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Thomas–Fermi-type dielectric screening of statistical atomic models of donor-specific impurities in a semiconductor-like valence electron gas at zero temperature

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Abstract. Thomas–Fermi (TF-) type theories are applied to the problem of static dielectric screening in a semiconductor at absolute zero when the impurity-charge-density distribution is given by a variational statistical approximation. This treatment of the external perturbation is consistent with the valence electron-gas formulation of the host crystal and in contrast with the point-charge probe and other donor-specific or pseudocharge distributions that have been previously studied in this context. One-parameter exponential bound-electron charge densities are employed in this report. For purposes of illustration, atomic parameters specifying the chemical identity of an impurity are characteristic of phosphorus (group V) and sulphur (group VI) substitutional single and double donors, respectively, and a reference silicon ion. Linearized TF and Thomas–Fermi–Dirac (TFD) screening equations for the exponential case and its point-charge limit are solved in closed analytical form with silicon as the host semiconductor. The corresponding nonlinear TF and TFD equations are solved numerically and nonlinear screened impurity potentials are compared with linear results. Dielectric screening of statistical impurities follows the same general trend as noted for a point charge, that is, the nonlinear theory is more effective than its linear approximation. Furthermore, for a given statistical impurity, with a given degree of ionization, the ion potential is more effectively screened in the following order: linear TF, linear TFD, nonlinear TF, and nonlinear TFD. Corresponding screening radii decrease in this order. Within the set of statistical ions under consideration, linear and corresponding nonlinear screening radii and their differences decrease as the degree of ionization decreases. Further development is planned to test the usefulness of this approach to donor and host potentials in conventional and generalized effective-mass calculations of isocoric and nonisocoric binding energies.

1. Introduction

The electronic structure and properties of ionized impurities in semiconductors is a subject of considerable theoretical and experimental interest [1]. The study of binding energies involves the construction of individual impurity potentials which can be used directly with various methods of solution, including effective-mass variational procedures, numerical integration of Schrödinger's equation, and Green function techniques. The valence electrons in a semiconductor will respond to the presence of an ionized atom by screening its bare potential. It is well known [1, 2] that an accurate description of the screening effect is indispensable for the calculation of the ground states of donors in semiconductors. From the viewpoint of wave-vector space (k -space), the screened impurity potential is given by the

Fourier transform of the bare potential divided by a k -space-dependent dielectric function which is obtained from linear response theory. Accurate dielectric functions are worked out numerically and the results fitted to an analytic expression. Integrating back to configuration space (r -space) to obtain the screened impurity potential is very complicated, if not in some cases impractical.

A more transparent approach to the problem of dielectric screening involves the TF method which has the advantage of working directly in r -space and readily adapts to a nonlinear treatment [3]. This popular description of the microscopic response of a semiconductor to an external perturbation treats the valence electrons as a degenerate Fermi gas of nonuniform, spherically symmetric density $n(r)$ in a positive background. Semiconductor-like behaviour is simulated in this model homogeneous and isotropic metallic medium by the *ad hoc* prescription of a finite radius R of incomplete screening at and beyond which the electron density assumes its uniform background value n . The available screening charge $-(1 - 1/\epsilon)Z_a$ is wholly contained within a spherical boundary of radius R where Z_a is the external charge and ϵ is the static macroscopic dielectric constant of the semiconductor [4]. The original formulation of this particular screening theory adopts a point-charge probe, $Z_a\delta(r)$, for which it is possible to define a spatial dielectric function, $\bar{\epsilon}(r)$, as the ratio of the bare Coulomb potential, $-Z_a/r$, to the screened potential, $V(r)$. Characteristically, $\bar{\epsilon}(r)$ increases monotonically from unity at the origin to ϵ for $r \geq R$. The corresponding linear and nonlinear TF screening equations have been solved analytically [3] and numerically [5], respectively, subject to continuity requirements on the potential and the electric field at $r = R$, and the condition at the origin generally applied to a Coulomb divergence. Semiconductor input data consist of ϵ and the valence Fermi momentum, k_F . Basic features of this theory are the following: (i) the screening radius is of the order of a single bond length in covalent solids; (ii) the TF linear response functions are numerically quite close to the pseudopotential random-phase-approximation calculations of the same functions; (iii) nonlinear response functions manifest important deviations from the results of linear theory. In particular, screening radii are correspondingly smaller (larger) in the former case, implying that attractive (repulsive) potentials are screened more (less) effectively.

Modifications of the TF theory include exchange–correlation in the Dirac–Slater X_α approximation [6] and a Weizsäcker-type gradient correction to the kinetic energy functional [7]. In the former case, an exchange–correlation potential of a shallow-donor impurity and the exchange interaction of the donor electron with the valence electrons are used in an effective-mass variational calculation of the binding energy. The same problem has been investigated in terms of a numerical integration of Schrödinger’s equation whereby best results for the binding energy in silicon and germanium are obtained with nonlinear screening in the TFD approximation [8]. A natural generalization of the present screening theory considers the dielectric relaxation of a doped semiconductor at nonzero temperature [9]. Under these conditions, the Fourier transform of the screened potential is reduced to an effective wave-vector-dependent dielectric function which combines the zero-temperature response due to the valence electrons with a temperature-dependent part due to the free carriers. In effect, this amounts to a summation of the susceptibilities due to these various sources of charge. This extension of the theory has been applied to the problem of calculating the ionized-impurity scattering mobility in silicon [10].

Self-consistent TF-type approximations require the screened potentials to satisfy Poisson’s equation. The displacement of the inhomogeneous electron density $n(r)$ from the uniform background density n provides a source term in this equation. Another contribution is due to the presence of the external charge density which, in its simplest

form, is a point charge. More realistic screening situations, such as arise for donors in multivalley semiconductors such as silicon, require the introduction of an impurity with a spatially extended charge or pseudocharge distribution. A linearized version of the TF theory incorporates donor-specific, bare-impurity pseudopotentials [11]; some consequences of linearization are examined in a nonlinear treatment using the same pseudopotentials [12]. Another application of the theory, including a boundary condition on the electric field at the origin, studies three different model potentials and their corresponding pseudocharges [13]. It is pointed out in the second citation under [13] that the continuity conditions, applied at the screening radius when all of the external charge resides within the screening boundary, will not be strictly correct with the use of smooth pseudocharges that are nonvanishing beyond R . In that case, the screened potential for $r \geq R$ is the sum of the bare potential and the term $(1 - 1/\epsilon)Z_a/r$ due to the screening charge, rather than simply the former reduced by ϵ .

