Electron correlation effects in screened hydrogenic impurity states in many-valley semiconductors

Antonio Newton Borges

Departamento de Física, Universidade Federal de Goiás, 74000-000 Goiânia, Brazil

Oscar Hipólito

Departamento de Física e Ciência dos Materiais, Instituto de Física de São Carlos, Universidade de São Paulo,
Caixa Postal 369, 13560-970 São Carlos, São Paulo, Brazil

Vera Beatriz Campos

Departamento de Física, Universidade Federal de São Carlos 13565-905 São Carlos, São Paulo, Brazil

The critical concentration of donor hydrogenic impurities in a screened Coulomb potential is calculated, considering the effects of exchange, correlations, and mass anisotropy of the bound electron. We used the random-phase approximation and a self-consistent scheme proposed by Singwi, Tosi, Land, and Sjölander with variational solutions in the effective mass equation. Our results are compared with other theoretical calculations and with experimental measurements of the metal-semiconductor transition in n-type impurities of silicon and germanium. The agreement with the experimental results let us conclude that in many semiconductor systems the short-range correlations need to be taken into account in a more effective way.

I. INTRODUCTION

There has been a considerable interest in the investigation of critical densities of shallow donor impurities in group IV semiconductors, from both theoretical and experimental points of view. For sufficiently low impurity concentration Kohn and Luttinger[1] and several other authors[2] have solved the Hamiltonian of the impurity in the effective mass approximation, using a trial function of the hydrogenic type in a variational calculation. However, it is known that if the donor impurity concentration in a semiconductor is increasing, there occurs a superposition of the electronic wave functions of the neighboring impurity atoms, which allow the electrons to become relatively free and move from one impurity site to another. Consequently, these free carriers screen the electron-ion Coulomb interaction. In this sense, within the effective mass approximation, the electronic properties have been calculated using different approaches for the dielectric function: Thomas-Fermi (TF),[3-5] Lindhard,[5-7] and Hubbard-Sham (HS).[8]

The electronic system under consideration can be characterized only by a single dimensionless variable $r_s = r_0/a_0^*$, where $r_0 = (3/4\pi n)^{1/3}$ is the average interparticle separation, n is the number density, and $a_0^* = \epsilon_0 \hbar^2/m^* e^2$ is the effective Bohr radius. m^* and ϵ_0 are the electron effective mass and the dielectric constant of the semiconductor, respectively. For doped semiconductors the critical densities are usually low, ranging from about 10^{17} to 10^{19} cm^{-3}. Then, in this range of densities and using the appropriate values of effective mass and dielectric constant for silicon and germanium, we find r_s that corresponds to the metallic densities of the electron gas, $2 \leq r_s \leq 6$. This means that a better calculation than the random-phase approximation (RPA) should be performed.

In the present paper we investigate some electronic properties of semiconductors by using a self-consistent-field approximation proposed by Singwi, Tosi, Land, and Sjölander[9] (STLS) for a degenerate electron gas. This approach is one of the best improvements of the RPA formalism by virtue of including the short-range correlations which arise from the Coulomb repulsion potential. The short-range correlations responsible for the local field corrections are calculated in a self-consistent way by making the density-density response function dependent upon the pair-correlation function.[10] The method consists in making a decoupling of the two-particle distribution function in the Liouville equation, replacing it by the product of two one-particle distribution functions and a pair-correlation function.

In order to determine the critical density n_c for which the semiconductor-metal transition occurs, we have applied the STLS to calculate the ground-state energy, as a function of the carrier density, of an electron bound to an ion of a donor impurity. The mass anisotropy of the bound electron is taken into account in the dielectric function, which is obtained within the self-conssitent approximation method. We have used a trial wave function that reflects the cylindrical symmetry of the system. The numerical results for the critical densities, for silicon and germanium, are compared with those obtained through different approaches for isotropic and anisotropic systems as well as with the experimental results.

