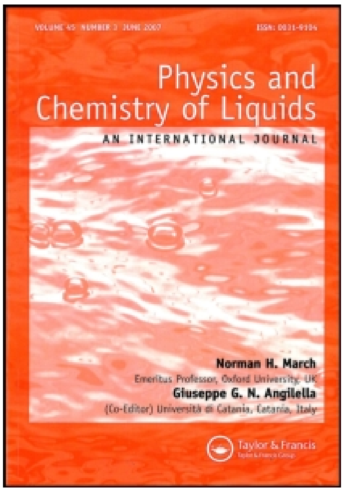

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Relativistic Correction to the Electronic Charge Density of an Atom Embedded in Jellium

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A relativistic correction to the electronic charge density of an atom embedded in jellium is investigated within the framework of a relativistic Thomas–Fermi theory. A numerical solution is obtained by successive approximation for Li, Rb and Hg atoms. The relativistic correction for a heavy atom in jellium is found to be significant not only in the vicinity of the nucleus but also at greater distances from it.

1 INTRODUCTION

The electronic states of an atom embedded in solid and liquid metals have recently been the subject of an extensive study by the density functional formalism. In such study, host metals are usually replaced by jellium[1,2] for simplicity, or by an effective medium in which the electron potential is averaged spherically around the nucleus of an embedded atom.[3,4,5] The latter method, called as a spherical-solid model, has recently been generalized so as to apply to an impurity ion dissolved in a simple liquid.[5]

An investigation of the electronic states of an atom embedded in jellium or effective medium can serve also as a first step towards a better, quantitative understanding of various physical properties of rather complicated solid and liquid alloys which have recently been revealed to show an interesting metal–nonmetal transition, such as Cs-Au, Mg-Bi and Li-Pb alloys. Since such alloys are composed of very heavy elements, it is essential to take into account the relativistic effect on the electronic states of an embedded atom. As far as we know, however, no work has been published on it, though the relativistic effect has been studied on an isolated atom or ion in the Thomas–Fermi approximation[6,7] and in the Hartree–Fock–Slater approximation.[8,9]

In this paper, we investigate the relativistic effect on the electronic charge density around an atom embedded in jellium within the framework of a relativistic Thomas–Fermi approximation. As a result, we consider that we can understand qualitative feature of the relativistic effect in this simple model, and that results are useful as a proper reference for our next, more elaborate calculation of the electronic and the transport properties using the density function formalism.

2 FORMALISM

2.1 Model

We consider the jellium model of metals, where the ions are thought to form a uniform positive background of charge and the valence electrons are treated as an electron gas. Furthermore, we make a vacancy, which is a spherical hole in the positive background, and embed an atom at the centre of the vacancy. We denote the positive and the electronic charge densities by $\rho_+(\mathbf{r}) = en_+(\mathbf{r})$ and $\rho_e(\mathbf{r}) = -en_e(\mathbf{r})$, respectively, where $n_+(\mathbf{r})$ and $n_e(\mathbf{r})$ are corresponding number densities. In our model, there are three parameters: Z_A; an atomic number of the embedded atom, Z; the valency of the host metal and $n_0(=\frac{3}{4}\pi^{-1}(r_s a_0)^{-3}$, a_0 being the Bohr radius); the number density of the uniform background. In terms of these parameters, the positive number density of our model is given by

$$n_+(\mathbf{r}) = n_0 \theta(r - R_{\mathrm{WS}}) + Z_A \delta(\mathbf{r}), \tag{1}$$

where $\theta(r)$ is the step function and R_{WS} is the Wigner–Seitz radius satisfying the condition

$$\tfrac{4}{3}\pi R_{\mathrm{WS}}^3 n_0 = Z. \tag{2}$$

2.2 Thomas–Fermi theory

The total charge density must satisfy the Poisson equation

$$\nabla^2 \phi(\mathbf{r}) = -4\pi(\rho_+(\mathbf{r}) + \rho_e(\mathbf{r})) = -4\pi e(n_+(\mathbf{r}) - n_e(\mathbf{r})), \tag{3}$$

where $\phi(\mathbf{r})$ is the electrostatic potential. In the Thomas–Fermi theory, the electronic number density is expressed in terms of the electrostatic potential as follows:

$$n_e(\mathbf{r}) = n_0\left(1 + \frac{e}{\mu}\phi(\mathbf{r})\right)^{3/2}. \tag{4}$$