The model proposed in [3] for screening in semiconductors starts from an electron-gas formulation of the host crystal. On the other hand, the impurity charge or pseudocharge distributions employed thus far in the literature are prescribed in some other way. The purpose of the present paper is to follow a theoretical approach in which the bound electrons associated with the impurity are treated in a statistical variational approximation. Similar considerations have been applied to the problem of stopping power and straggling of ionic projectiles in condensed matter [14]. The size parameter of the fixed electron cloud in the ion and the internal energy of the ion are determined by a minimization of the total ground-state energy functional with respect to the total number of electrons and the size parameter. An obvious advantage of this approach is that it permits the use of *a priori* charge densities that possess some of the essential features of real atoms, such as being finite at the nucleus and monotonically decreasing. Exponential impurity-charge densities will be employed in this paper to describe the electrons bound in the bare atom or ion.

Section 2 is concerned with statistical models of the external charge distribution. The corresponding energy functional accounts for the classical Coulomb potential energy of electron–electron and electron–nucleus interactions and the kinetic energy in the TF approximation. The electron–electron interaction is weighted for correlation in an average manner by a parameter β . Optimization of the total ground-state energy, with respect to the size parameter α associated with the prescribed donor charge density, leads to an expression for this parameter in terms of the total number of bound electrons N_a , the nuclear charge Z , and the correlation parameter. Another expression for α is obtained from the definition of the chemical potential for a neutral atom. These results determine a numerical value for β which feeds into final expressions for the internal energy and α . A comparison is made between experimental total ground-state energies for free ions and neutral atoms and results predicted by numerical solution of the customary TF equation, statistical models, and Hartree–Fock theory.

Section 3 deals with TF-type dielectric screening of statistical atoms or ions in the model semiconductor. Minimization of the corresponding total ground-state energy functional with respect to the electron number density, $n(r)$, subject to the constraint that the total number of valence electrons remains constant, yields an Euler–Lagrange equation which must be solved self-consistently with Poisson’s equation for the screened potential, $V(r)$. It is seen that $V(r)$ is the sum of the dopant-dependent bare impurity potential and the potential due to the induced electron-charge density. Linear and nonlinear TF-type screening equations are formulated in this section. A closed analytical expression is derived for $V(r)$ in the former approximation. It reduces to the dielectric screening of a point charge and the metallic screening of an extended charge density in the formal limits $\alpha \rightarrow 0$ and $R \rightarrow \infty$,

respectively. Taken together, these limits recover the well known result of Mott for the TF metallic screening of a point charge.

Numerical solutions of the nonlinear screening equations are presented in section 4. This section includes a comparison between linear and nonlinear results for statistical models of phosphorus, sulphur, and a reference silicon ion in a model semiconductor of silicon. Screened potentials and corresponding screening radii for these ions and their point-charge limits are displayed in graphical and tabular form, respectively. The two sets of solutions (linear and nonlinear TF and TFD) are compared by illustrating the relationship between the screening radius and the degree of ionization for phosphorus in silicon. Lastly, a sequence of nonlinear TFD screened potentials, with the degree of ionization as parameter, are shown for phosphorus in silicon. Section 5 gives some concluding remarks.

2. Atoms or ions in the variational statistical approximation

2.1. Bound-electron charge density and total ground-state energy

The three basic components of the ground-state energy functional of a many-electron system are its kinetic energy, the electron–electron repulsive energy, and the attractive electron–nuclear energy. The second contribution can be expressed as the sum of the classical Coulomb repulsive energy and the exchange–correlation energy. This section adopts a simplified version of this energy functional for statistical models of donor atom or ions embedded in a medium with macroscopic dielectric constant ϵ . The kinetic energy density is considered to be proportional to the five-thirds power of the bound-electron density $\rho_c(r)$ as in the original TF theory. The electron–electron interaction is weighted for correlation in an average manner as in [14], and the exchange–correlation part is formally neglected. Under these conditions, the total ground-state energy is

$$E_a = c_k \int \rho_e^{5/3}(r) d\tau + \frac{1}{\epsilon} \int \rho_e(r) v_n(r) d\tau + \frac{1}{2\epsilon} \beta \int \rho_e(r) v_e(r) d\tau. \quad (1)$$

The coefficient c_k is an abbreviation for $(3/10)(3\pi^2)^{2/3}$. If $v(r)$ denotes the total potential energy of the atom or ion, then

$$v(r) = v_e(r) + v_n(r) \quad (2a)$$

where

$$v_n(r) = -Z/r \quad (2b)$$

and

$$v_e(r) = \int \frac{\rho_e(r') d\tau'}{|\mathbf{r} - \mathbf{r}'|}. \quad (2c)$$

Similarly, if $\rho_a(r)$ denotes the total impurity charge density, then

$$\rho_a(r) = Z\delta(r) - \rho_e(r). \quad (3)$$

Integration of this quantity over all space gives

$$Z_a = \int \rho_a(r) d\tau = Z \left(1 - \frac{N_a}{Z}\right) \equiv Zp \quad (4)$$

where p is defined as the degree of ionization.

Two simple one-parameter forms of $\rho_e(r)$ are studied here in connection with the minimization of E_a . Obvious choices are the exponential and screened-Coulomb functions. [15] shows that the former is especially appropriate because Hartree–Fock electron densities

and presumably exact densities for the ground states of selected atoms are well represented by continuous piecewise exponential decaying functions of r with as many different exponential regions as there are principal quantum numbers. Results in [15] for ground-state energies and electron densities of first-row and some second-row atoms show that shell structure is accessible through simple energy functionals. For the present discussion, it is convenient to assume that $\rho_e(r)$ is described by a single exponential distribution

$$\rho_e(r) = \frac{N_a}{8\pi\alpha^3} e^{-r/\alpha} \quad (5)$$

where the screening length or size parameter α is treated as a variational parameter. Alternatively, various estimations of the electronic stopping power and straggling of the free electron-gas model solid for a projectile atom have employed the screened Coulomb form

$$\rho_e(r) = \frac{N_a}{4\pi\alpha^2} \frac{e^{-r/\alpha}}{r}. \quad (6)$$

For the purpose of calculating α in a statistical way, the projectile has been treated as an isolated neutral atom located in a vacuum [14]. Other considerations [16] have used an improved value of α in a metallic-like medium by taking into account the screening of corresponding $v_a(r)$ and $v_e(r)$, by the background electron gas. In either case, this form of $\rho_e(r)$ permits analysis of α without recourse to numerical methods, as does (5).

