ ЭФФЕКТИВНЫЙ ПОТЕНЦИАЛ В РАСЧЁТАХ СЕЧЕНИЙ РАССЕЯНИЯ ЭЛЕКТРОНОВ НА АТОМЕ И НА ПОВЕРХНОСТИ ЗОЛОТА

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Предложен эффективный релятивистский l-зависимый потенциал $V^{(a)}$ взаимодействия электрона и атома золота. Данный потенциал получен на основе обобщения ранее предложенного модельного релятивистского взаимодействия электрона и положительного атомного иона $V(+)$. Мы применили потенциал $V^{(a)}$ к расчётам, относящимся к упругому рассеянию электронов на атоме золота. Результаты расчётов сечений рассеяния при энергии столкновения 400 эВ—30 КэВ согласуются с аналогичными результатами, полученными с помощью двух других эффективных потенциалов при энергиях столкновений бóльших, чем 400 эВ. Мы показали, что первое и второе приближения Борна неприменимы в случае рассеяния электронов атомами золота в широком интервале энергий столкновения, вплоть до 1 МэВ. Мы исследовали эффект, возникающий при ограничении области действия эффективного потенциала. При помощи такого ограниченного потенциала мы моделировали взаимодействие электронов с поверхностью металла. Библиогр. 19 назв. Ил. 3. Табл. 1.

Ключевые слова: эффективный потенциал, электрон, атом, золото, рассеяние, сечение рассеяния, интеграл, дифференциал, расчёт, парциальные волны, полуклассическое приближение, релятивистское приближение, уравнение Дирака.

1. Introduction. The atom of Gold and Gold systems such as semi-infinite media, thin films, quantum wires, nanoparticles are widely used in different fields of science and technology, see for example, Gold Bulletin (World Gold Council, London). Considerable efforts were directed to experimental and theoretical studies of Gold atom and Gold systems and processes with them including electron—atoms scattering. There is the special type of experimental study — the elastic peak electron spectroscopy (EPES) [1], dealing with electron scattering from targets surface at intermediate and high (but nonrelativistic) impact energy. The goal of the present paper is to consider the elastic electron — Gold scattering

at intermediate and high collision energies E_0, approximately 200 eV $< E_0 <$ 10 keV by suitable theoretical approach. The theoretical study of electron atom collisions includes relativistic close-coupling method combined with partial wave expansion [2], the relativistic method of R-matrix [3], the Dirac—Hartree—Fock method [4], effective potential methods [5–9] and first Born and distorted wave approximations [10]. Not all theoretical approaches are suitable for application to electrons — heavy atom (Au) scattering at collision energies 200 eV $< E_0 <$ 10 keV. The accurate but cumbersome close-coupling approach [2] and R-matrix method [3] are limited by impact energies are not exceeding few tens eV. Note, that the first and the second Born approximations are not valid for e^-—Au scattering calculations at non-relativistic impact energies E_0 [8]. The method of effective potential is seemed to be the most suitable for the application to fast electron—atom collisions.

2. Electron — heavy atom effective interaction potential. We compose the effective electron — neutral atom interaction $V^{(a)}$ as the sum of three potentials: electron — positive ion $V^{(+)}$ interaction, scattering electron — outer bound atomic electron $V_n^{(\mathrm{out})}\lambda$, and polarization—correlation V_{pc} terms [6]:

$$V^{(a)} = V^{(+)} + V_{n\lambda}^{(\mathrm{out})} + V_{pc}. \tag{1}$$

2.1. Static potential. The sum of two first terms in (1) is known as static potential: $V_{\mathrm{stat}} = V^{(+)} + V_{n\lambda}^{(\mathrm{out})}$. We believe that the term $V^{(+)}$ should reproduce values of atomic orbital energies in bound states calculations as precised as it is possible. The known electron — heavy atom effective potentials give orbital energy values with the deviations from experimental these as 5–87 %, meanwhile the effective potential $V^{(+)}$ developed in work [11], gives deviations 0,006–8 % (see [11, table 3]), so we apply the electron — positive Gold ion $V^{(+)}$ from there:

$$V^{(+)}(\vec{r}) = \sum_l V_l^{(+)}(r)|l\rangle\langle l|, \tag{2}$$

where $|l\rangle\langle l|$ is the projection operator in the Hilbert space onto the subspace with fixed orbital momentum l. The polarization, exchange and Coulomb potentials of valent atomic electron and positive core are included in the $V^{(+)}(\vec{r})$. Radial potentials $V_l^{(+)}(r)$ are fitted in [11] by the sum of Yukawa, Slater, Coulomb terms and the special potential

$$V_h = C_{-2}^l \frac{\exp\left(-q_{-2}^{(l)} r\right)}{r(r+h)}.$$

We calculate the electron—electron term in (1) $V_{n\lambda}^{(\mathrm{out})}$ by the expression:

$$V_{n\lambda}^{(\mathrm{out})}(\vec{r}) = \frac{1}{4\lambda+2} \sum_{j=|\lambda-1/2|}^{\lambda+1/2} \int \frac{(P_{n\lambda j}^2(\vec{r}') + Q_{n\lambda j}^2(\vec{r}'))(2j+1)}{|\vec{r}-\vec{r}'|}\, dr', \tag{3}$$

where $P_{n\lambda j}^2$, $Q_{n\lambda j}^2$ are large and small components of Dirac wave function. In (3) we average the interaction over fine structure configuration. In the case interaction with Gold atom we get:

$$V_{6s}^{(\mathrm{out})}(\vec{r}) = \frac{1}{r}\int_0^r S_{6s_{1/2}}^2(r')r'^2 dr' + \int_r^\infty S_{6s_{1/2}}^2(r')r' dr'.$$

For ground state of Gold atom $S^2_{6s_{1/2}} = P^2_{6s_{1/2}} + Q^2_{6s_{1/2}}$. To find components $P^2_{n\lambda j}$, $Q^2_{n\lambda j}$ of relativistic wave function we solved Dirac equation with effective potential $V^{(+)}$, parameterized in [11]. We fitted the radial function (3) by the sum of Yukawa, Slater and Coulomb terms:

$$V^{(\mathrm{out})}_{n\lambda} = \sum_{i=-1}^{1} C^{(l)}_{i,n\lambda} r^i \exp\left(-q^{(l)}_i r\right) + \frac{1}{r}. \tag{4}$$

Note, that for the best fitting we included in the sum (4) the electron-electron Coulomb rejection $1/r$ accordingly the limit of $V^{(\mathrm{out})}_{n\lambda}(r)$ on large r. Small values of fitting errors allow us to keep values of parameters $q^{(l)}_i$ in (4) the same as in [11], coefficients we find by the minimum square fit. Combining (2) and (4) we obtain the final expression for static potential:

$$V^{(+)} + V^{(\mathrm{out})}_{n\lambda} = \sum_l V_l |l\rangle\langle l|, \tag{5}$$

$$V_l = C^{(l)}_{-2} \frac{\exp\left(-q^{(l)}_{-2} r\right)}{r(r+h_i)} + \sum_{i=-1}^{1} C^{(l)}_i r^l \exp\left(-q^{(l)}_i r\right). \tag{6}$$

Values of parameters in (7) are presented in Table.

Parameters of effective electron — Gold atom static potential (2), all values are in atomic units

	i	$q^{(l)}_i$	$C^{(l)}_i$
$l = 0$ $h_0 = 0.068$	-2	2.174	-1.182
	-1	3.020	-67.189
	0	3.429	24.003
	1	2.224	-21.234
$l = 1$ $h_1 = 0.0615$	-2	2.310	-1.211
	-1	2.890	-61.794
	0	2.900	17.636
	1	2.135	-24.060
$l > 1$ $h_l = 0.02954$	-2	2.300	-0.438
	-1	2.800	-64.414
	0	2.800	34.828
	1	2.030	-26.005

2.2 Polarization—correlation potential V_{pc}. For the potential V_{pc} in (1) we applied the expression [5, 12]:

$$V_{\mathrm{pol}}(r) = -\frac{\alpha_p}{2r^4}\left(1 - \exp(-r^6/r_p^6)\right), \tag{7}$$

where α_p is the polarization constant of Gold atom; r_p is the polarization radius. Different kinds of experiment give different values of polarization constant: 30.4 a. u. $\leqslant \alpha_p \leqslant$ 36.06 a. u. [13]. In present calculations we applied the moderate value of $\alpha_p = 35.1$ a. u. [13]. The exchange potential from bound — continues electron interaction is included in polarization—correlation term semi-empirically through the known value of the outer electron bound energy E_a in negative atomic ion. We varied the value of polarization radius r_p in the Dirac equation for bound state of outer electron in the field of effective potential

summed with $V_{\rm ex}$ in order to reach the known value of bound energy of the outer electron to be equal to the electron affinity of Gold atom: $E_a = 2.3$ eV [14], $V_{\rm ex}$ is nonlocal singlet exchange potential formed by 6s-wave function of Au atom and outer electron orbital, see for example [15, Eq. (101)]. As the result we obtained the value $r_p = 1.9\ a_0$.

