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SEMICLASSICAL LONG-RANGE BEHAVIOUR OF HARTREE-FOCK ORBITALS

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A b s t r a c t

Semiclassical solutions of one-dimensional inhomogeneous Schrödinger and Dirac equations are obtained. Using these solutions, the asymptotic behaviour of the Hartree-Fock and Hartree-Fock-Dirac orbitals is found. The asymptotic solution in atom coincides, within the accuracy of a few per cent, with the numerical solution in the region after the classic turning point. Two questions concerning the influence of the exchange interaction are discussed: 1) the change of the long-range behaviour of wave functions, 2) the violation of the oscillation theorem (additional nodes).

It have been shown (Handy and Marron 1969, Handler and Smith 1980) the Hartree-Fock atomic orbitals at large r to behave like $exp(-\frac{1}{\hbar}\sqrt{2m|E|}\,r)$, where E is the highest occupied orbital energy. Such a behaviour of the wave function takes place only within the range which is an asymptotic one for all atomic electrons, i.e. at $r > a_{out}$, where a_{out} is the outer electron orbit radius. In this paper we have found the semiclassical asymptotic solution of the Hartree-Fock equation which is also applicable in intermediate range $r > a_{in}$. Here a_{in} is the orbit radius of the inner electron whose wave function we try to find.

Consider first the one-dimensional inhomogeneous Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + (U - E)\right]\varphi(x) = F(x) \qquad (1)$$

Suppose that the semiclassical conditions

$$\left|\frac{d\lambda}{dx}\right| \ll 1\,, \quad \left|\frac{\lambda}{F}\frac{dF}{dx}\right| \ll 1\,, \qquad (2)$$

where

$$\lambda = \frac{\hbar}{P(x)}\,, \quad |P(x)| = \sqrt{2m|E-U|}$$

are satisfied. A solution of equation (1) is a sum of a free solution of the homogeneous equation and the induced solution:

$$\varphi = \varphi_{ind} + \varphi_{fr} \qquad (3)$$

Consider, for example, a classically forbidden region where $P(x) = \sqrt{2m(U-E)}$. Here the free solution is of the form:

$$\varphi_{fr} = \frac{const}{\sqrt{P}}\, e^{\pm\frac{1}{\hbar}\int P\,dx} \qquad (4)$$

Condition (2) implies that the function $F(x)$ varies not so rapidly as the solution of the homogeneous equation. Therefore, we can find a slowly varied induced solution in the zero approximation by neglecting the derivatives in (1), i.e.

$$\varphi_0 = \frac{F(x)}{U(x)-E} \qquad (5)$$

Then equation (1) can be written as follows:

$$\varphi_{ind} = \varphi_0 + \frac{\hbar^2}{2m(U-E)}\frac{d^2}{dx^2}\varphi_{ind} \qquad (6)$$

This equation can be solved by the iteration method. The result of iterations is also representable as a series

$$\varphi_{ind} = \left(1 - \frac{\hbar^2}{2m(U-E)}\frac{d^2}{dx^2}\right)^{-1}\varphi_0 = \varphi_0 + \frac{\hbar^2}{2m(U-E)}\frac{d^2}{dx^2}\varphi_0 + \cdots \qquad (7)$$

Similarly one can find the solution of the inhomogeneous radial Dirac equation ($\hbar = C = 1$)

$$\left(-\frac{d}{d\tau} + A\right)\begin{pmatrix} f \\ g \end{pmatrix} = \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} \qquad (8)$$

where the matrix A is

$$A = \begin{pmatrix} -\frac{\varkappa}{\tau} & E + 2m - U \\ -E + U & \frac{\varkappa}{\tau} \end{pmatrix}$$

If the semiclassical conditions are satisfied, one obtains

$$\begin{pmatrix} f \\ g \end{pmatrix}_{ind} = \left(1 - A^{-1}\frac{d}{d\tau}\right)^{-1}\begin{pmatrix} f_0 \\ g_0 \end{pmatrix} = \begin{pmatrix} f_0 \\ g_0 \end{pmatrix} + A^{-1}\frac{d}{d\tau}\begin{pmatrix} f_0 \\ g_0 \end{pmatrix} + \cdots \qquad (9)$$

where

$$\begin{pmatrix} f_0 \\ g_0 \end{pmatrix} = A^{-1}\begin{pmatrix} F_1 \\ F_2 \end{pmatrix}$$

It is necessary to point out that in the cases of interest the series (7) and (9) turn out to be asymptotic ones. In view of this, in the following we shall use two or three first terms only.