After calculation with (1)–(5), it is found that

$$E_a = b \frac{N_a^{5/3}}{\alpha^2} - \frac{N_a Z}{2\alpha\epsilon} + \frac{5\beta N_a^2}{32\alpha\epsilon} \quad (7)$$

where b is an abbreviation for $2(3\pi)^{2/3}(3/10)^4$. It remains to minimize E_a with respect to N_a ($= Z$) and α . As a result of these operations, the first of which expresses the vanishing of the chemical potential for a neutral atom, it follows that

$$E_a(Z, p) = -Z^{7/3}(1-p)^{1/3}(6+p)^2/784b\epsilon^2 \quad (8)$$

$$\alpha(Z, p) = 28b\epsilon(1-p)^{2/3}/Z^{1/3}(6+p) \quad (9)$$

and $\beta = 48/105$. The correlation parameter is less than unity, as it should be. From (5), (8) and (9), the ground-state energy and the bound-electron charge density are determined now in terms of the parameters Z , p and ϵ . A parallel calculation of β , E_a and α in terms of the screened Coulomb form of $\rho_e(r)$ given by (6) shows that $\beta = 4/7$, while the only changes in (8) and (9) are the replacement of the numerical quantities $784b$ and $28b$ by $196c$ and $14c$, respectively, where c is an abbreviation for $(1/2)(3\pi/4)^{2/3}(3/5)^{7/3}\Gamma(4/3)$. Not surprisingly, it is found in general ($p \neq 1$) that the exponential density distribution leads to atomic energies (screening lengths) that are less negative (smaller) than their screened Coulomb counterparts. It is interesting to make a numerical comparison of these results for the atomic energy with the prediction of the TF model for neutral atoms ($p = 0$) in free space. The following formulae summarize these various cases:

$$E_a(Z, 0) = -0.6353Z^{7/3} \quad (10a)$$

$$E_{SC}(Z, 0) = -0.7653Z^{7/3} \quad (10b)$$

$$E_{TF}(Z, 0) = -0.7687^{7/3}. \quad (10c)$$

The energies $E_{SC}(Z, 0)$ and $E_{TF}(Z, 0)$ are essentially coincident. Table 1 gives the degree of ionization and atomic screening length for the modified TF model of atoms and ions in silicon. From table 2, it is seen that the total ground-state energies for free ($\epsilon = 1$),

neutral ($p = 0$) atoms of Si, P and S, derived from the exponential form of the bound-electron density distribution, are a considerable improvement over those predicted by the numerical solution of the TF equation and the screened Coulomb distribution. This trend can be shown as well for other atoms, such as the inert gas group which is frequently used in comparison testing [15, 17] with Hartree–Fock results as standard. For values of Z up to about 20, the known experimental total binding energies are closely reproduced by Hartree–Fock theory. Of course, such comparisons will be misled by relativistic influences which are more important for larger Z . It is amusing that the simple expression given above for $E_a(Z, 0)$ yields energies in respectable agreement with corresponding Hartree–Fock values given by C F Fischer. The results of tables 2 and 3 show that total ground-state energies for the free atoms and ions under consideration are good to about 3.6%.

Table 1. Degree of ionization p and atomic screening length $\alpha(Z, p)$ for model atoms and ions in silicon.

Ion	p	$\alpha(Z, p)^a$
S ⁶⁺	0.375	1.100
P ⁵⁺	0.333	1.181
Si ⁴⁺	0.286	1.275
S	0	1.598
P	0	1.633
Si	0	1.671

^a $\alpha(Z, p)$ is calculated from (9).

Table 2. Ground-state energies (au) for free neutral atoms from modified and original TF model, Hartree–Fock theory and experiment.

Atom	E_{TF}^a (% of error) ^b	E_a^c (% of error) ^b	E_{HF}^d (% of error) ^b	E_{exp}^e
Si	−363.12 (−25.3)	−300.11 (−3.54)	−288.85 (+0.35)	−289.86
P	−426.55 (−24.6)	−352.53 (−2.99)	−340.72 (+0.46)	−342.31
S	−495.87 (−24.3)	−409.82 (−2.70)	−397.50 (+0.38)	−399.03

^a E_{TF} is calculated from (10c).

^b Errors are relative to experimental energies, E_{exp} .

^c E_a is calculated from (10a).

^d Hartree–Fock energies are from Froese-Fischer C *The Hartree–Fock Method for Atoms* (New York: Wiley).

^e E_{exp} is found from ionization potentials given by Moore C E *Analysis of Optical Spectra* NSRDS-NBS 34 (Washington, DC: National Bureau of Standards).

Finally, some remarks are appropriate concerning other formulations of the ground-state energy functional. It is noted that values of E_a , even less accurate than the TF values, are obtained with the present procedure when the correlation part of the electron–electron interaction is formally neglected, while the exchange part is given in the Dirac approximation. On the other hand, small reductions in the values of E_a are obtained when the kinetic energy functional is extended to include the first gradient correction as some fraction of the original Weizsäcker term. More sophisticated TF-type energy functionals

Table 3. Ground-state energies (au) for free ions from modified TF model.

Ion	$E_a^a(Z, p)$ (% of error)	E_{exp}^b
Si ⁴⁺	-294.44 (-2.92)	-286.07
P ⁵⁺	-343.19 (-2.20)	-335.81
S ⁶⁺	-395.61 (-1.73)	-388.87

^a $E_a(Z, p)$ is calculated from (8).

^b E_{exp} is found from ionization potentials given by Moore C E *Analysis of Optical Spectra* NSRDS-NBS 34 (Washington, DC: National Bureau of Standards).

with higher-order gradient corrections to the kinetic energy and more accurate descriptions of the exchange–correlation energy are available [17]; however, variational derivatives will lead to rather unwieldy equations for E_a and the variational parameters contained in $\rho_e(r)$. It remains for further investigation to refine the values of E_a and the expressions for $\rho_e(r)$ used in the variational statistical approximation insofar as the associated dielectric screening problem remains mathematically and numerically tractable.