3. Electron—Gold elastic scattering cross sections. For electron — Au atom elastic scattering calculations at intermediate and high impact energy range (100 eV $< E_0$ $< 3 \div 5$ keV) we applied the method of partial waves [15], semiclassical phase approximation [16], and the first Born formula for scattering phases with high l in polarization potential [17] (Appendix I). The difference between results of nonrelativistic and relativistic partial waves results is vanished at impact energies E_0 exceeded several tens eV, as it was shown in the example of e—Hg scattering [2]. Bearing in mind results of [2], we calculate the scattering amplitude by nonrelativistic partial wave method (PW), see Appendix.

3.1. Differential cross section (DCS). In Fig. 1 we show the comparison of results of DCS obtained with presently developed effective potential $V^{(a)}$ (1)–(5) and with two other known model potentials: $V^{(a)}_{IPM}$ (Independent Particle Model potential, we applied formula from [9]) and $V^{(a)}_{ADHFS}$ (Analytical Dirac—Hartree—Fock—Slater potential, the expression is given in [8]). One can see in the equivalence of all effective potentials in DCS calculation at impact energies $E_0 \geqslant 400$ eV at in spite of their different shapes and ways of development. Note, that our results are in excellent agreement with these ADHFS, presented in [19] at $E_0 = 500$ and 1000 eV, see Fig. 1, *a, b*.

3.2. DCS of electron scattering from Gold surface. To investigate electron—surface scattering features we approximated correspondent interaction by confined potential $V^{(a)}$ with the help of cut off radius $r_{\rm cut}$ of effective interaction (1):

$$V^{(a)}(r)\Big|_{r>r_{\rm cut}} = 0.$$

Results of DCS calculations at different values of $r_{\rm cut}$ are presented in Fig. 2. We reveal oscillations in angular dependenses of DCS at impact energies less than 5 keV. Oscillations become more prominent at intermediate collision energies E_0 at scattering angle not exceeded 90°. At large impact energies ($E_0 = 1200$ eV) and $r_{\rm cut} > 2a_0$ the cutting effect almost is absent. As one can see, oscillations are vanished at $r_{\rm cut} = 3a_0$ at all E_0 under consideration. At the value of $r_{\rm cut}$ being in order of Wigner—Zeitz cell size in metallic gold, $2.99a_0$ [18], DCS results are similar to these for free Gold atom. Thus, the effect of potential cutting is liked to "solid state" effect in e^- — solid Au scattering, investigated in muffin-tin approximatiion [19]. Note, that revealed oscillations in DSC appieard due to confinement of interaction potential, did not neither observed, nor calculated before.

3.3. Integral cross section and single Yukawa potential approximation. We examine the validity of first and second Born approximations in the electron—Gold integral cross section (ICS) calculations despite it is was done before present work [2], however with another effective potential and by another way. We substitute the potential $V^{(a)}$ (1) by the single Yukawa one: $V_{\rm Yuk}$: $V_{\rm Yuk} = C\exp(-ar)/r$, $C = -79$ in order to applying analytical expressions for scattering amplitudes. For example, in the case of second Born approximation, we employ the Dalitz formula [10]. Parameter α of Yukawa interaction we determine from the adjusting of ICS, obtained with single Yukawa potential, to that, obtained with our effective potential (1), (5), (7) at impact energies 500 eV $< E_0 <$ 40 keV, Fig. 2. One can compare the present Yukawa constant $\alpha = 2.4a_0^{-1}$ with the value of $2.1a_0^{-1}$, obtained from [10, table II and formula (68)]. Small deviation in values one can explain by the difference in impact energies in either event: we consider $E_0 <$ 40 keV and E_0= 15 MeV in [10]. Basing

