Genuine converging solution of self-consistent field equations for extended many-electron systems

A.Ya. Shul’man
Institute of Radio Engineering and Electronics of the RAS, 125009 Moscow, Russia
E-mail: ash@cplire.ru

Abstract. Calculations of the ground state of inhomogeneous many-electron systems involve solving of the Poisson equation for Coulomb potential and the Schrödinger equation for single-particle orbitals. Due to nonlinearity and complexity this set of equations, one believes in the iterative method for the solution that should consist in consecutive improvement of the potential and the electron density until the self-consistency is attained. Though this approach exists for a long time there are two grave problems accompanying its implementation to infinitely extended systems.

The first of them is related with the Poisson equation and lies in possible incompatibility of the boundary conditions for the potential with the electron density distribution renewed by means of the Schrödinger equation. Rigorously speaking, it means the iteration process cannot be continued. The resolution of this difficulty is proposed for both infinite conducting systems in jellium approximation and periodic structures. It provides the existence of self-consistent solution for the potential at every iteration step due to realization of a screening effect.

The second problem results from the existence of continuous spectrum of Hamiltonian eigenvalues for unbounded systems. It needs to have a definition of Hilbert space basis with eigenfunctions of continuous spectrum as elements, which would be convenient in numerical applications. It is proposed to insert a limiting transition into the definition of scalar product specifying the Hilbert space. It provides self-adjointness of Hamiltonian and, respectively, the orthogonality of eigenfunctions corresponding to the different eigenvalues. In addition, it allows to normalize them effectively to delta-function and to prove the orthogonality of the ‘right’ and ‘left’ eigenfunctions belonging to twofold degenerate eigenvalues.

1. Problem definition
Ground-state calculations of inhomogeneous many-electron systems involve generally a solving of the Poisson equation for averaged Coulomb potential $u(r)$ at given spatial electron density $n(r)$ and the Schrödinger equation for single-particle orbitals $\psi_E(r)$ in the potential $u_{eff}$ accounting by some approximation for the difference between $u(r)$ and the microscopic local field. In the density functional theory the corresponding set of Kohn-Sham equations for the spin-unpolarized electron gas has the form (in atomic units $|e| = m = \hbar = 1$)

$$-\frac{1}{2} \nabla^2 \psi_E(r) + u_{eff}(r) \psi_E(r) = E \psi_E(r) \tag{1}$$

$$u_{eff}(r) = u(r) + u_{xc}(r) \tag{2}$$

$$\nabla^2 u(r) = 4\pi (N_+(r) - n(r)) \tag{3}$$

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Here \( E \) is the energy eigenvalue of the single-particle Hamiltonian, \( E_F \) is the Fermi energy of the electrons, \( N_+ \) is the density of the positive background, \( u \) is the Coulomb potential energy of the electron, and \( u_{\text{xc}} \) is the exchange-correlation potential energy, which is assumed in the local-density approximation \( u_{\text{xc}}(r) \equiv u_{\text{xc}}[n(r)] \).

Due to nonlinearity and complexity of this set of equations, one believes in the iterative solution procedure that should consist in consecutive improvement of \( u(r) \) and \( n(r) \) until the self-consistency is attained. While this approach exists for a long time and as if were used in many articles there are two grave problems accompanying its applications and pertinent to very background of the iterative method in the case of infinitely extended many-electron systems.

The first of them is related with Poisson equation and lies in possible incompatibility of the boundary conditions for \( u(r) \) with the distribution \( n(r) \) renewed by means of the Schrödinger equation solutions and substituted to the right-hand side of the Poisson equation (3). Rigorously speaking, it means the iteration process cannot be continued. To manage this difficulty there were several empirical techniques suggested (see e.c. [1]) but their shortcomings are either lack of iteration convergence and a transfer to some kind of variation solution instead (see [2], Appendix B), or an appearance of solution instability [3] or a change in the positive charge distribution [1] that violates the derivation conditions of self-consistent field equations as variational equations. In the case of extended but finite systems, the effect may result in the non-physical growth of the electric field far away from the inhomogeneity region [4]. The compliance of obtained solution with true one is an open question in all cases. The suggested approach to deal with this problem are described in Section 2 for systems with Fermi level given at the infinity and in Section 4 for systems with given number of electrons.

The second problem results from the existence of continuous spectrum of Hamiltonian eigenvalues for unbounded systems. It is necessary to have such a definition of Hilbert space with eigenfunctions of continuous spectrum as elements, which would be convenient in numerical applications. A limiting transition to Hamiltonian operator with continuous spectrum by means of the unlimited increase in system size is used to build up mathematically the Hilbert space of singular self-adjointed operators (see e.c. [5]). However, this way is practically inappropriate for inhomogeneous systems.