2.2. Potential energy in the exponential bound-electron-density approximation

This subsection is concerned with the potential energy $v(r)$ due to the atom or ion charge distribution when the core electrons have the one-parameter exponential functional form. The total donor-charge density, accompanying $v(r)$, provides the source term in the corresponding Poisson equation,

$$\nabla^2 v(r) = 4\pi\rho_a(r). \quad (11a)$$

Because of spherical symmetry, (11a) becomes

$$v''(r) + \frac{2}{r}v'(r) = 4\pi Z\delta(r) - \frac{N_a}{2\alpha^3} e^{-r/\alpha} \quad (11b)$$

where the prime denotes differentiation with respect to r . The boundary conditions on (11b) are such that $rv(r) = -Z$ and $v(r) = 0$ at $r = 0$ and $r = \infty$, respectively. From the definition $w(r) = rv(r)$, it is found that the general solution of the equation for $w(r)$ is

$$w(r) = c_1 + c_2 r - (N_a/2) e^{-r/\alpha} (2 + r/\alpha) \quad (12)$$

where the integration constants $c_1 = -(Z - N_a)$ and $c_2 = 0$ are determined by the boundary conditions. Finally,

$$v_{z,p}(r) = -(Z/r) \{1 - (1-p)[1 - e^{-r/\alpha(Z,p)}(r/2\alpha(Z,p) + 1)]\}. \quad (13)$$

It is readily shown by direct integration of (2c), for $\rho_e(r)$ given by (5) and with $v_n(r)$ given by (2b), that (2a) also leads to (13), as expected. In the case of complete ionization ($p = 1$), (13) reduces to the bare ion potential

$$v_{z,1}(r) = -Z/r \quad (14)$$

studied in [1]. If the core electrons are placed at the origin so that $\rho_e(r) = N_a\delta(r)$, then

$$v_{z,p}(r) = -Zp/r. \quad (15)$$

Formally, (15) follows from (13) by allowing the screening length of $\alpha(Z, p)$ to vanish.

3. Thomas–Fermi-type dielectric screening of atoms or ions in semiconductors

3.1. Euler–Lagrange and Poisson equations

Consider the many-electron system that results when a statistical model atom or ion is immersed in a semiconductor-like electron gas. It consists of mobile valence electrons in a positive background plus the nucleus and fixed electrons of the impurity. A procedure for developing a corresponding TF-type equation for the self-consistent screened potential of the impurity has been outlined in a previous paper [18]. Minimization of the total ground-state energy functional E with respect to the screening charge density $n(r)$, subject to the constraint that the total number of valence electrons

$$N = \int n(r) d\tau \quad (16)$$

is constant, yields a nonlinear Euler–Lagrange equation relating to $V(r)$ and $n(r)$. The functional to be made stationary is $E - [E_F + V(R)]N$ where E_F is the Fermi energy, $[E_F + V(R)]$ plays the role of the Lagrange multiplier, and

$$E = c_k \int n^{5/3}(r) d\tau + \int n(r) V_n(r) d\tau + \int n(r) V_e(r) d\tau - c_e \int n^{4/3}(r) d\tau. \quad (17)$$

c_e is an abbreviation for the constant $(3/4)(3/\pi)^{1/3}$ appearing as a prefactor in the Dirac exchange energy. The nuclear potential energy created by the donor nucleus and the background positive charge is given by

$$V_n(r) = v_n(r) - \int \frac{n d\tau'}{|\mathbf{r} - \mathbf{r}'|}. \quad (18)$$

Similarly, the potential energy due to the bound and valence electrons is expressed as

$$V_e(r) = v_e(r) + \frac{1}{2} \int \frac{n(r') d\tau'}{|\mathbf{r} - \mathbf{r}'|}. \quad (19)$$

The variational principle yields the Euler–Lagrange equation

$$\frac{5}{3} c_k n^{2/3}(r) - \frac{4}{3} c_e n^{1/3}(r) + V(r) - E_F - V(R) = 0. \quad (20)$$

This equation expresses the constancy of the electrochemical potential, $E_F(r) + V(r) = E_F + V(R)$, where the first two terms on the left-hand side of (20) are identified with the local Fermi energy $E_F(r)$. As for the total electrostatic potential $V(r)$, it corresponds to the sum $V_n(r) + 2V_e(r) - v_e(r)$. Equation (20) also embodies the boundary condition $E_F(R) = E_F$, or equivalently $n(R) = n$, that simulates semiconductor-like behaviour of the valence electron gas.

Self-consistency requires that $V(r)$ satisfies Poisson's equation

$$\nabla^2 V(r) = 4\pi[n - n(r)] + 4\pi\rho_a(r) \quad (21)$$

where the square brackets on the right-hand side of (21) enclose the screening charge density and $\rho_a(r)$ is the impurity atom or ion charge density appearing in (11a) and (11b). It is clear from (11a) and (21) that the difference $V(r) - v_{z,p}(r)$ denotes the potential due to the induced electron charge. Electrostatic considerations show that

$$V(r) = v_{z,p}(r) - \int \frac{[n - n(r')] d\tau'}{|\mathbf{r} - \mathbf{r}'|}. \quad (22)$$

Clearly, this statement coincides with the definition of $V(r)$ given above in the context of the variational principle. Before proceeding to the TF and TFD theories of dielectric screening of statistical models of donor impurities, it is emphasized that the basic equations

for $n(r)$ and $V(r)$ presented here are the same as those used in previous works [6, 18] for the point-charge-impurity case of (14). The significant new feature here is the dependence of a nonpointlike $v_{z,p}(r)$ on natural parameters identifying the donor atom or ion.

3.2. Linear and nonlinear Thomas–Fermi equations

When the exchange contribution in (20) is neglected, the resulting equation expresses $n(r)$ in terms of $V(r)$ as

$$n(r) = \frac{2^{3/2}}{3\pi^2} \left[E_F + v_{z,p}(R) + \left(1 - \frac{1}{\epsilon} \right) \frac{Zp}{R} - V(r) \right]^{3/2} \quad r \leq R. \quad (23)$$

This relationship shows $V(R)$ as the sum of the bare ion potential $v_{z,p}(R)$ and the potential $(1 - 1/\epsilon)(Zp/R)$ due to the screening charge which is totally confined within the screening radius R . In the case when all of the external charge Zp also resides within the screening boundary, $V(R)$ reduces to $-Zp/\epsilon R$, as previously mentioned. At and beyond R , the electron density takes on its uniform background value

$$n(r) = n = (2E_F)^{3/2}/3\pi^2 \quad r \geq R \quad (24)$$

where, in the TF approximation, $E_F = (1/2)k_F^2$. Equation (23) combines with (21) to form a nonlinear differential equation for $V(r)$ given by

$$\nabla^2 V(r) = (2^{7/2}/3\pi) \left\{ E_F^{3/2} - [E_F + V(R) - V(r)]^{3/2} \right\} + 4\pi\rho_a(r) \quad r \leq R. \quad (25)$$

Continuity of the potential in (25) with the external potential

$$V(r) = v_{z,p}(r) + (1 - 1/\epsilon)Zp/r \quad r \geq R \quad (26)$$

and its derivative (the electric field) with

$$V'(r) = v'_{z,p}(r) - (1 - 1/\epsilon)Zp/r^2 \quad r \geq R \quad (27)$$

at $r = R$, and the behaviour at the origin generally attributed to a Coulomb divergence, i.e.,

$$\lim(r \rightarrow 0)rV(r) = -Z \quad (28)$$

are the corresponding boundary conditions.