Let us now proceed to the asymptotic of the solution $X_i(\tau) = \tau \cdot \varphi_i(\tau)$ of the radial Hartree-Fock equation:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{d\tau^2} + (U_{eff} - E_i)\right]X_i(\tau) = K_i(\tau) \qquad (10)$$

$$U_{eff} = U + \frac{\hbar^2 \ell(\ell+1)}{2m\tau^2},$$

$K_i(\tau)$ is the exchange contribution. Within the range $\tau > a_i$ (a_i is the classic turning point) $X_i(\tau)$ strongly vanishes and the main contribution to the exchange integrals comes from the sphere $\tau \leq a_i$. Thus, at $\tau \gg a_i$, $K_i(\tau)$ is practically independent of the values of $X_i(\tau)$ in this region and equation (10) is similar to equation (1). Let us show that at $\tau > a_i$ the conditions (2) are satisfied, too. U_{eff} in atoms rapidly decreases with increasing τ. Therefore,

$|E_i| \gg |U_{eff}|$ and $\frac{d\lambda}{d\tau} \ll 1$. $K_i(\tau)$ is the sum of the integrals

$$C_{n\kappa}X_n(\tau)\left[\frac{1}{\tau^{k+1}}\int_0^\tau y^k X_n(y)X_i(y)\,dy + \tau^k\int_\tau^\infty \frac{1}{y^{k+1}}X_n(y)X_i(y)\,dy\right] \qquad (11)$$

where $C_{n\kappa}$ are standard (angular momentum dependent) coefficients in the exchange term. If $\tau \gg a_i$, the second term can be neglected and the exchange integral (11) takes the form

$$C_{n\kappa}\,b_{n\kappa}\cdot\frac{X_n(\tau)}{\tau^{k+1}} \qquad (12)$$

where $b_{n\kappa} = \int_0^\infty y^k X_n(y)X_i(y)\,dy$. If $\kappa = 0$ $b_{n\kappa} = 0$ due to the orthogonality of radial wave functions with the same angular momentum. So, the minimal κ equals 1.

If $\tau \gg a_i$, the wave functions with $|E_n| \geq |E_i|$ are very small and the terms with $|E_n| < |E_i|$ in $K_i(\tau)$ are the only nonvanishing terms. The behaviour of $X_n(\tau)$ determines the variation rate of expression (12). Therefore, the ratio of the second term to the first one in (7) is about $(E_n - U_{eff})/(E_i - U_{eff})$. As it has been noted above, $|U_{eff}| \ll E_i$. Hence, the accuracy of expression (7) is determined by the ratio $E_n/E_i < 1$.

Thus, the asymptotic solution of the Hartree-Fock equation is ($e = 1$)

$$X_i(\tau) = \frac{A}{\sqrt{p}}\,e^{-\frac{1}{\hbar}\int_{a_i}^{\tau} p\,dx} + \left(1 - \frac{\hbar^2}{2m(U_{eff}-E_i)}\frac{d^2}{d\tau^2}\right)^{-1}\frac{K_i(\tau)}{U_{eff}-E_i} \qquad (13)$$

$$K_i(\tau) = \sum_{k\geq 1,n} C_{n\kappa}\,b_{n\kappa}\,\frac{X_n(\tau)}{\tau^{k+1}}$$

The constant in the free solution can be determined by comparison of Fq. (13) with a computational solution of exact Hartree-Fock equation. For a rough estimation of this constant one can use the expression (Gol'dman and Krivchenkov 1957)

$$A = \sqrt{\frac{1}{2\pi}\frac{m}{\hbar}\frac{dE_n}{dn}} \qquad (14)$$

where E_n is the energy, n is the principal quantum number.

As has already been pointed out, the first term in (13) vanishes more strongly than the second. But usually the exchange interaction is small enough compared to U_{eff}. Therefore, the free and induced solutions become comparable only at the

distances where the typical relation $E_n/E_i \ll 1$. Thus, the accuracy of the expression (13) is about a few per cent even if we use only two terms in the expansion of induced solution. For heavy atoms the Hartree-Fock-Dirac equation should be used instead of the Hartree-Fock equation. In this case, one can repeat all the arguments with no important changes. Note only that for the Dirac equation every two terms in the series (9) correspond to one term in (7). In practice, at $\tau > a_i$ it is more convenient to use the Schrödinger-type equation which can be obtained from the Dirac one if $U_{eff} \ll mc^2$:

$$-\frac{\hbar^2}{2m+\frac{E_i}{c^2}}\frac{d^2}{d\tau^2}f_i + \frac{\hbar^2\varkappa(\varkappa+1)}{(2m+\frac{E_i}{c^2})\tau^2}f_i + (U-E_i)f_i = K_i \qquad (15)$$

$$g_i = \frac{\hbar}{c}\,\frac{\frac{d}{d\tau}f_i + \frac{\varkappa}{\tau}f_i}{2m+\frac{E_i}{c^2}}$$

