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ASYMPTOTIC CONTINUUM WAVE FUNCTIONS FOR TWO-CENTER PROBLEM OF QUANTUM MECHANICS

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1 Introduction

In the last few years the investigation of the continuum state of Coulomb three-body problem has been attracting attention of researchers. A simple wave function when all three interparticle distances tend to infinity, first was proposed by P.J. Redmond [1] as sited in L. Rosenberg [2] and R.J. Peterkop [3]. A more general asymptotic continuum wave function has been stated by M. Brauner, J.S. Briggs, H. Klar [4] and S.P. Merkuriev [5]. This function is referred to as 3C, because it is producted of three Coulomb wave functions. In this model, the initial three-body system is splited into two-body subsystems which are uncoupled.

The construction problem of the solution, when the distance between any two particle is small as compared to the distance of the third particle, is considered by E.O. Alt and A.M. Mukhamedzhanov [6]. They have shown that the correct description requires an introduction of a local relative momentum [7]. New additional terms in the wave function were derived recently by Y.E. Kim and A.L. Zubarev [8].

J. Berakder and J.S. Briggs [9] corrected the 3C wave function introducing momentum-dependent Sommerfeld parameters. They used an invariance of the total potential under overall rotation in parabolic- hyperspherical coordinates.

A particular case of the Coulomb three-body problem is a two-center problem of quantum mechanics. This problem is devoted to investigation of the electronic state, moving in the field of two fixed point charges and has lost of applications to molecular scattering, slow atom-ion collision and mesic atom processes.

The two-center problem is separable in spheroidal coordinates and solved further only numerically. However, in this case, the momentum of scattered electron is not defined. It is well known that in the statement of the scattering problem, it is adequate to use the wave functions having the asymptotic momentum $\vec{k}$.

In this paper, we will consider a possibility of finding the asymptotic wave functions with definite momentum for the electron, scattered from the two fixed Coulomb center.

In Sec.2 we construct a 3C-type solution for the two-center problem and show that this solution satisfies Schrödinger equation asymptotically up to the terms of order $O(1/(kr)^2)$. In Sec.3, we calculated the terms of order $O(1/(kr)^2)$ in Schrödinger equation and we modified the 3C-type solution, too. In a point dipole approximation, the slow electron scattering is considered in Sec.4. Conclusions are given in Sec.5.

2 3C-type solution for the two-center problem of quantum mechanics

Let us consider the electron moving in the field of two fixed charges with values Z_1, Z_2 and having a separation R. The coordinates of the two-center problem are shown in Fig.1.

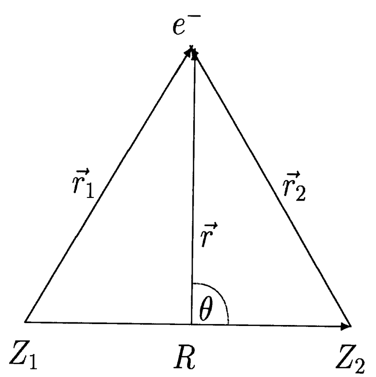


FIG.1.The Fig coordinates as used in the text

The vectors $\vec{r}_1$ and $\vec{r}_2$ refer to the positions of the electron with respect to the centers, while the position from the middle of separation is labeled by $\vec{r}$.

In the atomic units ($e = \hbar = m = 1$) the electronic Hamiltonian has the form

$$H = -\frac{1}{2}\Delta_r - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}. \tag{1}$$

We seek a solution to the Schrödinger equation

$$(H - E)\Psi(\vec{r}) = 0 \tag{2}$$

as a product of the functions

$$\Psi(\vec{r}) = \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2), \tag{3}$$

where

$$\Psi_l(\vec{r}_l) = e^{i\vec{k}\vec{r}_l/2} Q_l(\vec{r}_l) \tag{4}$$

and $\vec{k}$ is the momentum of the electron.