First, consider a binomial-expansion perturbation-series approach in which the square of the quantity $[V(R) - V(r)]/E_F$ is negligible in comparison with unity. This procedure leads to a linearized [19] form of (25), namely

$$\nabla^2 V(r) = q_0^2 [V(r) - V(R)] + 4\pi\rho_a(r) \quad (29)$$

where

$$q_0^2 = 4k_F/\pi. \quad (30)$$

Because of spherical symmetry, the general solution of (29) is found to be

$$V(r) = V(R) + \frac{1}{r} (c_+ e^{q_0 r} + c_- e^{-q_0 r}) - \frac{N_a}{2\alpha(1 - \alpha^2 q_0^2)} \frac{e^{-r/\alpha}}{r} \left(r + \frac{2\alpha}{1 - \alpha^2 q_0^2} \right) \quad (31)$$

for $4\pi\rho_a(r)$ given by the right-hand side of (11b). The constants c_{\pm} are fixed by continuity of the potential at $r = R$ and the divergence condition of the origin. Lastly, continuity of the electric field at $r = R$ is used to determine R . It follows for $r \leq R$ that

$$V(r) = V(R) - Z(1 - P_1) \frac{\sinh q_0(R - r)}{r \sinh q_0 R} + Z \frac{[(P_0 R + P_1)e^{-R/\alpha} \sinh q_0 r - (P_0 r + P_1)e^{-r/\alpha} \sinh q_0 R]}{r \sinh q_0 R}. \quad (32)$$

The quantities P_0 and P_1 are defined by

$$P_0 = \frac{(1-p)}{2\alpha(1-\alpha^2q_0^2)} \quad P_1 = \frac{(1-p)}{(1-\alpha^2q_0^2)^2}. \quad (33)$$

The condition for the determination of R is given by

$$q_0R(1-P_1) + q_0R(P_0R + P_1)e^{-R/\alpha} \cosh q_0R - (p/\epsilon) \sinh q_0R + \{(R/\alpha)(P_0R + P_1) - P_0R - (1-p)/2[1 + (1+R/\alpha)^2]\} e^{-R/\alpha} \sinh q_0R = 0. \quad (34)$$

Equations (32)–(34) summarize the solution, in closed analytical form, of the screening equation in the linearized TF theory. Input parameters characterizing the semiconductor and the dopant type are k_F , ϵ and Z , p (or N_a), respectively. The quantities q_0 and α appearing in these equations are given in terms of these parameters by (30) and (9), respectively.

Numerical illustrations of linear and nonlinear TF results for various donors in silicon are displayed in subsection 4.1. It remains here to examine (13), (26) and (32)–(34) in certain limiting cases. By formally letting $\alpha \rightarrow 0$, these equations reduce to their point-charge (Zp) forms first reported in [1]. In that case, the solution of the TF equations for linear dielectric screening is given by

$$V(r) = -Zp/\epsilon R - \frac{Zp \sinh q_0(R-r)}{r \sinh q_0R} \quad r \leq R \quad (35)$$

$$V(r) = -Zp/\epsilon r \quad r \geq R \quad (36)$$

and

$$\epsilon q_0R = \sinh q_0R. \quad (37)$$

Metallic-like behaviour of the valence electron gas is recovered in the limit $R \rightarrow \infty$ where (32) becomes

$$V(r) = -Z(1-P_1)e^{-q_0r}/r - Z(P_0r + P_1)e^{-r/\alpha}/r. \quad (38)$$

This expression, in turn, is connected to the well known Mott [20] potential for the TF metallic screening of a point charge (Zp) by letting $\alpha \rightarrow 0$. In the short-range limit, the interior ($r \leq R$) semiconductor potential and the metal potential approach the nuclear charge $-Z$. For the long-range limit, the exterior ($r \geq R$) semiconductor potential approaches $-Zp/\epsilon r$. When the valence screening effect is neglected ($q_0 = 0$), the long-range limit of (38) is $-Zp/r$.

3.3. Linear and nonlinear Thomas–Fermi–Dirac equations

It is seen that (20) is a quadratic in the cube root of $n(r)$ and because of the exchange term it predicts a connection between $n(r)$ and $V(r)$ that differs from (23). Indeed,

$$n(r) = (2^{3/2}/3\pi^2) \left[\gamma + \sqrt{(-\gamma)^2 + E_F + v_{Z,p}(R) + (1-1/\epsilon)Zp/R - V(r)} \right]^3 \quad r \leq R \quad (39)$$

where γ is a definition for $1/\pi\sqrt{2}$. In the rest of space, from R to infinity, the electron density is given by

$$n(r) = n = (2^{3/2}/3\pi^2) \left[\gamma + \sqrt{\gamma^2 + E_f} \right]^3 \quad r \geq R \quad (40)$$

where, in the TFD approximation, $E_F = (1/2)k_F^2 - k_F\gamma\sqrt{2}$, only the positive square-root solution of (20) is retained as this is the physical choice. Formally, the TF versions of (39) and (40) are recovered when the exchange effect is neglected ($\gamma \rightarrow 0$). The nonlinear TFD screening equation follows from (21) and (39). Together they give

$$\nabla^2 V(r) = (2^{7/2}3\pi) \left\{ \left[\gamma + \sqrt{\gamma^2 + E_F} \right]^3 - \left[\gamma + \sqrt{(-\gamma)^2 + E_F + V(R) - V(r)} \right]^3 \right\} + 4\pi\rho_a(r) \quad r \leq R. \quad (41)$$

For $r \geq 0$, the screened potential has the same form shown already in (26). The boundary conditions associated with (41) are the same as those stated in the previous section for the TF equation.