To estimate an accuracy of the asymptotic expressions, we have compared the asymptotic wave functions with the numerical solutions of the Hartree-Fock equations for the $1S_{\frac{1}{2}}^2 2P_{\frac{1}{2}}^2$ configuration of Be and of the Hartree-Fock-Dirac equations for the ion C_s^+ ground state. Figure 1 shows the ratio of asymptotic solution to exact one for the 1S orbital in the $1S_{\frac{1}{2}}^2 2P_{\frac{1}{2}}^2$ Be configuration for the zeroth approximation and after the first iteration in (6). In both cases the accuracy is the same as it is expected, i.e. $E_2/E_1 \approx 0{,}04$ and $(E_2/E_1)^2 \approx 0{,}0016$. In C_s^+ the accuracy is about a few per cent for all orbitals after the first iteration.

As known, the additional nodes occur sometimes in Hartree--Fock orbitals in the asymptotic range (see e.g. Froese Fischer, 1977). The appearance of these nodes is easy to understand using the asymptotic solution obtained in this paper. Let us, for example, discuss 1S orbital of $1S_{\frac{1}{2}}^2 3P_{\frac{1}{2}}^2$ Be configuration. The 3P wave function has a node at $\tau \approx 3a_B$ (a_B - Bohr radius). Therefore, the induced solution for 1S changes the sign near this point, too. But at $\tau = 3a_B$ the free solution for 1S is larger than the induced one. The node of 1S orbital occurs only at $\tau \approx 4a_B$, where the free solution becomes equal to the induced one. The functions 1S and 3P are shown in Fig. 2. The exchange interaction with 3P electron leads also

to the appearance of the first node in the 1S orbital in C_s^+ ground state. As is shown in Fig. 3, the total number of nodes of this function is equal to three.

Of course, these additional nodes are in the region where the wave function is very small. Therefore, the contribution of this tail of function to the matrix elements of physical operators is usually negligible.

If the radius is larger than the size of atom, there is only one nonvanishing term in expression (13), i.e. $\chi = const \cdot \tau^{\rho} \cdot exp(-\frac{1}{\hbar}\sqrt{2m|E_n|}\,\tau)$, where the E_n is the energy of the outer electron. The value of ρ is the same as in paper by Handler and Smith (1980).

Interesting results can be obtained for the asymptotic behaviour of the wave function of an inner electron in the atom placed into a crystal. The wave function of the electron from the conduction band does not vanishes at large distances. In the weak coupling approximation this function equals $\frac{1}{\sqrt{V}}exp(i\vec{K}\vec{\tau})$. Therefore, due to the exchange interaction, the wave function of inner electron vanishes only as a power of τ

$$\varphi(\tau) \sim \frac{\sin(K_0\tau) - (K_0\tau)\cos(K_0\tau)}{\tau^5}\,, \qquad (16)$$

where the K_0 is the Fermi momentum.

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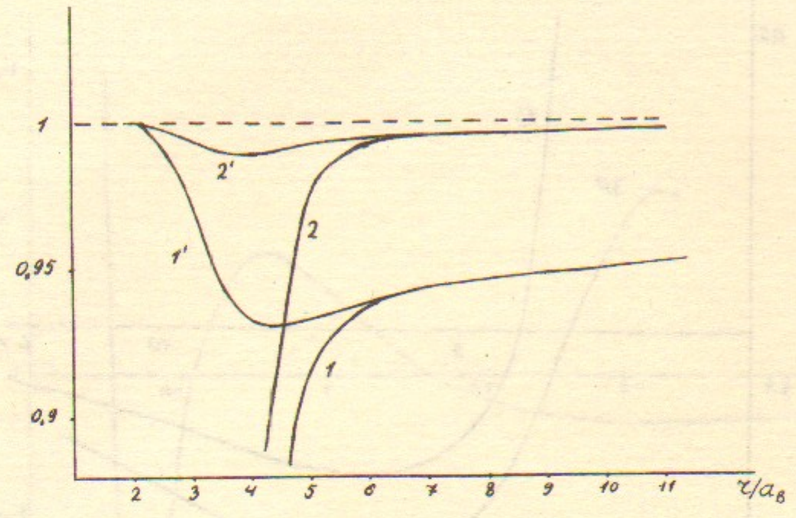

Fig. 1. Induced solutions for the zeroth (curve 1) and first (curve 2) approximation divided by the exact solution. Curve 1' and 2' are corresponding functions including the free solutions.