Equation (4) is derived from the expression for the chemical potential

$$\mu = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2 k_F^2(\mathbf{r})}{2m} - e\phi(\mathbf{r}), \tag{5}$$

together with the relations $k_F = (3\pi^2 n_0)^{1/3}$ and $k_F(\mathbf{r}) = (3\pi^2 n_e(\mathbf{r}))^{1/3}$. By substituting Eq. (4) into Eq. (3), we obtain the Thomas–Fermi equation for the electrostatic potential as

$$\nabla^2\phi(\mathbf{r}) = -4\pi e\left\{n_+(\mathbf{r}) - n_0\left(1 + \frac{e}{\mu}\phi(\mathbf{r})\right)^{3/2}\right\}. \tag{6}$$

We have solved this nonlinear differential equation by the successive approximation, which proved to be an effectual method for the vacancy problem.[10] The recursive solution is given for the i-th iteration by

$$\begin{aligned} f^{(i+1)}(r) = e^{-kr} &+ \frac{1}{2k}\int_0^\infty \mathrm{d}r'(e^{-k(r+r')} - e^{-k|r-r'|}) \\ &\times \left\{\frac{4\pi}{Z_A} r'(n_e^{(i)}(r') - n_0\,\theta(r' - R_{\mathrm{WS}})) - k^2 f^{(i)}(r')\right\}, \end{aligned} \tag{7}$$

where

$$f(r) = \frac{r}{Z_A e}\phi(r). \tag{8}$$

Following Arponen *et al.*[10] we equate k to the Thomas–Fermi inverse screening length: $k = (4k_F/\pi a_0)^{1/2}$. Here both charge density and potential are assumed to be spherically symmetric with respect to the nucleus of the embedded atom. As the initial spatial form of $\phi(r)$ for a self-consistent iteration procedure, we use Latter's interpolation formula.[11] We find that the self-consistent calculation is quite stable and the convergence is fast.

2.3 Relativistic Thomas–Fermi theory

Following the method of Vallarta and Rosen,[6] we replace the kinetic energy term in Eq. (5) by the relativistic expression. Then, the chemical potential is given by

$$\mu = (c^2\hbar^2 k_F^2(\mathbf{r}) + m^2c^4)^{1/2} - mc^2 - e\phi^R(\mathbf{r}), \tag{9}$$

where the superscript R stands for the quantities in the relativistic Thomas–Fermi theory. With the relation $k_F(\mathbf{r}) = (3\pi^2 n_e^R(\mathbf{r}))^{1/3}$, we obtain the relativistic electronic number density as

$$n_e^R(\mathbf{r}) = n_0\left(1 + \frac{e}{\mu}\phi^R(\mathbf{r})\right)^{3/2}\left[1 + \frac{\mu}{2mc^2}\left(1 + \frac{e}{\mu}\phi^R(\mathbf{r})\right)\right]^{3/2}. \tag{10}$$

The second term in the square bracket is the relativistic correction. As is seen from Eq. (9), the relativistic effect in the Thomas–Fermi theory means the relativistic variation of mass with velocity. It is known that $n_e^R(\mathbf{r})$ cannot be normalised because $n_e^R(r)$ is proportional to r^{-3} when r approaches zero. This difficulty can be avoided by introducing the finite size of the nucleus as pointed out by March.[7] For this purpose we change the lower limit of the integration in the recursive solution from zero to r_c, where r_c is the effective radius of nucleus and we use the well-known relation $r_c = r_0 A^{1/3}$, $r_0 = 1.1 \times 10^{-13}$ cm and A being the mass number.