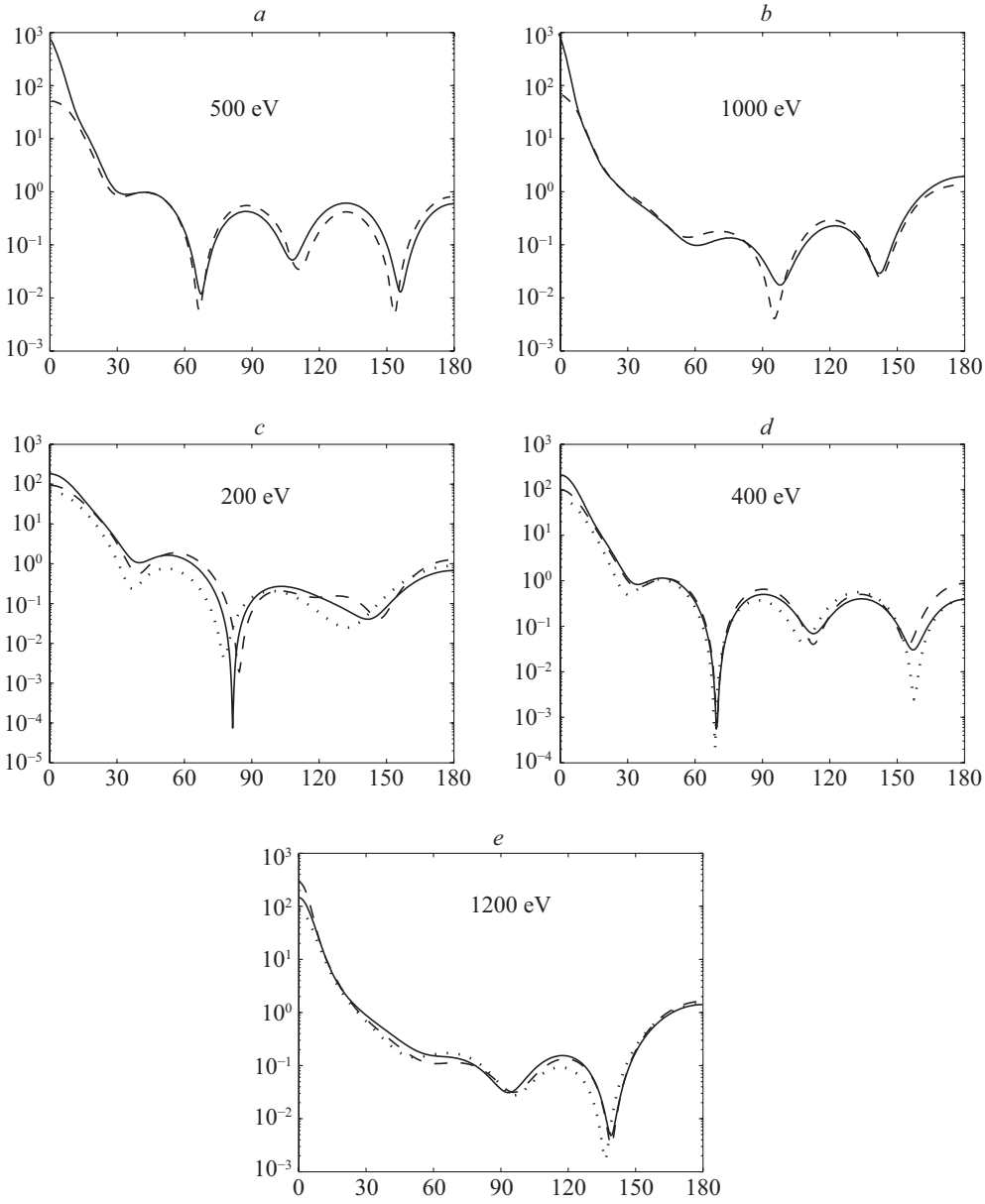

Fig. 1. e^-—Au elastic DCS in units of a_0^2/sr versus E_0, eV:
lines — results obtained with present relativistic effective potential; dashes and points — results with potentials ADHFS and IPM correspondingly; at $E_0 = 500$ and 1000 eV (*a, b*) dashes correspond to results from [19]

on results, presented in Fig. 3, one can conclude, the first and the second Born approximations are not valid for electron — Gold atom scattering calculations at all nonrelativistic impact energies. This conclusion agrees with the condition of Born approximations validity for Yukawa potential [10]: $(|C|/\sqrt{2E_0})^n \ll 1$, C is the coefficient in Yukawa potential, $n = 1$