II. THEORY

The conduction band energy surfaces in the $\vec{k}$ space for germanium and silicon are ellipsoids of the form

$$E(\vec{k}) = \hbar^2 \left(\frac{k_x^2 + k_y^2}{2m_\perp} + \frac{k_z^2}{2m_z} \right) \quad , \tag{1}$$

where $m_\perp$ and m_z represent the effective masses perpendicular and parallel to the anisotropic direction, k_z. We have assumed mass isotropy in the plane xy. Then the Hamiltonian of the system we are working on, within the effective mass approximation, can be written as

$$H = -\frac{\hbar^2}{2} \left(\frac{1}{m_\perp} \frac{\partial^2}{\partial x^2} + \frac{1}{m_\perp} \frac{\partial^2}{\partial y^2} + \frac{1}{m_z} \frac{\partial^2}{\partial z^2} \right) + U(\vec{r}) \quad . \tag{2}$$

By making a scale transformation[12] on the vector $\vec{k}$ we obtain an isotropic electron gas with wave vector $\vec{\xi} = (k_x R^{-1/6}, k_y R^{-1/6}, k_z R^{1/3})$ and effective mass $m^* = (m_z m_\perp^2)^{1/3}$, where $R = m_\perp/m_z$ is the mass ratio between the values of the mass in the plane xy and the mass in the direction z. $U(\vec{r})$ is the interaction potential between an electron and an impurity given by

$$U(\vec{r}) = \int \frac{d\vec{\xi}}{(2\pi)^3} \frac{\Phi(\vec{\xi})}{\epsilon(\vec{\xi},0)} \exp(i\vec{\xi} \cdot \vec{r}) \quad , \tag{3}$$

and its Fourier transform is

$$U(\vec{\xi}) = \frac{\Phi(\vec{\xi})}{\epsilon(\vec{\xi},0)} = \frac{4\pi e^2}{\varepsilon_0 \xi^2 \epsilon(\vec{\xi},0)} \quad , \tag{4}$$

where $\Phi(\vec{\xi})$ is the Fourier transform of the Coulomb potential without screening, ε_0 is the static dielectric constant of the host crystal, and $\epsilon(\vec{\xi},0)$ is the static dielectric function of the system. In the general case, the dielectric function in the STLS approximation is given by

$$\epsilon(\vec{\xi},\omega) = 1 + \frac{Q_0(\vec{\xi},\omega)}{1 - G(\vec{\xi})Q_0(\vec{\xi},\omega)} \quad , \tag{5}$$

where

$$Q_0(\vec{\xi},\omega) = -\Phi(\vec{\xi})\chi_0(\vec{\xi},\omega) \tag{6}$$

is the electronic polarizability and $\chi_0(\vec{\xi},\omega)$ is the density-density response function for a noninteracting electron gas with isotropic mass m^*. The local field correction $G(\vec{\xi})$ can be expressed as a function of the structure factor $S(\vec{\xi})$ as

$$G(\vec{\xi}) = -\frac{3}{8\pi} R^{\frac{1}{2}} \xi_F^{-3} \int d\vec{\xi}' \, \frac{\vec{\xi} \cdot \vec{\xi}'}{|\vec{\xi}'|^2} \left[S(|\vec{\xi} - \vec{\xi}'|) - 1 \right] \quad , \tag{7}$$

and is related to the self-consistent effective potential $\psi(\vec{\xi})$ through the expression

$$\psi(\vec{\xi}) = \Phi(\vec{\xi}) \left[1 - G(\vec{\xi}) \right] \quad . \tag{8}$$

By now it is worth noting that the RPA results correspond to the zeroth-order approximation, where $\psi(\vec{\xi})$ is taken as the bare Coulomb interaction potential, $\Phi(\vec{\xi})$.

Closing the self-consistent scheme, the structure factor $S(\vec{\xi})$ can be obtained from the dielectric function $\epsilon(\vec{\xi},\omega)$, with the help of the exact expression

$$S(\vec{\xi}) = -\frac{\hbar}{\pi n \Phi(\vec{\xi})} \int_0^\infty d\omega \, \text{Im} \left[\epsilon^{-1}(\vec{\xi},\omega) \right] \quad , \tag{9}$$

where n is the electronic density.

We have then Eqs. (5), (7), and (9), which constitute the set to be solved self-consistently in order to obtain the dielectric function $\epsilon(\vec{\xi},\omega)$.