It is suggested here to introduce a limiting transition into the definition of the scalar product specifying the Hilbert space. The adopted form of the scalar product provides self-adjointness of Hamiltonian operator and, respectively, the orthogonality of all eigenfunctions corresponding to the different eigenvalues. In addition, it allows to normalize them effectively to delta-function and to prove the orthogonality of the "right" and "left" current-carried eigenfunctions belonging to twofold degenerate eigenvalues. This is particularly of the essence for the problem of tunneling through a self-consistent barrier considered as an example in Section 3. Also this approach is implemented to the Bloch wave functions of periodic solids in Section 4.

\[ n(r) = 2 \sum_{E \leq E_F} |\Psi_E|^2(r) \]  (4)

2. Poisson equation and iteration algorithm

Let us illustrate the neutrality problem with one-dimensional Poisson equation given on semi-axis \( z \in [0, \infty) \):

\[ u''(z) = 4\pi \rho(z), \ \rho = N_+(z) - n(z) \]  (5)

The simple integration results in

\[ u'(z) = u'(0) + 4\pi \int_0^z dz_1 \rho(z_1), \]  (6)

\[ u(z) = u(0) + zu'(z) - 4\pi \int_0^z dz_1 z_1 \rho(z_1). \]  (7)
The finiteness condition of \( u(\infty) < \infty \) requires \( \lim_{z \to \infty} z u'(z) = 0 \) and

\[
4\pi \int_{0}^{\infty} dz_1 \rho(z_1) = -u'(0),
\]

\[
4\pi \int_{0}^{\infty} dz_1 z_1 \rho(z_1) = u(0) - u(\infty)
\]

Assuming an energy scale such that \( u(\infty) = 0 \) it is easily to see the existence of the direct relationship between the total charge and a boundary condition for the electric field \( u'(0) \) in Eq.(6) or between the total dipole moment and a boundary condition for the potential \( u(0) \) in Eq.(7). However, the electron density \( n^{(i)}(r) \) in Eq.(4) obtained after the solution of the Schrödinger Eq.(1) at an \( i \)-th iteration step may not satisfy the imposed boundary conditions for the Poisson equation as usually it takes place. In this case there is no possibility to solve the Eq.(5) and the iteration procedure should be stopped.

In the presented approach this difficulty is removed by partition of full density \( n(r) \) in two terms

\[
 n(z) = n_{\text{ind}}[u(z)] + n_{Q}(z),
\]

where \( n_{\text{ind}} \) is defined as a function of the Coulomb potential \( u \) via its relation to the effective potential \( u_{\text{eff}} = u(z) + u_{\text{xc}}[n(z)] \) by the known quasi-classical expression

\[
n_{\text{ind}}(u, n) = \frac{2^{3/2}}{3\pi^2} [E_{F} - u_{\text{eff}}(z, n(z))]^{3/2}
\]

and

\[
n_{Q}(z) = n(z) - n_{\text{ind}}(z)
\]

is named as the quantum correction. Using the definition (10), the Poisson equation (5) can be rewritten in the form

\[
u'' + 4\pi n_{\text{ind}}[u, n_{Q}] = 4\pi(N_{+} - n_{Q}(z)).
\]

If the pair functions \( n(z) \) and \( u(z) \) is the true self-consistent solution of the problem (1-4) then the Eq.(13) is the simply rearranged Eq.(5). However, the Eq.(13) is much more appropriate for the iterative procedure since, due to the screening effect, the induced electron density \( n_{\text{ind}}^{(i)} \) depending on the unknown Coulomb potential provides the existence of self-consistent solution \( u^{(i)}(r) \) at every iteration step and any possible spatial dependence of right-hand side of Eq.(13).

It is useful to note that the expression (11) is a good approximation of the solution of Schrödinger equation for the smooth part of the \( u_{\text{eff}} \) and produces the true screening of the long-range part of the Coulomb potential since the \( n_{\text{ind}} \) is found simultaneously with \( u \) in the course of self-consistent solution of the Poisson equation. The rest short-range variations of the density \( n(z) \) are exactly described by \( n_{Q}(z) \), which is to be found in the usual iterative cycle after the solution of Schrödinger equation. This is the root cause of the algorithm efficiency. It will be convenient to designate the Eq. (13) as self-consistent Poisson equation.

The full iteration algorithm in the case of the one-dimensional inhomogeneity of the charge distribution can be described now as following

\[
i = 0, 1, \ldots; \quad n_{Q}^{(0)} = 0,
\]

\[
u''^{(i)} + 4\pi n_{\text{ind}}[u^{(i)}, n_{Q}^{(i)}] = 4\pi(N_{+} - n_{Q}^{(i)}(z)),
\]

\[
n_{Q}^{(i)}(z) = n_{\text{ind}}[u^{(i)}, n_{Q}^{(i)}] + n_{Q}^{(i)}(z); \quad u_{\text{eff}}^{(i)}(z) = u^{(i)}(z) + u_{\text{xc}}(n_{Q}^{(i)}(z)),
\]
\frac{1}{2} \psi_i''(z) + \left( \frac{1}{2} k^2 + u_{\text{eff}}(\infty) - u_i(z) \right) \psi_i(z) = 0, \quad (17)

E = \frac{1}{2} (k^2 + k_\parallel^2 + u_{\text{eff}}(\infty)); \quad \Psi_E^{(i)}(r) = \frac{1}{2\pi} \exp(ik_\parallel r_\parallel) \psi_i(z); \quad n^{(i)}(z) = 2 \sum_{E \leq E_F} |\Psi_E^{(i)}(r)|^2, \quad (18)

n^{(i+1)}_Q(z) = n^{(i)}(z) - n_{\text{ind}} \left[ u^{(i)}(z), n^{(i)}(z) \right]. \quad (19)

Here $n^{(i)}_Q(z)$ is the electron density that is self-consistent with the Coulomb potential $u^{(i)}(z)$ at the given quantum correction density $n^{(i)}_Q(z)$. The self-consistent Poisson equation (15) is solved as the boundary problem and the Schrödinger equation (17) is solved as the Cauchy problem.