In this case, Eq.(2) converts to the following form:

$$\left[\frac{1}{2}\Delta_1 Q_1 + i\vec{k}\vec{\nabla}_1 Q_1 + \frac{Z_1}{r_1}Q_1 + \frac{(\vec{\nabla}_1 Q_1)\vec{\nabla}_2}{2}\right] Q_2(\vec{r}_2) +$$

$$+\left[\frac{1}{2}\Delta_2 Q_2 + i\vec{k}\vec{\nabla}_2 Q_2 + \frac{Z_2}{r_2}Q_2 + \frac{(\vec{\nabla}_2 Q_2)\vec{\nabla}_1}{2}\right] Q_1(\vec{r}_1) = 0, \tag{5}$$

where $\Delta_l = \Delta_{r_l}$ and $\vec{\nabla}_l = \vec{\nabla}_{r_l}$.

Now we suppose that each expression in the middle bracket is zero, separately. Then

$$\left[\frac{1}{2}\Delta_l Q_l + i\vec{k}\vec{\nabla}_l Q_l + \frac{Z_l}{r_l}Q_l + \frac{(\vec{\nabla}_l Q_l)\vec{\nabla}_n}{2}\right] Q_n(r_n) = 0 \quad l \neq n; \quad l, n = 1, 2. \tag{6}$$

If we neglect the term which contains a product of nabla, then we have an exact solution

$$Q_l(r_l) = F(i\eta_l, 1, i[kr_l - \vec{k}\vec{r}_l]), \tag{7}$$

where $F(i\eta_l, 1, i[kr_l - \vec{k}\vec{r}_l])$ is the Kummer confluent hypergeometric function. In this approximation the solution of Eq.(2) reads

$$\Psi_{\vec{k}}(\vec{r}) = \frac{e^{(i\vec{k}(\vec{r}_1+\vec{r}_2))/2}}{(2\pi)^{\frac{3}{2}}} N_1 N_2 F(i\eta_1, 1, i[kr_1 - \vec{k}\vec{r}_1]) F(i\eta_2, 1, i[kr_2 - \vec{k}\vec{r}_2]). \tag{8}$$

We normalize this function by condition

$$< \Psi_{\vec{k}'}(\bar{r}) | \Psi_{\vec{k}}(\bar{r}) >= \delta(\vec{k} - \vec{k}'), \tag{9}$$

then

$$N_l = e^{\frac{\pi\eta_l}{2}} |\Gamma(1 - i\eta_l)|, \tag{10}$$

in this case $\eta_l = Z_l/k$ is the Sommerfeld parameter.

The expression (8) is just a 3C-type (exactly: 2C-type, because two Coulomb centers have no motion) solution to the two-center problem of quantum mechanics. In the limit $kr \to \infty$ from Eq.(8) we arrive to Redmond asymptotic:

$$\Psi(\vec{r}) \approx e^{i\bar{k}\frac{\bar{r}_1+\bar{r}_2}{2}} e^{-i\eta_1 ln(kr_1 - \overline{kr}_1)} e^{-i\eta_2 ln(kr_2 - \overline{kr}_2)}. \tag{11}$$

The derived solution (8) satisfies the Eq.(6) within the accuracy of order $O\left(\frac{1}{(kr)^2}\right)$. Now, we analyze the term $\nabla Q_l \nabla Q_n$ neglected in (6). Since

$$\vec{\nabla} Q(\bar{r}) = -\eta(k\hat{r} - \vec{k})F(i\eta + 1, 2, i[kr - \bar{k}\bar{r}]) \tag{12}$$

we have at $kr \to \infty$

$$\bar{\nabla} Q(\bar{r}) = \frac{\Gamma(2)}{\Gamma(1-i\eta)} \frac{\eta(\hat{r} - \hat{k})}{i(1-\hat{k}\hat{r})} \frac{e^{-\frac{\pi\eta}{2} - i\eta \ln[kr - \bar{k}\bar{r}]}}{r}\left[1 + O\left(\frac{1}{kr}\right)\right]. \tag{13}$$