Linearization [19] of (41) entails a binomial expansion in which the square of $[V(R) - V(r)]/(\gamma^2 + E_F)$ is neglected in comparison with unity. The resulting equation is a replica of the linearized TF equation, with the difference that q_0 appearing in (29) is replaced by q where

$$q = q_0 \sqrt{k_F / (k_F - \gamma\sqrt{2})}. \quad (42)$$

Thus, the linearized TFD solution follows immediately from (32)–(34) by simply using q in place of q_0 in these equations. Remarks made in the concluding paragraph of the previous section concerning limiting cases are also valid in the present context. Linear and nonlinear TFD results are displayed numerically in subsection 4.2.

4. Screened potentials for ions of silicon, phosphorus and sulphur

4.1. Linear and nonlinear TF screened potentials

It is straightforward to formulate a strategy for solving the TF equations numerically. In the linearized theory, this involves only a routine for finding the zeros of the function given by the left-hand side of (34), thus securing the screening radius and the screened potential of (32). Another routine is needed to solve (25) and (41) numerically in conjunction with associated boundary conditions. This paper works with a scheme which rewrites a nonlinear second-order differential equation as two first-order equations. A third first-order differential equation is added for the purpose of finding R and the nonlinear screened potential in terms of an initial value problem. Such routines are readily found in many numerical software references including the one used here [21].

In forming the electron-gas model semiconductor it is assumed, for reference, that one host ion Si^{4+} is not included in the smearing out of the positive ion cores of the host crystal. It remains fixed at the origin and is screened like an impurity ion by the valence-electron gas. When an isocoric impurity ion enters the system, it is assumed to do so with one or fewer valence electrons and substitute for the Si^{4+} ion. In this way, the same number of valence electrons is maintained in the gas. Computations are reported here for Si^{4+} , P^{5+} and S^{6+} in silicon ($\epsilon = 11.94$, $k_F = 0.96$). Since the electronic cores of P^{5+} and S^{6+} are isoelectronic with the core of S^{4+} , the former have larger p and smaller α values.

For each impurity ion, the bare potential $v_{Z,p}(r)$ is calculated from (9) and (13). The corresponding screened potential for $r \geq R$ is given by (26). For $r \leq R$, linear and nonlinear screened potentials follow from the numerical procedures referenced above. Figure 1(a)–(c) shows $rV(r)$ against r for Si^{4+} , P^{5+} and S^{6+} and corresponding point charges +4, +5 and +6 in silicon. Each of these figures contains six curves, the lower (upper) three of which are associated with the statistical (point-charge, Zp) model of the impurity. The former (latter)

converge at $r = 0$ to $-Z$ ($-Zp$) in agreement with previous remarks. In these figures, dashed curves refer to bare ion potentials ($V(r) \rightarrow v_{Z,p}(r)$); dotted (solid) curves give the results of nonlinear (linear) TF screening. In the long-range limit, the dashed curves converge to $-Zp$, while the dotted and solid curves approach $-Zp/\epsilon$. All potentials are negative, monotonically increasing functions of r . The general trend seen in these figures is that nonlinear screening is more effective than the linear-screening approximation. This difference, first noted for a point charge [5], is here evident for statistical atomic models, and also has been shown for other impurity pseudocharges and corresponding pseudopotentials [11–13].

Table 4. Linear and nonlinear TF and TFD screening radii (au) for various ions and their point charge limits in silicon. Linear results are in parentheses.

Ion	TF	TFD
+4	3.732 (4.275)	3.110 (3.495)
+5	3.658 (4.275)	3.057 (3.495)
+6	3.593 (4.275)	3.011 (3.495)
Si ⁴⁺	0.666 (1.554)	0.618 (1.252)
P ⁵⁺	0.606 (1.422)	0.564 (1.151)
S ⁶⁺	0.538 (1.274)	0.502 (1.038)

Table 4 reports linear and nonlinear screening radii in silicon for the silicon and donor ions in table 3, including their point-charge limits. For comparison, both TF and TFD radii are compiled here. Screened potentials for these various ions in the TFD approximation are presented in subsection 4.2. A perusal of either TF or TFD results reveals some interesting features. (i) Linear and nonlinear screening radii for statistical defects exhibit the same property as noted for their point-charge limits, that is, the latter are correspondingly smaller, especially so for large charge in the point-charge case. (ii) For point charges, linear (nonlinear) radii are charge-independent (dependent). In the former case, this is clearly shown by (37). (iii) For statistical defects, linear and nonlinear radii are functions of the nuclear charge Z and the degree of ionization p . In the linear case this is evident from (34). These radii and their corresponding differences decrease as the degree of ionization decreases. (iv) TFD screening radii are smaller than their TF counterparts, indicating more effective screening in the TFD approximation. A measure of the magnitudes of these various screening radii may be visualized by comparing them with the nearest-neighbour distance, 4.44 au, in silicon.

4.2. Linear and nonlinear TFD screened potentials

The computational methods referred to in the previous section apply, *in toto*, for various values of Z and p , to the TFD screening equations. With q_0 replaced by q , the roots of (34) give the linear radii R . In turn, these are employed in (32), modified by the replacement referenced here, to secure the linearized screened potentials for $r \leq R$. As in the linearized TF approximation, (26) applies in the exterior region $r \geq R$. Nonlinear TFD screened potentials, for $r \leq R$, follow from the numerical solution of (41). Figure 2 shows $rV(r)$ against r for the same set of ions and corresponding point charges in silicon, as before. These figures are described in the same manner as in the previous section. To avoid going through a repetitious discussion of the results, suffice it to say, again, that nonlinear screening is more effective than linear screening.