It needs to say a few words relative to the speciality of the quasi-classical expression (11) for $n_{\text{ind}}$ in the case of density functional approach. Because $u_{\text{xc}}$ depends itself on the electron density the Eq.(11) determines $n_{\text{ind}}$ as the implicit function of the Coulomb potential $u$ when $n_Q$ is known. This function has the physical meaning only under condition $\partial n_{\text{ind}}/\partial u < 0$, which is the stability condition for solutions of the Eq.(15) (see a discussion in [6]).

The validity of the described method for semi-infinite electron systems was examined by calculations of surface properties of simple metals and quantum corrections to the capacity of barrier structures [7]. The expected convergency of the iteration procedure has been obtained and the true self-consistency of the solution has been successfully checked by the Budd-Vannimenus criterion [8].

3. Schrödinger equation and Hilbert space

Difficulties of calculations of wave functions of the continuous spectrum are also present in problems of type of surface properties of metals where one has deal with the semi-infinite inhomogeneous electron gas. Attempts to replace the unbounded system by a system of finite size give rise to serious complications both in analytical and in numerical computations (see e.g. [9]). However, it is more instructive to analyze here the problem by an example of the tunneling in many-electron system.

In this case the questions related to the eigenfunctions pertinent to the continuous spectrum of the Schrödinger equation (1) can be considered with a fair degree of details and usefulness. In such a system the self-consistent Coulomb and exchange-correlation potentials effect inevitably on the shape of the tunnel barrier. The resultant contribution to tunnel current-voltage characteristics can vary from insignificant, as in metal-insulator-metal junctions, up to decisive, as in the Schottky-barrier metal-semiconductor junctions (see [6] and references therein). The essential dependence of the transparency of self-consistent barrier on the energy of tunneling electrons and a reconstruction of the barrier with the applied bias voltage make in principal impossible the use of the tunnel Hamiltonian approach to describe such systems. Therefore it is necessary to formulate some regular scheme of tunnel current calculations that would form also a basis for the numerical realization of self-consistent solution.

3.1. Scalar product and orthonormal basis in single-particle continuous spectrum

Let two parts of system (left - L, right - R) occupy half-space $z < 0$ (metal) and $z > 0$ (semiconductor with a degenerate electron gas and the Schottky barrier), respectively. The effective potential energy $V(z)$ of electrons is considered as independent of coordinates in the $(x, y)$ interface plane. Then the single-particle Hamilton operator is:

\[ \hat{H} = \hat{T} + V(z), \]  

(20)
where \( \hat{T} \) is the kinetic energy operator. Let us assume following conditions for the asymptotes of \( V(z) \)

\[
V(z) \rightarrow V^L, \quad z \rightarrow -\infty; \quad V(z) \rightarrow 0, \quad z \rightarrow \infty.
\]

(21)

In the case of metal-semiconductor junctions one can accept \( V(z) \equiv V^L < 0 \) for \( z \leq 0 \). Due to constraints (21) the eigenfunctions of continuous spectrum \( \hat{H} \) have an oscillating behavior at the left or both infinities depending on the relation between the \( V^L \) and the energy eigenvalue \( E \). The second type eigenstates only give the contribution to the current. Let \( k \geq 0 \) is the wavevector of wave function oscillations at \( z \rightarrow \infty \) and \( q \geq 0 \) is the same at \( z \rightarrow -\infty \). The eigenfunctions obey the equation

\[
\hat{H} \Psi_E(x, y, z) = E \Psi_E(x, y, z)
\]

(22)

and, in view of the translation invariance along the interface, they can be taken in the form

\[
\Psi_E(x, y, z) = C_k \psi_k(z) \exp(i k |r|) / 2\pi,
\]

(23)

where \( E_R = (k^2 + q^2) / 2 \) is the energy spectrum of electrons in the bulk of semiconductor.

The wave functions of continuous spectrum should be normalized to the \( \delta \)-function of quantum numbers. The Eq.(23) provides already the normalization to \( \delta(k_\parallel - k'_\parallel) \) in the lateral plane. This result (2\pi in the denominator) is usually obtained by means of Born-Karman periodic boundary condition in the normalization box. Evidently, the system under consideration has no periodicity in \( z \) direction. To determine the constant \( C \) and to avoid cumbersome calculations of eigenfunctions for a finite-size system mentioned in Section 1 let us define the scalar product of the eigenfunctions by

\[
\langle \psi_k | \psi_{k_1} \rangle = \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} dz \exp(-\epsilon |z|) \psi_k^* (z) \psi_{k_1} (z)
\]