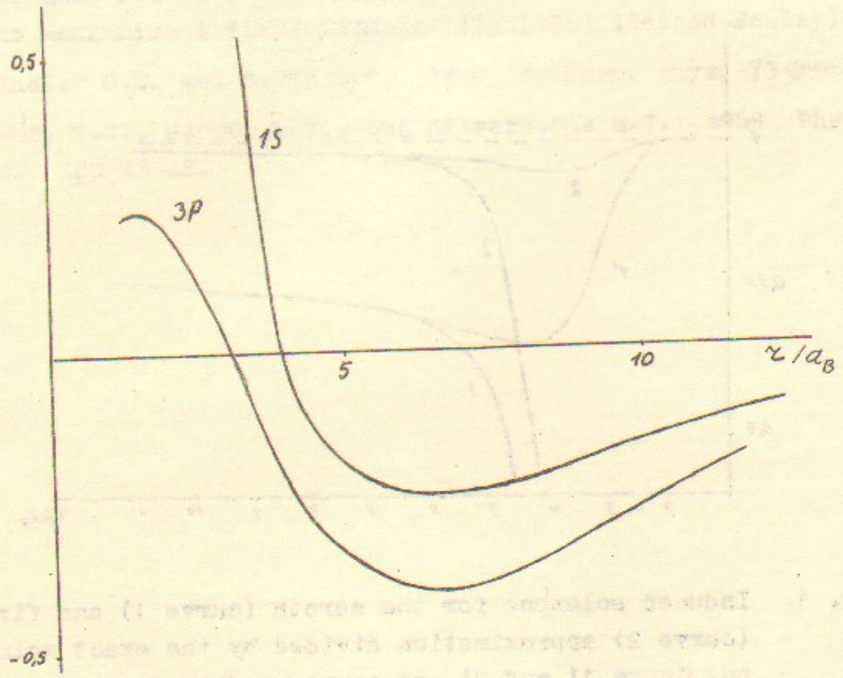

Fig. 2. The $1S_{1/2}$ orbital multiplied by the $10^2 \cdot (r/a_B)^2$ and $3P_{1/2}$ orbital in the $1S^2_{1/2}\ 3P^2_{1/2}$ Be.

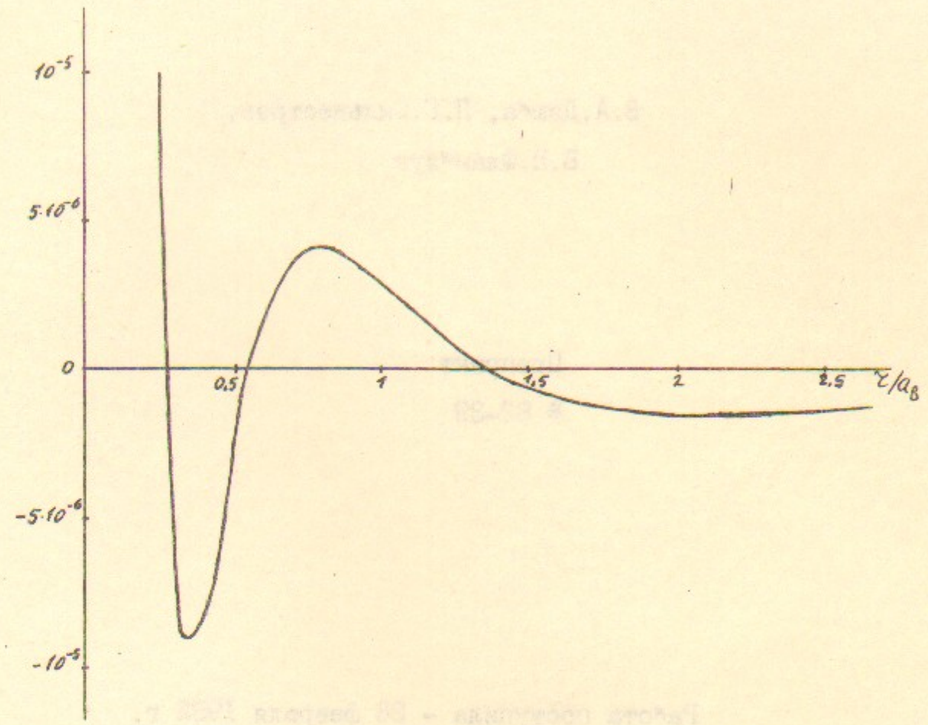

Fig. 3. The 1S orbital of C_s^+ ground state multiplied by the $(r/a_B)^2$.

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