From this the neglected terms will write following order

$$(\nabla_1 Q_1)(\nabla Q_2) \sim O\left(\frac{1}{(kr)^2}\right). \tag{14}$$

3 The modified 3C-type solution

Now, we will reconstruct to the solution of Eq.(6) approximately calculating the term $(\nabla Q_l)\nabla Q_n$. For this purpose we replace $(\nabla Q_l)\nabla Q_n$ by asymptotic expression (13). Then Eq.(6) reduces to

$$\frac{1}{2}\Delta_l Q_l + i\vec{k}\vec{\nabla}_l Q_l + k\frac{\eta_l}{r_l}Q_l - \frac{i\eta_n}{2}\frac{\hat{r}_l - \hat{k}}{1 - \hat{r}_l\hat{k}}\frac{\vec{\nabla} Q_l}{r_l} = 0. \tag{15}$$

When we write the fourth term of Eq.(15) we have replaced $\vec{r}_n$ by $\vec{r}_l$. This change has no influence on the terms of order $O\left(\frac{1}{(kr)^2}\right)$ in Eq.(2), because $1/r_n = 1/r_l + O(1/r_l^2)$.

To solve the new equation (15), we introduce a variable

$$x_l = i(kr_l - \vec{k}\vec{r}_l). \tag{16}$$

Then, taking into account

$$\nabla_l Q_l = ik(\hat{r}_l - \hat{k})Q_l',$$
$$\Delta_l Q_l = -\frac{2k^2}{x_l}(1 - \hat{k}\hat{r}_l)Q_l' - 2k^2(1 - \hat{k}\hat{r}_l)Q_l'' \quad , \tag{17}$$

(where the frame denotes the derivative with respect to x_l) we lead to the equation

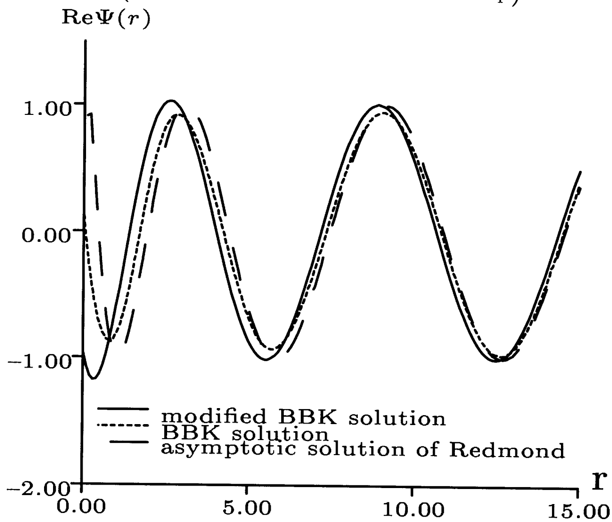
$$x_l Q_l'' + (1 - i\eta_n - x_l)Q_l' - i\eta_l Q_l = 0. \tag{18}$$

The latter equation has the solution

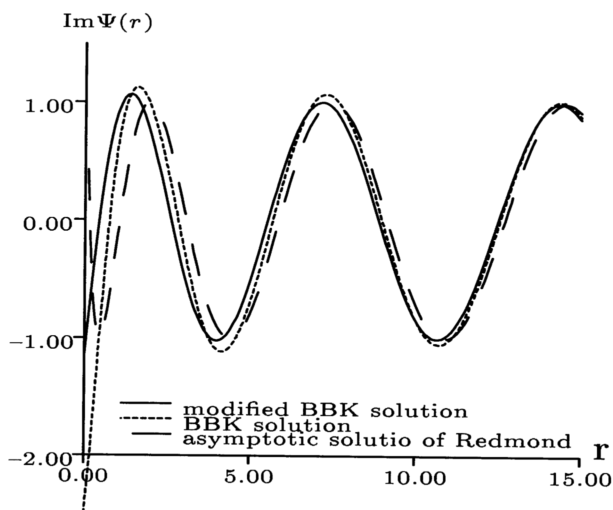
$$Q_l = F(i\eta_l, 1 - i\eta_n, x_l). \tag{19}$$