(24)

with the natural definition of the eigenfunction norm by

\[
\|\psi_k\|^2 = \lim_{k_1 \to k} \langle \psi_k | \psi_{k_1} \rangle.
\]

(25)

It is easily to check that the operator \( \hat{T} \) in Eq. (20) and, therefore, Hamiltonian \( \hat{H} \) are self-adjointed relative to the scalar product (24). Hence, the orthogonality of eigenfunctions for different eigenvalues is provided by the self-adjointness of \( \hat{H} \). However, the quantum number \( k \) for current-carrying eigenstates is twofold degenerate. Thus any complex solution \( \psi_k \) and its conjugate \( \psi_k^* \) form the linear-independent pair of solutions. In order to the degenerate pair of eigenfunctions do not violate the necessary orthonormality of the basis in the Hilbert space generated by Hamiltonian \( \hat{H} \) they must be orthogonalized and normalized.

Let us adopt as \( \psi_k \) the wave function describing tunneling from right half-space to the left one and having asymptotes of form

\[
\psi_k^R = C_k^R \left( e^{-ikz} + r_k^R e^{ikz} \right), \quad z \rightarrow \infty; \quad \psi_k^R = C_k^R i_k^R e^{-iqz}, \quad z \rightarrow -\infty.
\]

(26)

The usual continuity condition of the probability flow density

\[
j_k(z) = \psi_k^* (z) \left( \hat{\psi} + \hat{\psi}^+ \right) \psi_k (z) / 2 = \text{const}(z)
\]

gives the relation between amplitudes of the transmission and reflection coefficients

\[
\frac{\partial E^L(q, k_\parallel)}{\partial q} |t_k^R|^2 = \frac{\partial E^R(k, k_\parallel)}{\partial k} \left( 1 - |r_k^R|^2 \right).
\]

(28)
Here \( E^L(q, k_{\parallel}) \) and \( E^R(k, k_{\parallel}) \) are, respectively, the left and right energy spectrum, the velocity operator is defined by \( \hat{\mathbf{v}} = i \left[ \hat{H}, \hat{z} \right] \). The conservation of the total energy \( E \) and the transverse momentum \( k_{\parallel} \)

\[
E^L(q, k_{\parallel}) = E^R(k, k_{\parallel}) = E \tag{29}
\]
determines \( q(k) \) as a function \( k \) and vice versa. Accounting for Eq.(29), the Eq.(28) can be written in more compact form

\[
\frac{1}{\partial q/\partial k} |t_k^R|^2 = 1 - |r_k^R|^2 \tag{30}
\]

The contribution to the normalizing integral (25) is formed by infinite regions of the \( z \) axis where the asymptotic expressions (26) are valid. Using the definition (24) and the relation (30) the value of \( |C_k^R|^2 = 1/2\pi \) can be found that provides

\[
\lim_{k_{\parallel} \to k_{\parallel,1}} \langle \psi^R_k | \psi^R_{k_{\parallel,1}} \rangle = \delta(k - k_{\parallel,1}) \tag{31}
\]

The second normalized solution \( \psi^L_q \) which is linear-independent of \( \psi^R_k \) can be obtained by the similar procedure with the following results

\[
\psi^L_q = C^L_q \left( e^{iqz} + r^L_q e^{-iqz} \right), \quad z \to -\infty; \quad \psi^L_k = C^L_k t^L_k e^{ikz}, \quad z \to \infty, \tag{32}
\]

\[
\frac{1}{\partial q/\partial k} |t^L_q|^2 = 1 - |r^L_q|^2 \tag{33}
\]

\[
|C^L_q|^2 = 1/2\pi, \quad \lim_{q \to q_1} \langle \psi^L_q | \psi^L_{q_1} \rangle = \delta(q - q_1), \quad q = q(k). \tag{34}
\]

The other useful normalization

\[
\lim_{k_{\parallel} \to k_{\parallel,1}} \langle \psi^L_{q(k)} | \psi^L_{q_{\parallel,1}} \rangle = \delta(k - k_{\parallel,1}) \tag{35}
\]

is obtained under condition

\[
|C^L_k|^2 = \frac{\partial q/\partial k}{2\pi}. \tag{36}
\]

To elucidate a question about mutual orthogonality of \( \psi^R_k \) and \( \psi^L_{q(k)} \) it needs to know the interrelation between the pairs \( (t^R_k, r^R_k) \) and \( (t^L_{q(k)}, r^L_{q(k)}) \). The required relations can be found in general form independently of a particular barrier if one realizes \( \psi^L_{q(k)} \) as the linear combination of \( \psi^R_k \) and \( \psi^R_{k^*} \) that gives

\[
t^L_{q(k)} = \frac{1}{\partial q/\partial k} t^R_k, \quad t^L_{q(k)} = -i^R_k (t^R_k/i^R_{k^*}). \tag{37}
\]

Using Eq.(37) one can show that terms like \( \delta \)-function in scalar product \( \langle \psi^L_{q(k)} | \psi^R_{k_{\parallel,1}} \rangle \) cancel each other and hence

\[
\lim_{k_{\parallel} \to k_{\parallel,1}} \langle \psi^L_{q(k)} | \psi^R_{k_{\parallel,1}} \rangle = 0. \tag{38}
\]