By putting Eq. (10) into the Poisson equation

$$\nabla^2\phi^R(\mathbf{r}) = -4\pi e(n_+(\mathbf{r}) - n_e^R(\mathbf{r})), \tag{11}$$

we can obtain the relativistic Thomas–Fermi equation for the electrostatic potential as

$$\nabla^2\phi^R(\mathbf{r}) = -4\pi e\left\{n_+(\mathbf{r}) - n_0\left(1 + \frac{e}{\mu}\phi^R(\mathbf{r})\right)^{3/2}\left[1 + \frac{\mu}{2mc^2}\left(1 + \frac{e}{\mu}\phi^R(\mathbf{r})\right)\right]^{3/2}\right\}. \tag{12}$$

We have solved this relativistic Thomas–Fermi equation numerically by the same method as that employed to solve the non-relativistic Thomas–Fermi equation, Eq. (6). For an isolated neutral atom, i.e. $n_+(\mathbf{r}) = Z_A\,\delta(\mathbf{r})$, Vallarta and Rosen[6] solved the relativistic Thomas–Fermi equation by a first-order perturbation method, while we do not rely on a perturbation theory but determine the solution in a fully self-consistent manner.

3 NUMERICAL RESULTS AND DISCUSSIONS

We choose the parameters characterising the jellium as follows, $Z = 3$ and $r_s = 2.5$, which can be considered as an average polyvalent metal. As for the embedded atom, we choose the three atoms, i.e. Li($Z_A = 3$), Rb($Z_A = 37$) and Hg($Z_A = 80$), which correspond, respectively, to the atoms with small, intermediate and large atomic numbers, because we want to investigate the dependence of the relativistic effect on the atomic number. The values

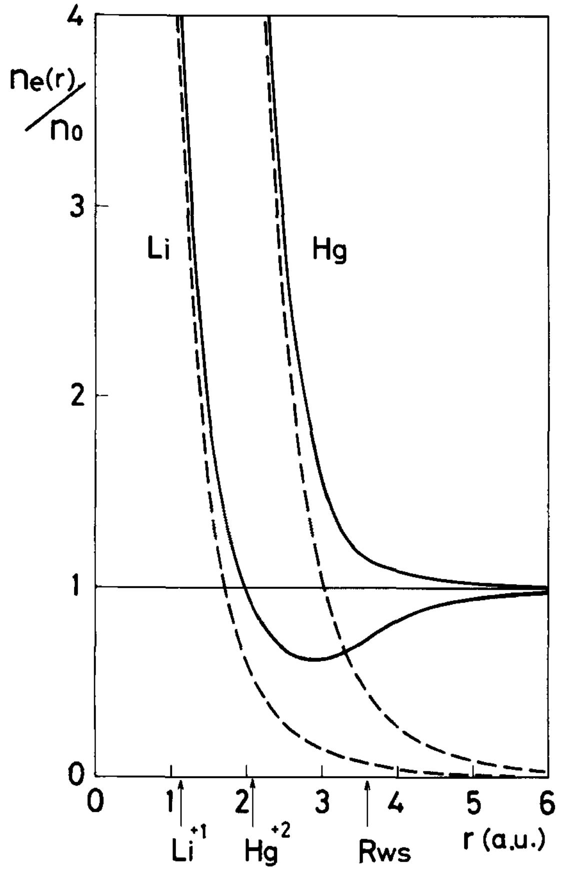

FIGURE 1 The non-relativistic Thomas–Fermi electronic number densities of the isolated neutral Li and Hg atoms (broken curves) and of those embedded in jellium (solid curves). The Wigner–Seitz radius R_{WS} (3.606 a.u.) and the Pauling ionic radii of Li^{+1} (1.13 a.u.) and Hg^{+2} (2.08 a.u.) are shown by arrows.

of r_c of Li, Rb and Hg atoms are 3.96×10^{-5}, 9.16×10^{-5} and 1.22×10^{-4} a.u., respectively. We use the atomic units in the following.