The real and imaginary parts of the density-density response function $\chi_0(\vec{\xi},\omega)$ are given by

$$\text{Re}\chi_0(\vec{\xi},\omega) = \frac{3n}{4E_F} \left\{ 1 + \left[\frac{E_F}{\lambda^3} \right] \left[(\lambda^2 - \Omega_+^2) \ln \left| \frac{\lambda + \Omega_+}{\lambda - \Omega_+} \right| \right. \right.$$
$$\left. \left. - (\lambda^2 - \Omega_-^2) \ln \left| \frac{\lambda + \Omega_-}{\lambda - \Omega_-} \right| \right] \right\} \tag{10}$$

and

$$\text{Im}\chi_0(\vec{\xi},\omega) = \frac{3\pi n}{4\lambda^3} [(\lambda^2 - \Omega_-^2)\Theta(\lambda - |\Omega_-|)$$
$$- (\lambda^2 - \Omega_+^2)\Theta(\lambda - |\Omega_+|)] \quad , \tag{11}$$

where we have defined $\Omega_\pm = \hbar\omega \pm E(\vec{\xi})$ and $\lambda = 2\sqrt{E(\xi)E_F}$. The Fermi energy is given by $E_F = \hbar^2\xi_F^2/2m^*$ with $\xi_F = (3\pi^2 n/\nu)^{\frac{1}{3}}$, ν being the number of valleys of the semiconductor. The unit step function is defined as $\Theta(x) = 1$ when $x > 0$, and zero otherwise.

Since the eigenvalues of the Hamiltonian of the system, Eq. (2), cannot be obtained in a closed form we used a variational approach to minimize the energy.

$$\langle E \rangle = \int d\rho \varphi^*(\rho) H \varphi(\rho) \tag{12}$$

with the trial wave function

$$\varphi(\rho) = \left(\frac{4 - \alpha^2}{4\pi\beta^{-3/2}\alpha^2} \right)^{1/2} \frac{2}{\rho} \sinh\left[-\rho(1 - \alpha/2) \right] \quad , \tag{13}$$

with $\rho = [(ma_\perp/m^*)(x^2 + y^2) + (m_z a_z/m^*)z^2]^{1/2}$, $a_\perp = \beta\gamma^{-1/3}$, and $a_z = \beta\gamma^{2/3}$. The variational parameters α, β, and γ must be determined by minimizing the ground-state energy of the system. This wave function is equivalent to the Hulthén wave function[13] when $\beta = \gamma = 1$. For this case, and taking the limit $\alpha = 0$, this trial wave function becomes hydrogenic. Throughout this work we express energies as multiple of the effective Rydberg $R^* = m^* e^4/(2\varepsilon_0^2 \hbar^2)$ and lengths in units of the effective Bohr radius. In these units, the result for the expected value for the total energy is given by

$$\langle E \rangle = \langle T \rangle + \langle U \rangle$$

$$= \frac{1}{24}(a_z + 2a_\perp)(4 - \alpha^2) - 8\pi \int d^3\xi \frac{W\left(\xi_x R^{-1/6}a_\perp^{-1/2}\xi_y R^{-1/6}a_\perp^{-1/2}, \xi_z R^{1/3}a_z^{-1/2}\right)}{\left(\xi_x^2 R^{1/3} + \xi_y^2 R^{1/3} + \xi_z^2 R^{-2/3}\right)\epsilon\left(\vec{\xi}, 0\right)}, \tag{14}$$

where

$$W(\xi) = \frac{[1 - 4/\alpha^2]}{(2\pi)^3\xi}\left[2\tan^{-1}\left(\frac{\xi}{2}\right) - \tan^{-1}\left(\frac{\xi}{2 - \alpha}\right) - \tan^{-1}\left(\frac{\xi}{2 + \alpha}\right)\right] \tag{15}$$