Fig.2. Comparison of the 3C-type solution, the modified 3C-type solution and the Redmond asymptotic. a). Real parts of solutions. b). Imaginary parts of solutions.

$$\left(Z_1 = 1, Z_2 = 1, |k| = 1, \angle(\overline{k}, \overline{r}) = \tfrac{3\pi}{4}\right)$$



a).



b).

Thus, for the total wave function we have

$$\Psi(\vec{r}) = \frac{e^{i\vec{k}(\vec{r}_1+\vec{r}_2)/2}}{(2\pi)^{\frac{3}{2}}}\tilde{N}_1\tilde{N}_2 F(i\eta_1, 1-i\eta_2, i[kr_1 - \vec{k}\vec{r}_1])F(i\eta_2, 1-i\eta_1, i[kr_2 - \vec{k}\vec{r}_2]). \quad (20)$$

If we normalize this function by the condition (9), then

$$\tilde{N}_l = \left|\frac{\Gamma[1-i(\eta_l+\eta_n)]}{\Gamma(1-i\eta_l)}\right| e^{\frac{\pi\eta_l}{2}}. \quad (21)$$

The modified function (20), as seen from the previous calculation, satisfies the Eq.(2) with accuracy of order $O(\frac{1}{(kr)^3})$. The substantial difference between the function (8) and the function (20) is that in the latter, part of the full function describing the electronic motion relatively to one of the Coulomb center, depends on Sommerfeld parameter of the other center. It is seen that the second argument of confluent hypergeometric function in (20) became 1-$i\eta$ instead of the previous value 1 in (8). Due to this, the normalization constant is changed, too.

Fig.2 compares the real and imaginary parts of the functions (20) ,(8) and Redmond asymptotic with $Z_1 = Z_2 = 1, R = 1$ and $\angle(\vec{r}, \vec{k}) = 135$. The difference between two solutions increases when r is small.

4 Scattering of slow electron

The major deficiency of the solutions obtained above, is no practical application for low electron energies $E = k^2/2$. Therefore, we need to pay particular attention to this case.

Expanding the electron-nuclear interaction in series of $1/r$ and maintaining a dipole term only, we recall to a reduced Schrődinger equation:

$$-\frac{1}{2}\Delta\Psi(\vec{r}) - \left(\frac{Z_1+Z_2}{r} + \frac{(Z_2-Z_1)}{2r^2}R\cos\theta\right)\Psi(\vec{r}) = E\Psi(\vec{r}). \quad (22)$$

Writing the solution as a product

$$\Psi(\vec{r}) = \Psi_1(\vec{r})\Psi_2(\vec{r}) \quad (23)$$

and requiring that $\Psi_1(\vec{r})$ satisfies the equation

$$\frac{1}{2}\Delta\Psi_1(\vec{r}) + \left(\frac{Z_1+Z_2}{r} + E\right)\Psi_1(\vec{r}) = 0, \quad (24)$$

we lead to the following equation for $\Psi_2(\vec{r})$:

$$\Psi_1(\vec{r})\left(\frac{1}{2}\Delta\Psi_2(\vec{r})+\frac{\alpha}{2r^2}\cos\theta\Psi_2(\vec{r})\right)+\nabla\Psi_1(\vec{r})\nabla\Psi_2(\vec{r})=0 \quad , \tag{25}$$

where $\alpha=(Z_2-Z_1)R$.