Figure 1 shows the non-relativistic Thomas–Fermi electronic number densities of the isolated Li and Hg atoms and of those embedded in the jellium. The Wigner–Seitz radius defined by Eq. (2) and the Pauling ionic radii[12] of Li^{+1} and Hg^{+2} are also shown by arrows. The number densities of the isolated and the embedded atoms are very similar inside the Pauling ionic radii and are quite different outside them. This result shows that the electronic states of the ionic cores of the isolated atoms change very little when they are embedded in the jellium. The different behaviours at large

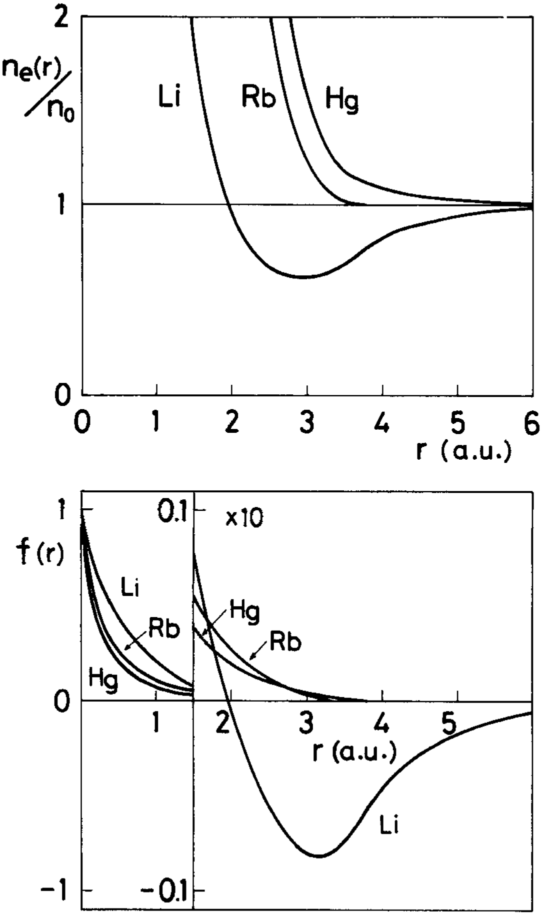

FIGURE 2 (a) The non-relativistic Thomas–Fermi electronic number densities of Li, Rb and Hg atoms embedded in jellium. (b) The function $f(r)$ related to the electrostatic potential by $f(r) = r\phi(r)/Z_A e$ for Li, Rb and Hg atoms.

distances originate from the different boundary conditions, i.e. when r increases $n_e(r)$ approaches zero for the isolated atom and n_0 for the embedded atom.

To examine the correlation between the electronic number density and the electrostatic potential for the embedded atom, we show, for Li, Rb and Hg atoms, the non-relativistic Thomas–Fermi electronic number densities in Figure 2(a) and the function $f(r)$ defined by Eq. (8) in Figure 2(b). The boundary conditions for $f(r)$ are: $f(r) \to 1$ when $r \to 0$ and $f(r) \to 0$ when $r \to \infty$. Physically speaking, the positive $f(r)$ corresponds to the attractive potential and the negative $f(r)$ to the repulsive potential for the electrons. Since the ionic radius of Li^{+1} is much smaller than R_{WS} and there are only three electrons in Li atom, there appears a repulsive-potential region for Li atom, where the electronic number density is less than that of the uniform background. In the small r region, the attractive force decreases as the atomic number increases, which is due to the screening effect. For larger r, the $f(r)$ for Hg has longer tail than that for Rb, corresponding to the longer tail of $n_e(r)$ of Hg atom.

To investigate the relativistic effect on the electronic number density and its dependence on the atomic number, we show in Figure 3 the ratios of the relativistic electronic number densities to the non-relativistic ones, $n_e^R(r)/n_e(r)$, for Li, Rb and Hg atoms. The characteristic features seen from Figure 3 are as follows:

i) The electronic number density increases in the vicinity of the nucleus due to the relativistic effect and becomes smaller than the non-relativistic one at larger distances, which results from the conservation of the number of electrons.