The proof of Eq.(38) completes the construction of the orthonormal basis in Hilbert space of single-particle Hamiltonian \( \hat{H} \).
3.2. Electron density and current density

In the case of an equilibrium system the single-particle density matrix is $\hat{\rho} = \hat{\rho}(H)$ and it has only diagonal non-zero elements $\rho^{LL} \equiv F^L$ and $\rho^{RR} \equiv F^R$ in the chosen basis due to the orthogonality relation (38). Therefore, 

$$n(z) = S\hat{p} \hat{n}(z) =$$

$$= 2\int_0^\infty dq \int_{-\infty}^{\infty} dk_{||} F^L \left( E^L(q, k_{||}) \right) \left| \psi^L_k(z) \right|^2 + 2 \int_0^\infty dk \int_{-\infty}^{\infty} dk_{||} F^R \left( E^R(k, k_{||}) \right) \left| \psi^R_k(z) \right|^2. \quad (40)$$

Since the Schottky barrier is completely situated in the semiconductor it is convenient to change the $q$-integration in Eq.(40) by $k$-integration because $k$ is the quantum number of the R-eigenstates. The result is

$$n(z) = 2 \int_0^\infty dk \int_{-\infty}^{\infty} dk_{||} \left\{ F^L \left( E^R(k, k_{||}) \right) \left| \psi^L_k(z) \right|^2 + F^R \left( E^R(k, k_{||}) \right) \left| \psi^R_k(z) \right|^2 \right\}. \quad (41)$$

Here the subindex $q(k)$ in $\psi^L$ was changed by $k$ to recall the necessity to use the normalization (35)-(36).

The diagonal elements $F^L$ and $F^R$ of the density matrix determine respectively the occupation of L- and R-eigenstates and are described by Fermi distributions. The choice of the L- R-states as the basis allows to account mathematically for the presence of two independent reservoirs of particles (thermostats) in the left and right infinites. The Fermi level $E^L_R$ of each reservoir is determined by the proper neutrality condition far away from the interface and they are different as the bias voltage is applied to the junction. It is important to stress that both $\psi^L_k(z)$ and $\psi^R_k(z)$ states extend to the both infinites and contribute to $n(z)$ at any point. Thus the bias applied changes the position of each Fermi level. Substituting asymptotic expressions (26) and (32) for $\psi^R_k$ and $\psi^L_k$ in Eq.(41) and using the neutrality condition $n(\infty) = N^R_\infty$ we obtain the equation determining the dependence of the Fermi level of electrons in semiconductor on the bias $U = -V$ (compare with Eq.(3.101) in [10])

$$n(z \to \infty) \equiv N^R_\infty + \frac{4}{(2\pi)^3} \int_0^\infty dk \int_{-\infty}^{\infty} dk_{||} \left| \psi^R_k(k, k_{||}) \right|^2 +$$

$$+ \frac{2}{(2\pi)^3} \int_{k_U}^\infty dk \int_{-\infty}^{\infty} dk_{||} \left( 1 - \left| r^R_k \right|^2 \right) \left\{ F^L \left( E^R(k, k_{||}) \right) \right\}.$$

$$\left( 1 - \left| r^R_k \right|^2 \right). \quad (42)$$

Here $V$ is the structure voltage drop, $k_U = \left[ 2 \max(E^L(0, 0) - U, 0) \right]^{1/2}$, $E^L_F = E^R_F - U$. At zero temperature $E^R_F = E^R(k_F)$ and this equation can be transformed into the equation for the Fermi wave vector of the right electrons

$$\frac{k^2_F}{3\pi^2} = N_\infty + 2\text{sgn}(U) \int \frac{dk d^2k}{(2\pi)^3} \left( 1 - \left| r^R_k \right|^2 \right). \quad (43)$$

The index R is suppressed here for short. It is easily to see from Eq.(43) that at $U > 0$ we have $k_F(U) > k_F(0)$ and vice versa as it should be. Under the low barrier transparency (the reflection coefficient is of order of 1) the Eq.(43) can be solved by simple iterative method.\(^1\)

\(^1\) In the case of metal-semiconductor junctions the relative correction to the solution of Eq.(43) due to a shift of the metal $E^F_F$ from the value $E^F_F - U$ by neutrality constraint is of order of $\approx (U/E^F_F)(1 - \left| r^R_F \right|^2)^2$ and can be neglected in calculations of $I - V$ characteristics of real structures with typical values $1 - \left| r^R_F \right|^2 < 10^{-4}$, $U < 1$ eV, $E^F_F \leq 10$ eV. Direct numeric calculations in Ref.[11] have shown that a violation of the equality $\Delta E_F = U$ becomes essential when the barrier height is $\lesssim E_F$ and barrier width is $\lesssim 2\pi/k_F$. 