The solution of Eq.(24) is given by

$$\Psi_1(\vec{r})=N_1e^{i\vec{k}\vec{r}}F\left(i\frac{Z_1+Z_2}{k},1,i(kr-\vec{k}\vec{r})\right) \tag{26}$$

and at a small electron momentum ($k\to 0$) it becomes

$$\Psi_1(\vec{r})\longrightarrow \overline{N}_1e^{i\vec{k}\vec{r}}J_0\left(2\sqrt{(Z_1+Z_2)(r-\hat{k}\vec{r})}\right) \quad ,$$

where $J_0(x)$ a zero order Bessel function.

In an asymptotic region, the function $\Psi_1(\vec{r})$ tends to zero by the low

$$\nabla\Psi_1(\vec{r})\underset{\substack{k\to 0\\ r\to\infty}}{\longrightarrow} O\left(r^{-\frac{3}{4}}\right) \quad . \tag{27}$$

Our goal is to find a solution to Eq.(25) which satisfies the constraint

$$\nabla\Psi_1(\vec{r})\nabla\tilde{\Psi}_2(\vec{r})\underset{\substack{k\to 0\\ r\to\infty}}{\longrightarrow} O\left(\frac{1}{r^\beta}\right), \quad \beta>2 \quad . \tag{28}$$

In this case, one can drop in (25) the term with the product of nabla and arrive to a more simple equation:

$$\Delta\tilde{\Psi}_2(\vec{r})-\frac{\alpha}{r^2}\cos\theta\tilde{\Psi}_2(\vec{r})=0. \tag{29}$$

Equation (29) is separable in spherical coordinates. Choosing the z axis along the dipole moment and putting

$$\tilde{\Psi}_2(\vec{r})=Q(r)\Theta(\mu)e^{im\phi}, \mu=\cos\theta, \tag{30}$$

we obtain two equations

$$\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial\Theta}{\partial\mu}\right)-\alpha\mu\Theta-\frac{m^2}{1-\mu^2}\Theta+\lambda\Theta=0 \tag{31}$$

$$\frac{\partial^2 Q}{\partial r^2}+\frac{2}{r}\frac{\partial Q}{\partial r}-\frac{\lambda}{r^2}Q=0. \tag{32}$$

Here $\lambda = \lambda_l(\alpha)$ is a separation constant and m is an integer.

If we look for solutions to Eq.(31) as a sum of Legendre polynomials

$$\Theta(\mu) = \sum_{l=0}^{\infty} d_l P_l^m(\mu), \tag{33}$$

then the coefficients d_l will be obtained by three-term recursion relations. From this, one can express eigenvalue $\lambda_l(\alpha)$ in terms of itself and the parameter α [8]. It has a discrete infinity of solutions which $l = 0, 1, 2, ...$ (we have already known for $\alpha = 0$: $\lambda_l(\alpha = 0) = l(l+1)$) . Thus, we can write

$$\lambda_l(\alpha) = l(l+1) + g_l(\alpha) \tag{34}$$

and suppose that $g_l(\alpha = 0) = 0$, for all l.

The solution of Eq.(32) bounded at the origin of coordinate system is given by

$$Q(r) = C_1 r^{s_l} \quad , \tag{35}$$

where

$$s_l = \frac{-1 + \sqrt{1 + 4\lambda_l}}{2}. \tag{36}$$

Note that $Re\{s_l\} \geq -0.5$.

Clearly that at R=0 ($\alpha = 0$), our problem reduced to the one center Coulomb continuum problem with unified charge $Z_1 + Z_2$. Therefore, we must require $\tilde{\Psi}_2(\overline{r}) \equiv 1$ in Eq.(35). This condition is fulfilled if $l = 0$ or $\lambda_0 = 0$. So, we need the lowest eigenvalue $\lambda_0(\alpha)$ only. The lowest eigenvalue is computed in [10] as

$$\lambda_0(\alpha) = -\frac{\alpha^2}{6} + \frac{11}{30}\left(\frac{\alpha^2}{6}\right)^2 - \frac{133}{450}\left(\frac{\alpha^2}{6}\right)^3 + \ldots$$

The function $\lambda = \lambda_0(\alpha)$ monotonically decreases with increasing $\alpha \in [0, \infty)$ as it has been shown in [11].