is the Fourier transform of the particle density $[\varphi^*(\rho)\varphi(\rho)]$ in the space of the momenta. Thus, in this way it is not necessary to know the analytical expression for the STLS potential in the spatial coordinates.
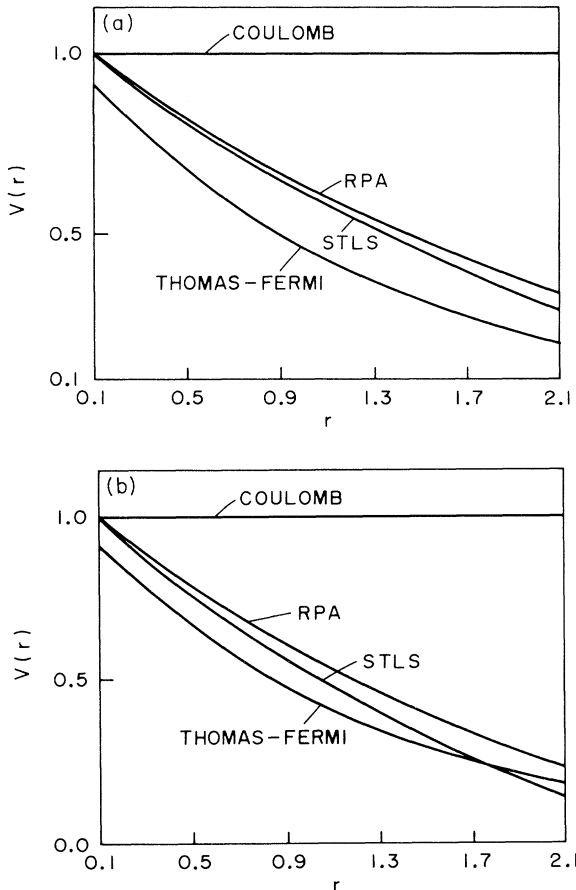

FIG. 1. Potential energy $V(\vec{r}) = rU(\vec{r})$, as a function of r, of an electron bound to an ion of a donor impurity in a semiconductor. Energy is in unit of effective Rydberg and length in unit of effective Bohr radius. (a) The results for germanium with density $n = 2.5 \times 10^{17}$ cm^{-3}, corresponding to $r_s = 4.1$, the electron ratio mass $R = 0.05$, and the valley degeneracy number $\nu = 4$. (b) The results for silicon, $n = 4.0 \times 10^{18}$ cm^{-3} ($r_s = 3.7$), $R = 0.2$, and $\nu = 6$. The corresponding results for Thomas-Fermi and RPA are also plotted for comparison.

III. RESULTS

For each concentration of free carriers we have numerically solved the self-consistent equations, Eqs. (5), (7), and (9), in order to obtain $\epsilon(\vec{\xi}, 0)$, which allows us to calculate the static structure factor, the electron-impurity potential, and the ground-state energy. The energy is calculated with the optimum values of the variational parameters α, β, and γ, for Si and Ge with densities in the range $2 \leq r_s \leq 7$.

Figure 1 represents the potential $V(\vec{r}) = rU(\vec{r})$ of an electron bound to an ion of a donor impurity, for the TF, RPA, and STLS potentials. Figure 1(a) shows the results for germanium with density corresponding to $r_s = 4.1(n = 2.5 \times 10^{17}$ cm$^{-3})$, $R = 0.05$, and $\nu = 4$, while Fig. 1(b) represents silicon, with $r_s = 3.7(n = 4.0 \times 10^{18}$ cm$^{-3})$, $R = 0.2$, and $\nu = 6$. We notice that for both materials the STLS potential curve takes values somewhat in between the RPA and the TF results. This fact indicates that STLS does not overestimate the screening effects, as TF does, nor underestimate these effects, as is the case of RPA. This happens due to the inclusion in STLS of the short-range correlations through the self-consistent local field correction.