After the Fermi level is found one can calculate the tunnel current, averaging the current density \((27)\) with density matrix and using the asymptotic representation of the wave functions at \(z \to \infty\). The result is

\[
I(U) = -2e \int_0^\infty \frac{dk}{2\pi} \int \frac{dk_{||}}{(2\pi)^2} \frac{\partial E}{\partial k} \left[ F(E) - F(E + U) \right] \left( 1 - |r_k|^2 \right).
\]

Here \(F(E)\) is the Fermi distribution at \(T \neq 0\), \(e = -1\) is the electron charge and \(E(k, k_{||})\) is the energy dispersion relation of the semiconductor electrons.

4. Many-electron structures with finite number of electrons

4.1. Many-electron atoms and molecules

The neutrality problem of iteration procedure in self-consistent field theory has been considered here for the extended many-electron systems with undetermined number of electrons and the solution is suggested in Section 2. In the case of the finite many-electron systems like atom or molecule the number of electrons is exactly known and the insolubility of iteration equations seems not present. Anyway, the required charge state can be prepared if there is sufficient number of bounded-state levels. However, the question is then transformed into the impossibility to find the Poisson equation solution with a given angle symmetry if the charge density at the right-hand side does not have the desired symmetry. Fertig and Kohn [12] has considered the problem and discussed its source and consequences. But the solution suggested consists in additional artificial constraints on the sought variational solution.

It seems, however, that separation of the induced charge in the self-consistent Poisson equation like it is done in Eq.(13) might also solve the problem in the case of finite Fermi systems. The induced charge can be taken in the form like in the Thomas-Fermi-Dirac theory [13] with correlation potential included.

4.2. Periodic electronic structures and supercells

The spatial periodicity of crystal solids makes possible to replace numeric simulations of infinitely extended system by computations for a finite fragment (cell) supplemented by periodic boundary conditions. To map the preceding analysis of the interrelation between the charge distribution and boundary conditions for Coulomb potential on such a case let us rewrite the Eqs. (6),(7) for the finite interval \((a, b)\)

\[
u'(b) - \nu'(a) = 4\pi \int_a^b dz_1 \rho(z_1),
\]

\[
u(b) - \nu(a) = (b - a)\nu'(b) - 4\pi \int_a^b dz_1 z_1 \rho(z_1).
\]

The periodicity demands the conditions for the total charge \(Q \equiv \int_a^b dz_1 \rho(z_1) = 0\) and the total dipole moment

\[
D \equiv \int_a^b dz_1 z_1 \rho(z_1) = (b - a)\nu'(b)/4\pi
\]

to be fulfilled. In the case of centrosymmetric structure there should be \(\nu'(a) = \nu'(b) = 0\) and therefore \(D = 0\) (see e.g., [14 §§6, 13]). At each \(i\)th iteration step it is easy to provide the neutrality condition \(Q^{(i)} = 0\) for the finite structure with a prescribed ionic charge by filling the necessary number of electronic states after solving the Schrödinger equation. However, the charge distribution with \(D^{(i)} \neq 0\) is the rather likely result that cannot be prevented. In this case the periodic boundary condition for the solution of the Poisson equation can be fulfilled only at \(\nu' \neq 0\) at the boundaries. At the same time the behavior of the potential should be
essential contorted in comparison with a “true” charge distribution at $D = 0$ that produces increasingly distorted charge distribution at the next iteration cycle. In the case of Fourier-series decomposition of the electron density and potential, the discontinuity of the potential at the boundaries entails a growth of the solution $u$ and, therefore, its derivative $u'$ again near the boundaries owing to the Gibbs effect [15].

In the case of two- or three-dimensional cell the Eqs. (45) and (46) should be replaced by

$$\oint_{S_{\text{cell}}} dv_s \cdot \nabla u = 4\pi \int_{\Omega_{\text{cell}}} d\mathbf{r} \rho(\mathbf{r}) \equiv 4\pi Q_{\text{cell}}, \text{ the Gaussian theorem,}$$

$$\oint_{S_{\text{cell}}} dS [v_s \cdot \nabla u - u(v_s \cdot \nabla)] \mathbf{r} = 4\pi \int_{\Omega_{\text{cell}}} d\mathbf{r} \mathbf{r} \rho(\mathbf{r}) \equiv 4\pi \mathbf{D}_{\text{cell}},$$

with the same conclusions as in the one-dimensional case above. Here $\Omega_{\text{cell}}$ and $S_{\text{cell}}$ are the volume and bounding surface of the cell, respectively, $v_s$ is the external unit normal to the cell surface. The formulae (47) and (48) are derived from the Poisson equation with the use of the Green theorem

$$\Delta u(\mathbf{r}) = 4\pi \rho(\mathbf{r}), \quad \int_{\Omega} d\mathbf{r} \Phi \Delta \Psi = \int_{\Omega} d\mathbf{r} \Psi \Delta \Phi + \oint_{S_{\Omega}} dS (\Phi \nabla \Psi - \Psi \nabla \Phi)$$

that requires for proper differentiability of the involved functions and correspondent smoothness of the bounding surface $S$ to be fulfilled [16].

The incompatibility of the boundary conditions with the right-hand-side of the Poisson equation makes the Dirichlet problem as ill-posed one with corresponding strong perturbation of the solution in response to insignificant perturbation of the initial data [17]. This mechanism may be responsible for the observed deterioration of current self-consistent iterative algorithms manifested in the long-wavelength charge instability, which is named as "charge sloshing" [18]-[20].

