Chapter 18
Cluster Embedding Method with Non-orthogonal Wave Functions for Simulation of Nanodevices

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Abstract Applicability of cluster embedding method with non-orthogonal wave functions for theoretical study of processes in nanodevices has been studied. Processes in nanodevices are treated in the framework of time-dependent DFT. We demonstrate that our cluster embedding method is compatible with DFT Kohn-Sham method and quantum transport theory based on time-dependent DFT. We conclude that the approach for electric current calculation developed for orthogonal wave functions may be applied for non-orthogonal wave functions if we transform the initial equations assuming that overlaps are small ($S^2 \ll S$).

Keywords Embedded molecular cluster model • Non-orthogonal wave functions • Quantum transport theory • Time-dependent DFT • Current in nanodevices

18.1 Introduction

It is expected that nanodevices will bring revolutionary changes into electronics with its all potential applications including monitoring of ecological security. Creation of nanodevices is a rapidly developing field of science and technology. To design nanodevices we should be able to perform their theoretical modeling. One of the approaches to theoretical description of nanodevices is quantum transport theory developed by Gross with co-workers [1–3]. This approach is based on the time-dependent density functional theory (TDDFT) and cluster model.

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When we theoretically describe nanodevices, we have to treat the whole quantum system as two subsystems: a small finite fragment of the system containing a nanodevice (cluster) and the rest of the system containing electrodes. The problem of the "cluster in the field of the rest of the system" is successfully solved in the framework of the embedded molecular cluster (EMC) model [4] with *orthogonal* wave functions. Such cluster embedding methods are well-developed [4–7] and successfully used for quantum-chemical simulations [6, 7].

There are many approaches [8–11] to construction of mutually orthogonal localized one-electron wave functions (Wannier functions). However, non-orthogonal one-electron wave functions of the system can be more localized than orthogonal ones. (See, for example, work of Anderson [12].)

Localization is very important for practical applications, because the expansion of a more localized wave function requires a smaller basis set. If we consider two overlapping electron densities and describe them by mutually orthogonal wave functions, we get wave functions with oscillating "tails" and need additional basis to reproduce these oscillations. But if we permit wave functions to be non-orthogonal, we may describe the overlapping densities by smooth wave functions without oscillations. Therefore, we need no additional basis. It is a significant advantage of non-orthogonal wave functions and it is the reason for a renewed interest in methods based on localized non-orthogonal wave functions. There are some recent approaches of this kind. For example, Kantorovich with co-workers [13] has proposed procedure of obtaining self-consistent localized non-orthogonal one-electron wave functions for perfect crystals. Iwata with co-workers [14] is developing the approach for molecular interaction treatment using Hartree-Fock-Roothaan equations without orthonormality constraints.

These reasons have stimulated us to develop cluster embedding scheme, treating the cluster embedding problem in the framework of one-electron approximation with *non-orthogonal* wave functions [15–18]. We have studied cluster embedding equations obtained in the framework of direct variational approach [15–17], when the total energy of the whole system (cluster + the rest of the system) is expressed in terms of *non-orthogonal* one-electron wave functions and equations for the cluster wave functions obtained *directly from variation* of the total energy expression. We have compared this approach with the approach of the theory of pseudopotentials [16, 18], when the total energy of the system is expressed in terms of *mutually orthogonal* wave functions. In the framework of the theory of pseudopotentials equations for the cluster wave functions are derived under orthogonality constraints and then these equations *are transformed* to obtain non-orthogonal solutions. Working in the framework of the direct variational approach we have proposed embedding equations for the case when mutually orthogonal one-electron wave functions of a cluster are not orthogonal to the wave function of the rest of the system [15, 16]. Using these equations we have developed a modified cluster embedding scheme and have demonstrated that consistent implementation of this scheme may radically reduce boundary effects in the EMC model [15, 19].

Our embedding scheme is based on Hartree-Fock (HF) method. In the last years HF one-electron equations are rarely used. Calculations usually are carried out in the

framework of the density functional theory (DFT) with one-electron Kohn-Sham equations [20, 21]. Moreover, for theoretical modeling of nanodevices we would apply the quantum transport theory based on DFT. Therefore, for our purpose we should generalize our cluster embedding method on the case of DFT Kohn-Sham approach. After this generalization we will study the possibility of combining our cluster embedding method with TDDFT approach of Gross et al. [1, 2] for simulation of processes in nanodevices.

18.2 Cluster Embedding Equations

Considering the system of N electrons within one-electron approximation, we may assume that a many-electron wave function of the system is represented by a single Slater determinant (it corresponds to calculations of an open shell system by the unrestricted HF method). A one-determinant wave function is known to be an invariant with respect to arbitrary non-singular linear transformation of one-electron wave functions (spin-orbitals) included in the determinant [22]. Non-singular transformation of one-electron wave functions keeps one-electron density unchanged [22]. It gives us possibility to transform delocalized one-electron wave functions to localized ones treating our N electron system both on HF and DFT Kohn-Sham levels.