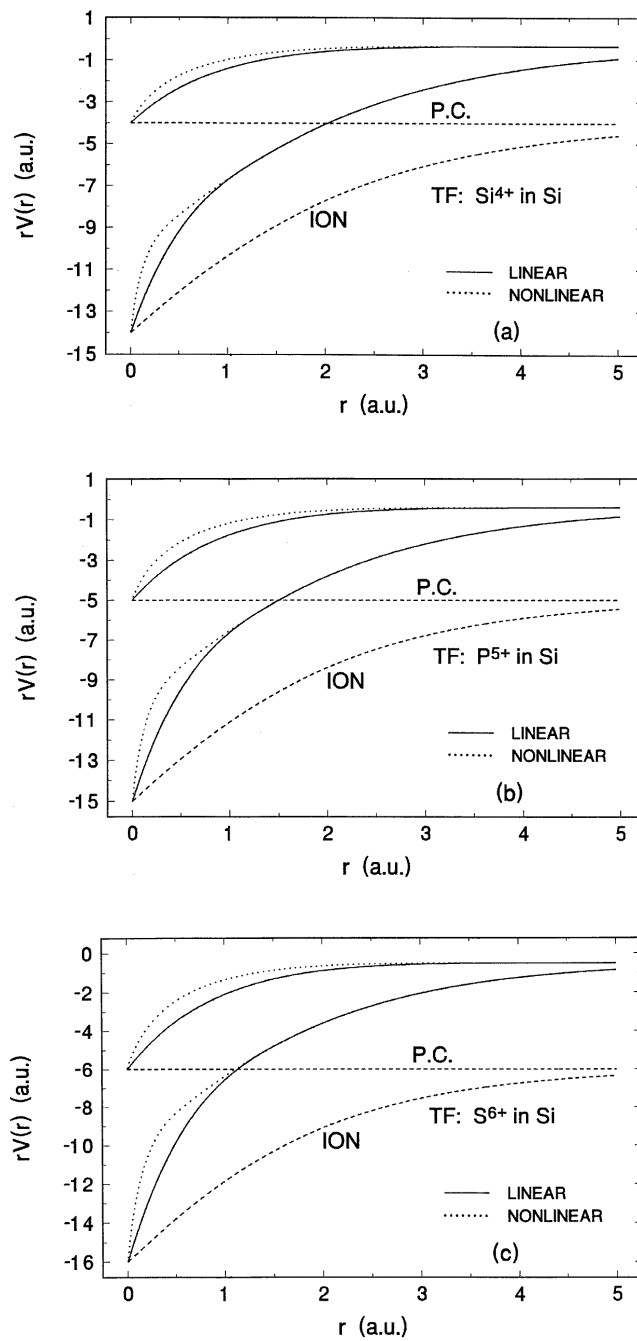


Figure 1. A comparison of linear (solid curves) and nonlinear (dotted curves) TF screened potentials for statistical impurities and their point-charge limits in silicon as follows: (a) Si^{4+} ; (b) P^{5+} ; (c) S^{6+} . The dashed curves represent corresponding bare potentials of point charge (P.C.) and ION.

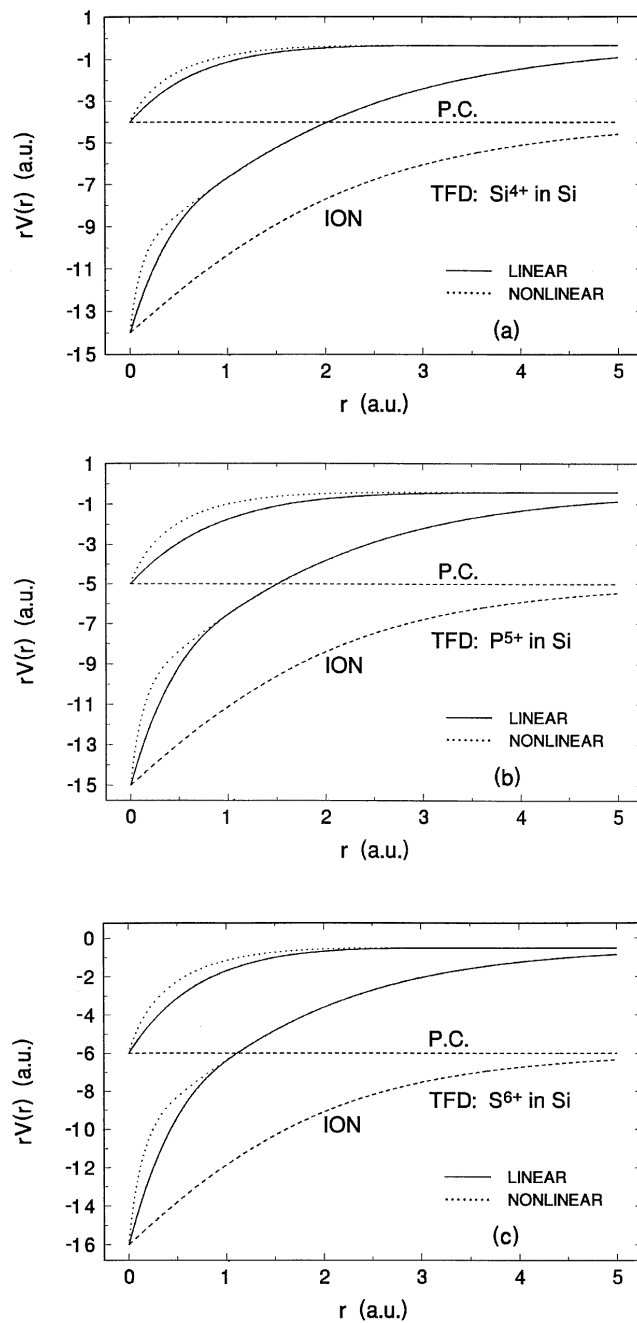


Figure 2. A comparison of linear (solid curves) and nonlinear (dotted curves) TFD screened potentials for statistical impurities and their point-charge limits in silicon as follows: (a) Si^{4+} ; (b) P^{5+} ; (c) S^{6+} . Dashed curves represent corresponding bare potentials of point-charge (P.C.) and ION.

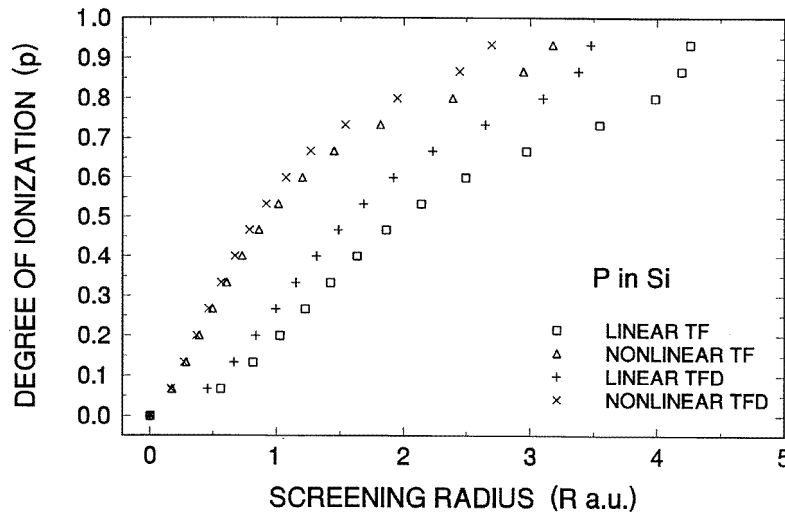


Figure 3. A comparison of linear (squares, TF; pluses, TFD) and nonlinear (triangles, TF; crosses, TFD), screening radii R against the degree of ionization p for a statistical model of phosphorus in silicon. (See also [22]).