In Figs. 2 and 3 we show the results for the static structure factor of the electron gas, for the RPA and STLS approximations, with different values for the mass ratio R and density r_s. Both results correspond to a valley degeneracy number $\nu = 1$. Figure 2 corresponds to $R = 0.2$ and two densities, $r_s = 1$ and $r_s = 4$. In Fig. 3 we considered $r_s = 2$ and $R = 1$, which corresponds to an isotropic system, and $R = 0.2$, which is about the experimental mass ratio for Si. From Fig. 2 one can notice

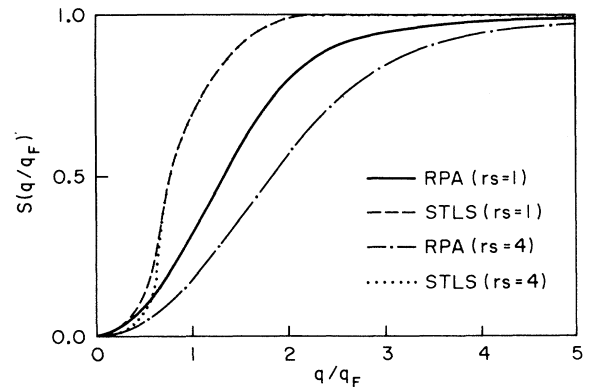

FIG. 2. Static structure factor $S(\vec{q})$ plotted as a function of q/q_F for an anisotropic electron gas, $R = 0.2$, for two different densities $r_s = 1$ and $r_s = 4$. The RPA results are also plotted for comparison.
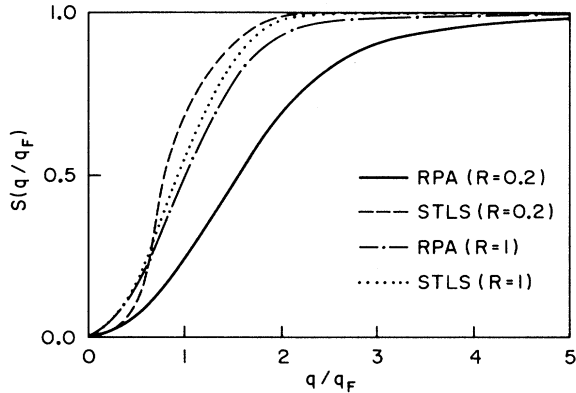
FIG. 3. Static structure factor $S(\vec{q})$ plotted as a function of q/q_F for an isotropic ($R = 1$) and an anisotropic ($R = 0.2$) electron gas with density $r_s = 2$. The corresponding results for RPA are also plotted for comparison.
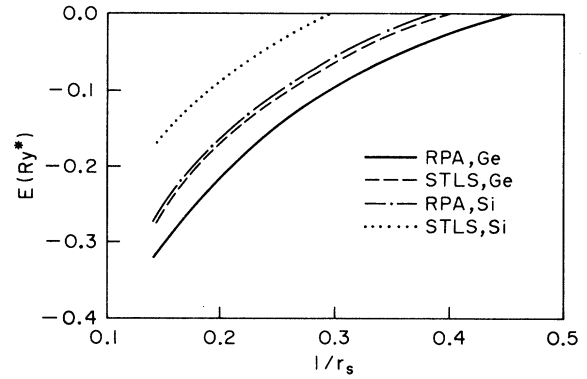

FIG. 4. Electron-impurity energies in units of effective Rydberg as a function of $1/r_s$ for germanium and silicon. The RPA results are plotted for comparison.

that, in the STLS approximation, for values of $q \geq q_F$ there is almost no dependence on the density. In the RPA, the values corresponding to the higher density systems (smaller r_s) are sensibly larger, getting closer to the STLS results as the density increases. This agrees with the fact that the RPA has proven to be a good approximation in the high density limit. Also, in the STLS approximation the structure factor reaches unity for values of q close to $2q_F$, which corresponds to a more structured system. Figure 3 shows that in the anisotropic systems there is a larger difference between the results obtained with each approximation. This fact should justify the use of the STLS approximation for anisotropic systems. We also note that for small values of q the results are almost independent of the approximation used.

The binding energies for an electron in the RPA and STLS potentials are shown in Fig. 4, for germanium ($R = 0.05$) and silicon ($R = 0.2$) as a function of the electronic density. In adimensional units ($a_0^* n_c^{1/3}$), the val-

ues for the critical densities for the metal-semiconductor transition are 0.284 for germanium and 0.243 for silicon, in the RPA, and 0.249 and 0.182, respectively, for the STLS approximation. It is worth mentioning again that the STLS values for the critical density are much closer to the experimental values, 0.23 and 0.20,[11,14–16] than the other approximations.