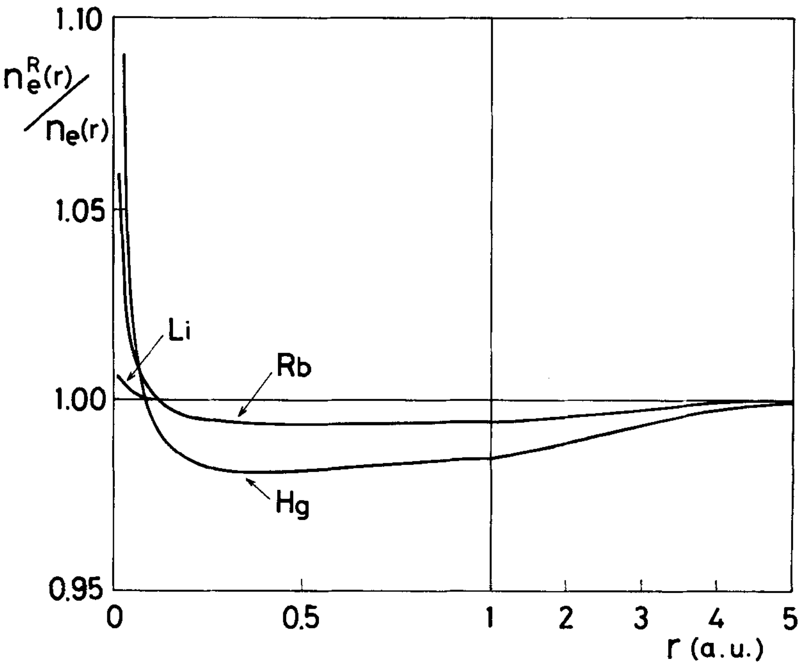

FIGURE 3 The ratio of the relativistic Thomas-Fermi electronic number densities of Li, Rb and Hg atoms embedded in jellium to the non-relativistic ones.

ii) The distance from the nucleus, where the ratio is extremely greater than unity, increases in proportion to the atomic number. This can be also derived from Eq. (10). Since $\mu/2mc^2 = \alpha^2 k_F^2/4 \ll 1$ (where $\alpha = 1/137.037$) in our model, the relativistic correction, i.e. the second term in the square bracket of Eq. (10), is negligibly small unless $|(e/\mu)\phi^R(r)| \gg 1$. Therefore the relativistic correction to the electronic number density is appreciable unless $(\mu/2mc^2) \times (e\phi^R(r)/\mu) \ll 1$, i.e. roughly speaking $r \gg Z_A/37558$.

iii) The larger the atomic number is, the slower the ratio approaches unity. This means that, for heavy atoms embedded in jellium, the relativistic correction to the electronic number density is important not only in the vicinity of the nucleus but also at larger distances from it.

To compare the result of our fully self-consistent method with that of a first-order perturbation method due to Vallarta and Rosen,[6] we show in Figure 4 the ratio $n_e^R(r)/n_e(r)$ for the isolated Hg atom calculated by both methods. In the vicinity of the nucleus, the relativistic correction to $n_e^R(r)$ is too large to treat by perturbation theory. For this reason, the ratio of theirs