To compare the two sets of solutions obtained from the TF and TFD theories, figure 3 shows the degree of ionization p against the screening radius R for phosphorus in silicon. Fifteen values of p , ranging from the neutral atom ($p = 0$, $N_a = 15$) to the hydrogen-like atom ($p = 0.933$, $N_a = 1$), and corresponding R -values, for linear and nonlinear TF and TFD solutions, are included in this illustration. The absence of screening ($R = 0$) is consistent with a neutral atom ($p = 0$). This is verified, for example, in the linear approximation by (34). For a given value of p , the statistical atom or ion is effectively screened, i.e., smaller radii are obtained in the following order of approximation: linear TF, linear TFD, nonlinear TF, and nonlinear TFD [22]. The same trend is found for the point ion except when its charge is less than $+7$, in which case linear TFD and nonlinear TF are interchanged in this sequence. For a given TF-type approximation, it is noted that the screening radii and the degree of ionization are related monotonically, the former reaching its maximum value in the point-charge limit of full ionization. Finally, figure 4 shows a sequence of nonlinear TFD potentials with p as parameter. The solid and short-dash-long-dash curves correspond to the limiting cases of a neutral atom ($p = 0$, $R = 0$) and a fully ionized atom ($p = 1$, $R = 2.731$), respectively. The other curves, in ascending order, are associated with five values of p (0.067, 0.20, 0.333, 0.467, and 0.60) and corresponding R (0.165, 0.368, 0.564, 0.785, and 1.071).

5. Concluding remarks

This paper considered analytical and numerical TF-type solutions of the dielectric screening problems that arise when a model impurity donor atom or ion is embedded in a semiconductor-like valence electron gas with the use of the variational statistical approximation of the bound impurity electrons. Theoretical results for ions of silicon and isocoric donors in silicon have been derived, tabulated, and plotted in parallel with corresponding point-charge limiting cases. It was found that the exponential charge

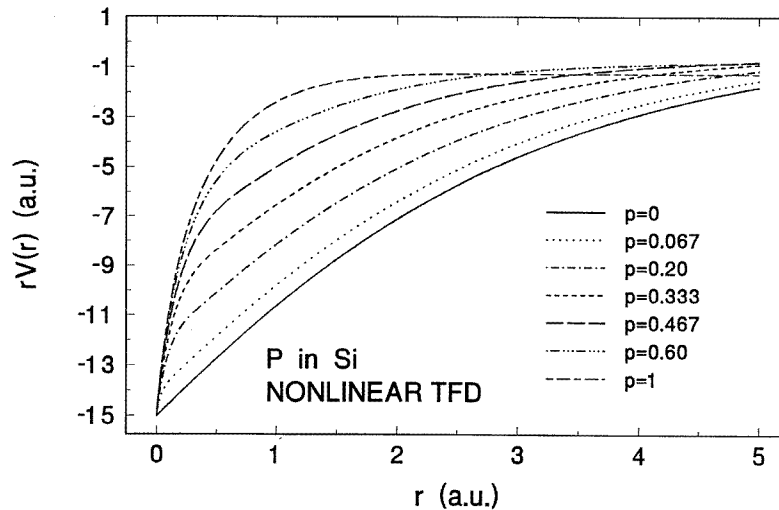


Figure 4. A comparison of nonlinear TFD screened potentials, parametrized by the degree of ionization p , for a statistical model of phosphorus in silicon. The solid curve and the short-dash-long-dash curve represent the neutral atom and the fully ionized atom, respectively. The other curves, in ascending order, are associated with increasing values of p .

distribution describing the electronic ground state of the impurity yields good results for the total internal energy of the free ions and neutral atoms. Given the donor (Z , p) and the host semiconductor (k_F , ϵ), the present formulation leads to linear and nonlinear screened impurity potentials with no adjustment of parameters. It is noted, however, since (4) does not involve a discrete summation, that p may be treated formally as a continuous variable. Figure 3 already reflects this possibility for p and, thus, R . Whereas the present work is concerned with the screening of individual bare impurity potentials, consistent binding energy calculations entail the screening of the difference between the bare impurity and host potentials, as shown, for example, in [11] and [13] where various charge and pseudocharge core distributions are used. The case of an interstitial donor is different in that only the bare impurity potential is screened.

For economy of presentation, this paper has focused on the screening of three model ions and their point-charge limits. It is clear that other host crystals and substitutional or interstitial impurities are readily incorporated in the present framework. Parallel calculations of the TF and TFD screening of other single donors and double donors have been carried out with similar results. In the case of isocoric impurities, where the difference between the bare potential or the donor and the host is small, the conventional effective-mass theory is a convenient approach to the binding energy problem [1]. For nonisocoric donor impurities, the difference between corresponding bare potentials shows considerable deviation from the point-charge model. Generalized effective-mass theories have been developed to handle this case and the special case of isocoric donors [1, 2, 13]. Another study is planned to report on the results of applying these formulations of the binding energy problem when the bare potentials of donor and host are based on charge-density distributions given by a variational statistical approximation.

Literature on TF-type screening theory covers linear and nonlinear screening of pointlike donors and acceptors in both elemental and compound semiconductors. The negative point-

ion case is complicated by the possibility of a ‘Coulomb hole’, a physical region inside which the valence electron density vanishes, leaving only the uniform background positive charge. For example, consider substituting (15) with $p < 0$ into (23). It is seen, then, that a sufficiently positive $V(r)$ will drive the term in square brackets negative. To remedy this situation, such a term must be dropped and (25) replaced by an alternative form of screening equation for $V(r) \geq E_F + V(R)$, where the equality holds at the Coulombic-hole radius $r = R$. Thus, there are three distinct regions and corresponding screened potentials surrounding the negative pointlike ion [23]. The occurrence of a Coulomb-hole problem, in the case of extended charge impurities, requires the same manner of treatment outlined here.

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