It is necessary to note that at initial iteration step the solution of self-consistent Poisson equation (13) with the induced electron distribution $n_{\text{ind}}$ defined by Eq.(11) should give a good starting guess for the potential and the valence electron distribution in the cell since they are self-consistent and meet the boundary conditions. However, the expression (11) is evidently inappropriate in the case of crystals with the filled energy bands and it needs to use a next quasi-classical approximation for the induced electron density expressed as a function of derivatives of the potential (see, e.g. [21]).

Let us consider now the application of the results of Sec. 3 to the continuum spectrum of infinitely extended periodic system. The eigenfunctions of single-particle Hamiltonian according to Bloch theorem can be taken in the form

$$\psi_{jk}(\mathbf{r}) = C \exp(i\mathbf{k} \cdot \mathbf{r}) \phi_{jk}(\mathbf{r}),$$

where $\phi_{jk}(\mathbf{r})$ is the cell-periodic part, $j$ is the energy band index, $\mathbf{k}$ is the wave vector, and $C$ is the normalizing constant. The definition of the scalar product like in Eq.(24) by the expression

$$\langle \psi_{jk} | \psi_{j_1 k_1} \rangle = \lim_{\epsilon \rightarrow 0} \int d\mathbf{r} \exp(-\epsilon |\mathbf{r}|) \psi^*_{jk}(\mathbf{r}) \psi_{j_1 k_1}(\mathbf{r})$$

and the eigenfunction norm like in Eq.(25) provides the self-adjointness of single-particle Hamiltonian and results in the orthonormal basis of the Hilbert space with $|C|^2 = (2\pi)^{-3}$

$$\langle \psi_{jk} | \psi_{j_1 k_1} \rangle = \delta (\mathbf{k} - \mathbf{k}_1) \delta_{jj_1}$$
under natural conditions \( \mathbf{k}, \mathbf{k}_1 \in \text{1st Brillouin zone} \) and

\[
\int_{\Omega_{\text{cell}}} d\mathbf{r} |\phi_{\mathbf{k}\mathbf{j}}(\mathbf{r})|^2 = \Omega_{\text{cell}}.
\]  

(53)

The relationships just obtained allow to determine the electron density inside the cell by

\[
n(\mathbf{r}) = 2 \sum_j \int_{\Omega_{\text{BZ}}} \frac{d\mathbf{k}}{(2\pi)^3} |\phi_{\mathbf{k}\mathbf{j}}(\mathbf{r})|^2 \Theta(E_F - E_j(\mathbf{k})),
\]

(54)

where the multiplier 2 takes into account the spin degeneration and \( k \)-integration is taken over the unit cell of the reciprocal lattice that is the first Brillouin zone. Because the volume of the Brillouin zone \( \Omega_{\text{BZ}} = (2\pi)^3 / \Omega_{\text{cell}} \) we have

\[
\int_{\Omega_{\text{BZ}}} \frac{d\mathbf{k}}{(2\pi)^3} = \frac{1}{\Omega_{\text{cell}}}.
\]

(55)

Thus the band filling and the position of the Fermi level can be determined from the neutrality condition

\[
\int_{\Omega_{\text{cell}}} d\mathbf{r} n(\mathbf{r}) = N_+, \quad (56)
\]

where \( N_+ \) is the ion charge of the unit cell.

The expressions (53)-(56) allow to abandon the use of unnecessary Born-Karman boundary condition for the eigenfunctions \( \psi_{\mathbf{k}\mathbf{j}}(\mathbf{r}) \), which limits admissible points in \( k \)-space by the discrete set. As a result, one can calculate the energy bands \( \varepsilon_j(\mathbf{k}) \) of perfect crystal or make integrations over Brillouin zone, using any set of \( k \)-points dictated by selected algorithm [22], and avoid disadvantages of the cell size extension beyond the size of the minimal unit cell to increase the sampling density of \( k \)-points [23].

Similarly, the artificial periodicity of the supercell [19] can be eliminated from the calculations of solid surface or imperfect crystal with a point defect and replaced by asymptotic boundary conditions at infinity for the Coulomb potential and wave functions. This removes the known difficulties introduced in calculations of extended systems by making use the slab [24] or supercell [25]-[26] geometries. In this case the induced charge resulted from the free carriers or nonuniform polarization of the valence electrons should be introduced into the self-consistent Poisson equation using the effective mass approximation or the macroscopic electric susceptibility, respectively.

5. Concluding remarks

The origin of all difficulties with self-consistency listed above is the long-range character of the Coulomb interaction that is responsible for an interdependence of the charge distribution with the boundary conditions on the potential. Thus large-scale self-consistent distributions can only result from the direct solution of the self-consistent Poisson equation itself because the boundary conditions take into account the reaction of distant charges that are exterior ones relative to the considered system. The separation of the induced charge as a function of the potential and the modification of the Poisson equation is only way in order to obtain the self-consistent distributions of potential and charge with due accounting for the boundary conditions.