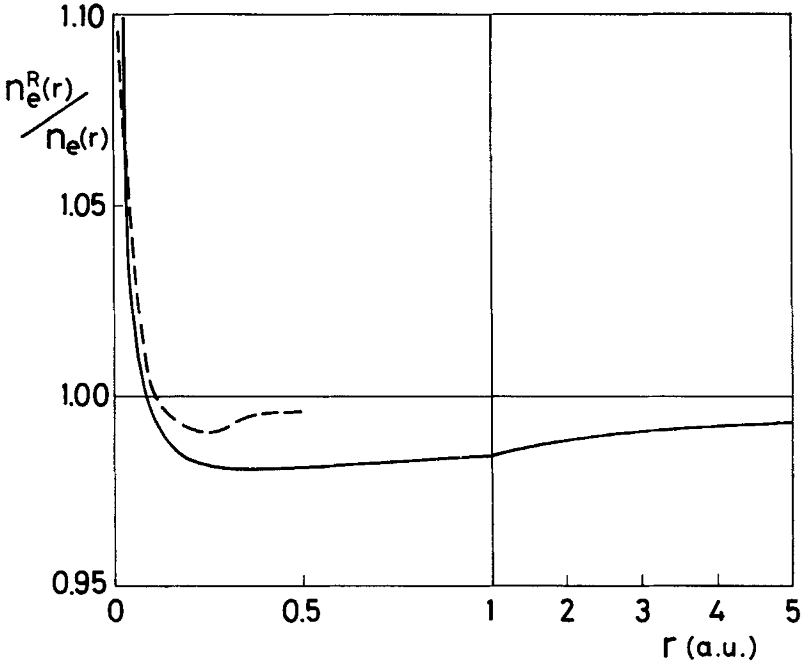

FIGURE 4 The ratio of the relativistic Thomas–Fermi electronic number density of the isolated Hg atom to the non-relativistic one. The solid curve shows the result of our fully self-consistent method and the broken curve shows that of a first-order perturbation method by Vallarta and Rosen.[6]

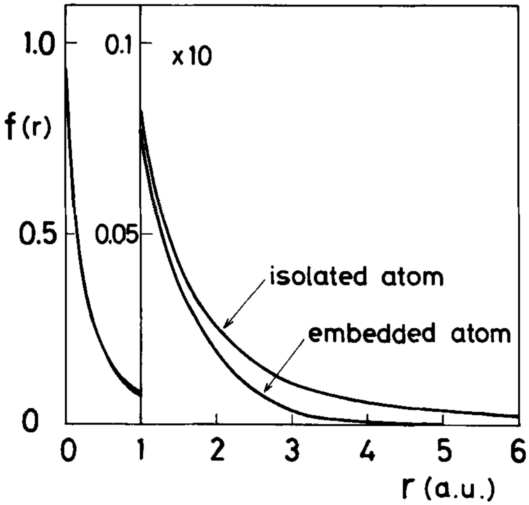

FIGURE 5 The function $f(r)$ for the embedded and the isolated Hg atoms.

is smaller than that of the present calculation. On the other hand, at larger distances, the ratio of ours is smaller than that of theirs. This reflects the fact that, from the conservation of the number of electrons, the larger the ratio is in the vicinity of nucleus, the smaller it is at larger distances.

By comparing the ratio of the embedded atom shown in Figure 3 with that of the isolated atom shown in Figure 4, we realise that the ratio of the embedded atom approaches unity at larger distances much faster than that of the isolated atom. The reason for this difference is the screening effect due to the electrons in jellium. As is shown in Figure 5, the function $f(r)$ decreases faster for the embedded atom than for the isolated atom. The characteristic length for the decay of $f(r)$ corresponds to the Thomas–Fermi screening length, $k^{-1} = 1.01$ a.u.

4 SUMMARY

We have investigated the relativistic correction to the electronic charge density of an atom embedded in jellium by solving a relativistic Thomas–Fermi equation with the self-consistent iteration method. We have shown that the relativistic correction becomes important as the atomic number of the embedded atom increases, and that the relativistic correction for a heavy atom in jellium is significant not only in the vicinity of the nucleus but also at greater distances from it.

In our theory the investigation is restricted to the total charge density inevitably by the Thomas–Fermi theory and absolute magnitude of the change in the charge density due to relativity seems actually small relative to the total charge density. However, if we go beyond the Thomas–Fermi theory and use a more refined theory such as the Dirac equation, the relativistic effect may be different from state to state, as Liberman *et al.*[9] have shown. Therefore, the relativistic correction to a certain electronic state can emerge more evidently. This tendency has been confirmed also by a relativisitic APW band structure calculation for the cesium-chloride type CsAu crystalline compound.[13,14] Thus, our next problem is to calculate quantitatively the electronic structure and the transport coefficients of Cs-Au alloys and others. An elaborate calculation based on the Dirac equation with the local-density approximation is now in progress.

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