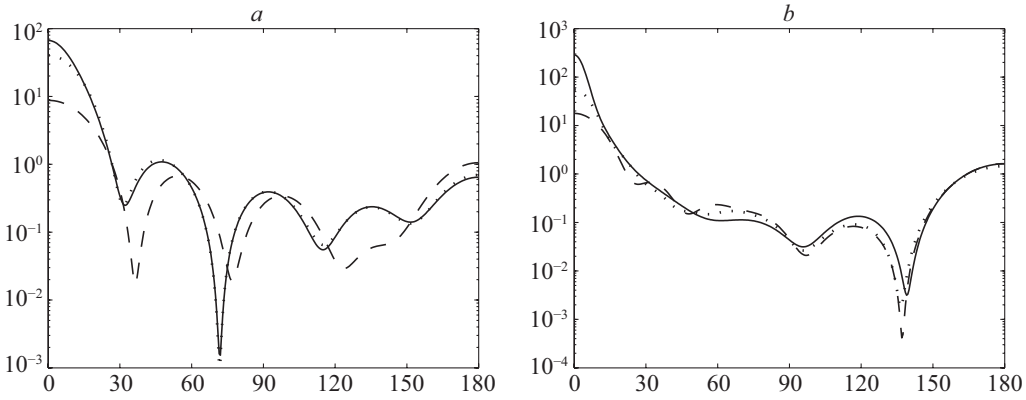

Fig. 2. Elastic e^-—Au DCS in units of a_0^2/sr calculated with present cut off potential at incident energies 300 eV (a) and 1200 eV (b) with values of cut-off radius:
$1a_0$ (dashes); $2a_0$ (dots); lines — without cut off

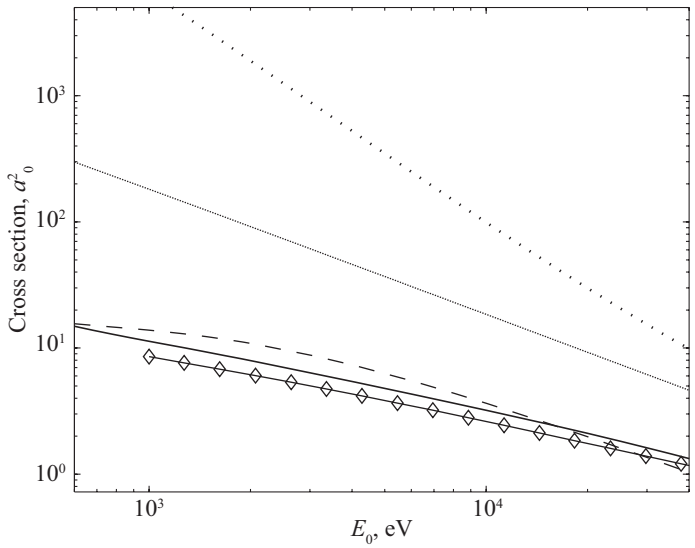

Fig. 3. Integral cross section of e—Au elastic scattering:
line — partial wave calculations with present effective potential; dashes — partial waves calculations with equivalent Yukawa potential; dash-dots and dots — the first and the second Born approximations accordingly with equivalent Yukawa potential; line with rhombuses — relativistic Dirac—Hartree—Fock—Slater PW calculations [19]

for the first and $n = 2$ for the second Born approximation. Note, that the later condition does not contain the parameter α of Yukawa potential.

4. Conclusions. We presented new effective l-dependent potential V_{ELP} for electron—Gold interaction. Our electron—Gold effective potential was been applied to elastic electron scattering problems in broad impact energy interval. Results obtained with presented effective potential are in excellent with other effective potential calculations at energies upper 400 eV. Intervals of validity of semiclassical phase approximation and Born polarization formula for electron — Gold atom scattering was been established. The equiva-

lence of present effective potential, V_{IPM} and V_{DHFS} effective potentials in DCS calculations at $E_0 > 400$ eV was been established.

We concluded that the first and the second Born approximations for electron—Gold cross section calculations at nonrelativistic collision energies are invalid. This result agrees calculations [8].