To elucidate the point in more detail let us consider the electrostatic part of the Kohn-Sham energy functional

\[
E_{\text{es}} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|.
\]

(57)
and the corresponding contribution to the effective potential in the Schrödinger equation [27]

$$u_{es} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$  \hspace{1cm} (58)

At first glance, there is no need for the Poisson equation since Eqs. (57) and (58) give us already the explicit relationships between the necessary quantities and the charge density. However, the function \(1/|\mathbf{r} - \mathbf{r}'|\) in the integrand of the Eq. (58) is the Green function of the Laplace equation with the zero boundary condition at the infinity. The expression (58) is the true solution of the Poisson equation if there are no charges outside the integration region. Evidently, this is not the case for infinitely extended systems or when periodic boundary conditions are specified.

Let us assume that there are two subsystems with non-intersected charge distributions

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r}); \rho_1(\mathbf{r}) \neq 0, \mathbf{r} \in \mathbf{Y}_1; \rho_2(\mathbf{r}) \neq 0, \mathbf{r} \in \mathbf{Y}_2; \mathbf{Y}_1 \cap \mathbf{Y}_2 = \emptyset$$  \hspace{1cm} (59)

and, respectively,

$$\varphi(\mathbf{r}) = \varphi_1(\mathbf{r}) + \varphi_2(\mathbf{r}); \Delta \varphi_{1,2} = -4\pi \rho_{1,2},$$  \hspace{1cm} (60)

where \(\varphi\) is the Coulomb potential. Substituting the expression (59) for \(\rho\) in Eq. (57) and using Poisson equations (60) together with Green theorem (49) we obtain

$$E_{es} = \int_{\mathbf{Y}_1} d\mathbf{r} \rho_1 \varphi + \frac{1}{8\pi} \int_{\mathbf{Y}_1} d\mathbf{r} \varphi \Delta \varphi + \int_{\mathbf{Y}_2} d\mathbf{r} \rho_2 \varphi + \frac{1}{8\pi} \int_{\mathbf{Y}_2} d\mathbf{r} \varphi \Delta \varphi \equiv E_{es1} + E_{es2}.$$  \hspace{1cm} (61)

Now it is possible to consider the total energy \(E_{tot1}\) of the subsystem 1 as the functional of \(\rho_1(\mathbf{r}), \Psi_{E1}(\mathbf{r}), \text{and} \varphi(\mathbf{r})\). Then the necessary conditions of the functional minimum are [27]

$$\frac{\delta E_{tot1}}{\delta \Psi_{E1}^{*}(\mathbf{r})} = 0, \frac{\delta E_{es1}}{\delta \varphi(\mathbf{r})} = 0$$  \hspace{1cm} (62)

that must be supplemented by the expression for the effective potential \(u_{eff1} = \delta E_{es1}/\delta \rho_1 + u_{xc1}\). The first equality gives rise to the Schrödinger equation and the second one is just the Poisson equation. The variation \(\delta \varphi\) and the sought potential \(\varphi\) have to satisfy such boundary conditions that ensure

$$\oint d\mathbf{S} (\varphi \nabla \delta \varphi - \delta \varphi \nabla \varphi) = 0$$  \hspace{1cm} (63)

at the surface confining the region \(\mathbf{Y}_1\) only. It implies that boundary conditions to Poisson equation must be properly fixed during the iterative process. If a realization of the equality (63) at given boundary conditions turns out to be impossible then the separate investigation of two subsystems is incorrect. This derivation shows that the solution of the Poisson equation cannot be replaced by direct variations of Eq. (57)-(58) in the course of searching for the \(E_{tot1}\) minimum for the infinitely extended electronic systems with the periodic or assigned asymptotically at infinity boundary conditions.

It is desirable to add some comment on the widely-used "mixing" method of fight against the charge instability. The very essence of the method lies in the use of some linear combination of results of previous iterative steps to make up the input for the next step. Such an approach is named as "iteration with memory" in the iterative calculus and it is destined to accelerate the convergence rate of the iterative process [28]. But this procedure cannot transform a divergent iteration scheme to convergent one. There are many reasons, including mentioned in the present work, to believe that charge instability observed in simulations of large electronic structures is rather sign of divergency than slow convergency of the simple iteration cycle of Poisson→Schrödinger→Poisson steps. The continuous appearance of new more and more
cumbersome and sophisticated mixing methods during the last three decades is the best evidence of this point of view (see some historic commentary in [1], [18]-[20], [29]). As a rule, the demonstration of the benefit of a new method is accompanied by illustrations of the lack of convergence of the old one as the structure size becomes larger. It is of interest, the mixing scheme based on some handmade modeled screening succeeds relatively [29], although it was constructed on the ground of rather formal mathematical reasoning than the underlying physics discussed here.

It needs also to note that mixing schemes may produce a spurious convergency (see [20], p. 11176). Thus it is necessary to check whether the norm of the functional derivatives $\|\delta E_{es1}/\delta \varphi(r)\|$ and $\|\delta E_{tot1}/\delta \Psi_1^{**}(r)\|$, which are residuals of Poisson and Schrödinger equations, are minimal along with the total energy $E_{tot1}$. Of course, $E_{tot1}$ is the total energy of sufficiently large but finite system that can be approximated by assignment of boundary conditions as in the infinitely extended one.

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