Thus, the solution of (29) is expressed by the sum

$$\tilde{\Psi}_2(\vec{r}, R) = C_1 r^{s_0} \sum_{l=0}^{\infty} d_l P_l(\mu) \tag{37}$$

(for convenience we choose m=0).

Now consider when the constrain (28) be fulfilled. Taking into account

$$\nabla \tilde{\Psi}_2(\overline{r}) \xrightarrow[r \to \infty]{} O\left(r^{s_0 - 1}\right) \tag{38}$$

Fig.3. Wave functions for slow electron scattering.

Dasher line:Solution given by Eq.(41), full line: one center function with

$Z = Z_1 + Z_2$. $\left(Z_1 + Z_2 = 3, \angle(\overline{k}, \overline{r}) = \frac{3\pi}{4}\right)$

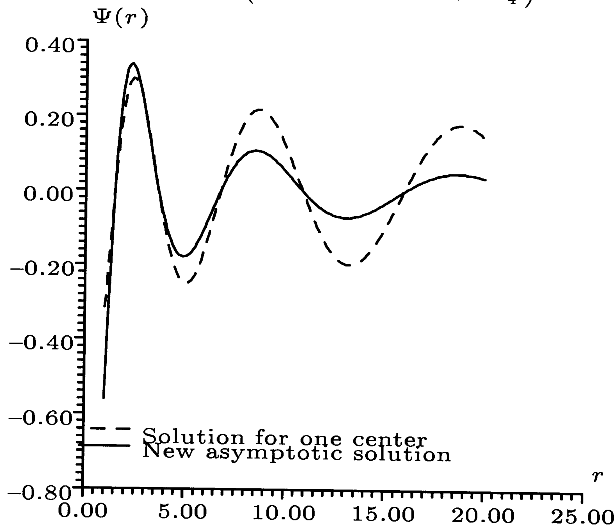


Table 1. The result of critical points ($Z_2 = -Z_1 = 1$).

Our results are shown in the lower lines. [11] results are shown in the upper lines.

	0	1	2	3	4	5	6	7
0	1.278630	7.583936	19.058055	35.724656	57.586409	84.643914	-	
	1.27862975	7.58393585	19.05805466	35.72465595	57.58640912	84.64391432	116.89737351	154.34687274
1	15.093911	28.224229	46.797070	70.670380	99.790199	134.133766	-	-
	15.09391142	28.22422919	46.79707021	70.67037995	99.79019900	134.13376699	173.69011671	218.45337381
2	42.601806	62.603396	88.132519	119.061744	155.311824	196.837449	-	-
	42.60180661	62.60339577	88.13251908	119.06174348	155.31182366	196.83744941	243.61214172	295.61974547
3	83.854611	110.730886	143.172019	181.078418	224.370210	272.991924	-	-
	83.85461430	110.73088570	143.17201864	181.07841765	224.37020975	272.99192390	326.90618101	386.08764044
4	-	-	-	-	-	-	-	-
	138.85677140	172.60811742	211.94395720	256.78710010	307.06533241	362.72148672	423.71277413	490.00766578

and the (27), we see the condition (28) is equal to

$$Re\left\{s_0\right\} < -\frac{1}{4}. \tag{39}$$

It seen from numerical calculation that the last inequality is true if

$$|\alpha| = R|Z_2 - Z_1| > 1.096. \tag{40}$$

Finally, at $k \to 0$ and $\alpha > 1.096$ the asymptotic solution to the two-center problem which includes the terms of order $O(1/r^{\beta})$ ($\beta > 2$), in Schrödinger equation is given by

$$\Psi(\vec{r}) = N_1 e^{i\vec{k}\vec{r}} J_0 \left(2\sqrt{(Z_1+Z_2)(r-\hat{k}\vec{r})}\right) r^{so} \sum_{l=0}^{N} d_l P_l(cos\theta), \tag{41}$$

where N is a cut off number of asymptotic series in (37).