Our computation results for the critical densties (Mott transition) for germanium and silicon are summarized in Table I, which also lists for comparison the values obtained through different approximation of calculations as well as the experimental values. All the results, except those from our work which are labeled by (a) and those using the Berggren model,[8] were obtained with the electrostatic screening in the Thomas-Fermi or Lindhard approximations. Inspection of the table shows that the present results for the metal-semiconductor transition densities are in good agreement with the experimental results, differing by less than 9% in both cases.

TABLE I. Comparison of theoretical and experimental values for the critical densities for germanium and silicon, as reported in the literature. The theoretical results marked by (a) correspond to this work. Numbers in parentheses are references.

Isotropic system	Germanium	Silicon
Thomas-Fermi (hydrogenic trial function) (5)	0.10	0.08
Lindhard (hydrogenic trial function) (5)	0.23	0.23
Thomas-Fermi (Hulthén trial function) (a)	0.142	0.108
Lindhard (Hulthén trial function) (a)	0.271	0.263
Hubbard-Sham (Hulthén trial function) (a)	0.299	0.290
Hubbard-Sham (numerical results) (17)	0.305	0.295
Anisotropic system		
Thomas-Fermi (6)	0.10	0.10
Lindhard (6)	0.22	0.25
Berggren's model (8)	0.206	0.202
RPA (a)	0.284	0.243
STLS (a)	0.249	0.182
Experimental results		
Experimental results (11,14,15,16)	0.23	0.20

IV. CONCLUSIONS

We have applied the self-consistent-field approximation which takes into account the short-range-correlations effects in order to study the impurity states in many-valley semiconductors. Numerical results for the effective electron-impurity interaction potential, the static structure factor of the anisotropic electron gas, and the electron binding energies were obtained as a func-

tion of the electron density for germanium and silicon. The metal-semiconductor transition densities were calculated and the agreement with the experimental results was found to be very good.

[1] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 1721 (1955); **98**, 915 (1955).

[2] C. Kittel and A. H. Mitchell, Phys. Rev. **96**, 1488 (1954); M. Lampert, *ibid.* **97**, 352 (1955); W. Kleiner, *ibid.* **97**, 1722 (1955).

[3] N. F. Mott, Proc. R. Soc. London **62**, 416 (1949); C. S. Lam and Y. P. Varshni, Phys. Rev. A **4**, 1875 (1971).

[4] F. J. Rogers, H. C. Graboske, Jr., and D. H. Harwood, Phys. Rev. A **1**, 1577 (1970).

[5] R. L. Green, C. Aldrich, and K. K. Bajaj, Phys. Rev. B **15**, 2217 (1977).

[6] J. B. Krieger and M. Nightingale, Phys. Rev. B **4**, 1266 (1971).

[7] C. Aldrich, Phys. Rev. B **16**, 2723 (1977).

[8] F. Marttino, G. Limdell, and V. F. Berggren, Phys. Rev. B **8**, 6030 (1973).

[9] K. S. Singwi, P. M. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. **176**, 589 (1968).

[10] V. B. Campos, O. Hipólito, and R. Lobo, Phys. Status Solidi B **81**, 657 (1977); O. Hipólito and R. Lobo, Phys. Rev. B **14**, 3892 (1976); N. Studart and O. Hipólito, Phys. Rev. A **19**, 1970 (1979); **12**, 2860 (1980).

[11] M. N. Alexander and D. F. Holcomb, Rev. Mod. Phys. **40**, 815 (1968).

[12] V. B. Campos and O. Hipólito, Phys. Rev. B **40**, 9306 (1989).

[13] L. Hulthén, Ark. Mat. Astron. Fhy. A **28**, No. 5 (1942).

[14] M. L. Kozhukh, N. S. Lipkina, and I. S. Shlimak, Sov. Phys. Semicond. **19**, 206 (1985).

[15] V. P. Dobrego, O. P. Ermolaev, and O. M. Khemeda, Sov. Phys. Semicond. **24**, 348 (1990).

[16] T. G. Castner and N. K. Lee, Phys. Rev. Lett. **26**, 1627 (1975).

[17] Y. P. Varshni and S. M. Khanna, Phys. Rev. B **43**, 9279 (1991).