The elastic scattering of electrons by cut-off effective potential was been examined. Oscillations in DCS were been detected. Ocsillations were neither explained, nor confirmed by other investigations by other authors. Probably oscillations could be explained by the application of a suitable model in future considerations. Of cause, new EPES experiments about electron—Gold surface scattering could be very useful.

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Appendix.

The partial wave method. In scattering cross section calculations we applied the expression for phase shift δ_i, that follows from [15, formula (17)]:

$$\tan\delta_l = \left.\frac{j_l(kr)(\gamma + l/r) - kj_{l-1}(kr)}{n_l(kr)(\gamma + l/r) - kn_{l-1}}\right|_{r=r_{\max}}, \tag{8}$$

$$\gamma = \frac{du_l(r_{\max})}{dr}(u_l(r_{\max}))^{-1},$$

where j_l, n_l are spherical Bessel and Neumann functions, $k = \sqrt{2E_0}$, δ_l is the phase shift. At distances $r \geqslant r_{\max}$ one can neglect values of potentials $V_l^{(a)}$ and $V_{\rm pol}$ relative to the kinetic energy $E_0 = k^2/2$ and orbital term $l(l+1)/(2r^2)$. The number of partial wave was determined form the accuracy of DCS values. We calculated DCS with the accuracy 0.1 %. At sufficiently large E_0 one needs a lot of partial phases. Meanwhile, calculations of phase shifts with formula (8) demand much time and in other hand they become less accurate at large l. To save calculation efforts we applied the semiclassical approximation for phase shifts at large l [16]:

$$\delta_l^{sc} = \int\limits_{R_t}^{r_{\max}} \left[k^2 - \frac{(l+1/2)^2}{r^2} - 2\left(V_l^{(a)}(r) + V_{\rm pc}(r)\right)\right]^{1/2} dr - \delta_{l0}^{sc}, \tag{9}$$

where R_t is the turning point; $r_{\max}$ can be determined from the condition, that at distances $r > r_{\max}$ one can neglect $V_l^{(a)}(r)$ and $V_{\rm pol}(r)$ in (9);

$$\delta_{l0}^{sc} = \int\limits_{(l+1/2)/k}^{r_{\max}} \left[k^2 - \frac{(l+1/2)^2}{r^2}\right]^{1/2} dr.$$

One can obtain:

$$\delta_{l0}^{sc} = (l+1/2)(A - \arctan A),\ A = \left(\frac{kr_{\max}}{(l+1/2)^2} - 1\right)^{1/2}. \tag{10}$$

Numerical calculations at energies 500 and 1000 eV give considerable small differences (less than 10^{-5}) of exact phase shifts (8) from semiclassical these (9) at sufficiently large orbital momentums $l > 10k$.

Analytical Born formula for phase shifts for asymptotic polarization potential. For large orbital momentum l the upper limit $r_{\max}$ in the integral in semiclassical phase (9) is shifted to large r. At sufficiently large r the short range potentials are vanished, polarization — correlation potential can be substituted by the asymptotic expression: $V_{\text{pc}}^{\text{asymp}} = -\alpha_p/(2r^4)$. One can apply the analytical formula for phase shifts for the potential V_p^{asymp} in the first Born approximation [17]:

$$\delta_l^{\text{Born}} = \frac{\pi k^2 \alpha_p}{(2l+3)(2l+1)(2l-1)}. \tag{11}$$

The comparison results of (11) and exact phase shifts (8) at energies 500 and 1000 eV shows that the absolute error in phase calculations with the polarization Born formula (11) is less than 10^{-5} at $l > 17k$.

The Dalitz formula. We applied the Dalitz formula for scattering amplitude by single Yukawa potential $V_{\text{Yuk}} = C\exp(-\alpha r)/r$ in second Born approximation [10]:

$$f_{II}^{(\text{Yuk})}(k,\vartheta) = \frac{2C^2}{kA\sin(\vartheta/2)}\left[\arctan\frac{\alpha k\sin(\vartheta/2)}{A} + \frac{i}{2}\ln\frac{A+2k^2\sin(\vartheta/2)}{A-2k^2\sin(\vartheta/2)}\right],$$

where $A = \alpha^4 + 4\alpha^2 k^2 + 4k^4\sin\vartheta/2$, ϑ is the scattering angle.

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