The constraint (40) is not fulfilled if $Z_1 = Z_2$. But in this case according to (22) and (24) we have

$$\Psi(\vec{r}) = N_1 e^{i\vec{k}\vec{r}} J_0 \left(2\sqrt{(Z_1+Z_2)(r-\hat{k}\vec{r})}\right). \tag{42}$$

In an other particular case, when $Z_1 + Z_2 = 0$, the low energy scattering wave function reads

$$\Psi(\vec{r}) = N_1 e^{i\vec{k}\vec{r}} r^{so} \sum_{l=0}^{N} d_l P_l(cos\theta). \tag{43}$$

Now let us compare the last expression with the Redmond asymptotic wave function given by Eq.(11). At $Z_1 + Z_2 = 0$ or $\eta_1 + \eta_2 = 0$. The Redmond wave function reduces transfers to a plane wave. Thus, there are two major differences between our Eq.(43) and the Redmond asymptotic wave function. First, our function contains the additional product r^s and secondly, has a certain angle dependence expressed by the sum or Legendre polynomials. See the comparison between the results of the one center wave function and the new wave function in Fig. 2.

We have calculated the critical points of Eq. (31) and used the continued fraction for the parameter α. See the results of the critical points in Table 1.

5 Conclusion

A 3C-type solution to the two-center problem of quantum mechanics is derived. We have shown that this function satisfies the Schrödinger equation asymptotically up to terms of order $O(1/(kr)^2)$.

By calculating all the terms of order $O(1/(kr)^2)$ in Schrödinger equation, the 3C-type solution is modified. A substantial feature of the modified solution is that part of the total wave function, which describes the electronic motion relatively to one of the Coulomb center, also depends on the Sommerfeld parameter of an other center. So, in this approximation, a correlation between two Coulomb subsystems is somewhat accounted.

The series type asymptotic solution for the slow electron scattering is found. These solutions satisfy the Schrödinger equation with accuracy $O(1/r^3)$. In the asymptotic region $r \to \infty$, the obtained solutions differ both from the Redmond wave function and from the one-center Coulomb continuum function with unified charge $Z = Z_1 + Z_2$.

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Чулуунбаатар О., Цоохуу Х. E11-2000-240

Волновые функции с асимптотическим континуумом для двухцентровой задачи квантовой механики

Асимптотические (r-большое) решения строятся для состояния континуума электрона, движущегося в области двух фиксированных кулоновских центров. Решения типа 3С получены для задачи двух центров квантовой механики. При приближенном вычислении члены порядка $O(1/(kr)^2)$ в уравнении Шредингера и решения типа 3С модифицируются. Отличительная черта модифицированного решения — это то, что волновая функция, которая описывает электронное движение относительно одного из кулоновских центров, также зависит от параметра Зоммерфельда другого центра.

В точечной дипольной аппроксимации асимптотические волновые функции получаются для медленного электронного рассеяния. Показано, что в конкретном случае $Z_1 + Z_2 = 0$ эта функция отличается от редмондского асимптотического члена r^s, где $Re\{s\} \geq -0{,}5$.

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Asymptotic Continuum Wave Functions for Two-Center Problem of Quantum Mechanics

Asymptotic (large-r) solutions are constructed for the continuum state of the electron moving in the field of two fixed Coulomb centres. A 3C-type solution is derived for a two-center problem of quantum mechanics. When calculating approximately, the terms of order $O(1/(kr)^2)$ in Schrödinger equation and the 3C-type solution are modified. The essential feature of the modified solution is that the wave function describing the electronic motion relatively to one of the Coulomb center, also depends on the Sommerfeld parameter of an other center.

In the point dipole approximation, the asymptotic wave functions are obtained for slow electron scattering. It is shown that in the particular case $Z_1 + Z_2 = 0$ this function differs from the Redmond asymptotic by a product r^s, where $Re\{s\} \geq -0.5$.

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