18.2.1 General Scheme for Variation Procedure

If transformation of delocalized one-electron wave functions to localized ones is carried out, we may use ideas of EMC model [4] and divide our N electron system into two subsystems: a cluster of finite size and the remaining system. Then spin-orbitals of the whole electron system $|\Psi_i\rangle$, $i \in$ c + r, may be split into two groups: $|\psi_i\rangle$, $i \in$ c: localized in the cluster region, and $|\varphi_i\rangle$, $i \in$ r: localized in the region of the remaining part of the system. The total energy of many-electron system described by non-orthogonal one-electron wave functions on both HF and DFT Kohn-Sham levels may be presented in the following way:

$$E = \int h(1)\rho(1|2)|_{2=1}d1 + \frac{1}{2}\int g(1,2)\rho(1|1)\rho(2|2)d1d2 + E_{XC}, \tag{18.1}$$

where $\rho(1|2) = \sum_{i,j\in c+r} \Psi_i(1)(S^{-1})_{ij}\Psi_j^*(2)$ is one-electron density and $S_{ij} = \langle \Psi_i \mid \Psi_j \rangle = \int \Psi_i^*(1)\Psi_j(1)d1$ is one-electron wave functions overlapping. Electron coordinates include both spatial and spin variables, integration is carried out on both of them.

The first term in the expression (18.1) is the energy of electron gas in the external potential; $h(1) = T(1) + V(1)$ includes electron kinetic energy operator $T(1)$ and Coulomb (electrostatic) potential $V(1)$ created by the nuclei. The second term in (18.1) is Coulomb (electrostatic) interaction energy of electrons; $g(1,2) = |\vec{r}_1 - \vec{r}_2|^{-1}$ is the operator for interaction between electrons. These two terms are the same for HF method and DFT Kohn-Sham method.

The third term E_{XC} is the exchange-correlation energy of electrons. HF and DFT Kohn-Sham methods differ only in the way of treating this term.

Variation of the total energy (18.1) is the following:

$$\delta E = \int h(1)\delta(\rho(1|2))|_{2=1} d1 + \int g(1,2)\rho(2|2)\delta(\rho(1|1))d1d2 + \delta E_{XC}. \quad (18.2)$$

We are searching for the minimum in the total energy of electron system under condition that the wave functions of the remaining system are known and are not varied. Because wave functions of the remaining system are frozen, $\delta\varphi_i = 0$, $i \in$ r. Hence, electron density variation is

$$\delta(\rho(1|2)) = \sum_{i\in c}\sum_{j\in c+r}(\delta\psi_i(1))\left(S^{-1}\right)_{ij}\Psi_j^*(2) +$$
$$+\sum_{i\in c+r}\sum_{j\in c}\Psi_i(1)\left(S^{-1}\right)_{ij}\left(\delta\psi_j^*(2)\right) + \sum_{i,j\in c+r}\Psi_i(1)\left(\delta\left(S^{-1}\right)\right)_{ij}\Psi_j^*(2). \quad (18.3)$$

According to the definition of the inverse matrix $S^{-1}S = I$, where I is the unit matrix. Therefore, on the one hand, $\delta I = 0$ while on the other hand, $\delta I = \delta(S^{-1}S) = S^{-1}\delta S + \delta(S^{-1})S$. Taking this into account, we get the following formula:

$$\left(\delta\left(S^{-1}\right)\right)_{ij} = -\sum_{k\in c}\sum_{l\in c+r}\left(S^{-1}\right)_{ik}\langle\delta\psi_k \mid \Psi_l\rangle\left(S^{-1}\right)_{lj} -$$
$$-\sum_{k\in c+r}\sum_{l\in c}\left(S^{-1}\right)_{ik}\langle\Psi_k \mid \delta\psi_l\rangle\left(S^{-1}\right)_{lj}. \quad (18.4)$$

18.2.2 HF Approach

For the HF approach, the exchange-correlation energy term contains only the exchange energy:

$$E_{XC} = -\frac{1}{2}\int g(1,2)\rho(1|2)\rho(2|1)d1d2.$$

Its variation is

$$\delta E_{XC} = -\int g(1,2)\rho(1|2)\delta(\rho(2|1))d1d2, \tag{18.5}$$

and for the HF approach, our variation procedure gives the following system of equations [15, 16]:

$$\sum_{l\in c+r}(1-\rho)F|\Psi_l\rangle\left(S^{-1}\right)_{lk} = 0, \quad k \in \mathrm{c}, \tag{18.6}$$

where ρ is one-electron density operator,

$$\rho = \sum_{i,j\in c+r}|\Psi_i\rangle\left(S^{-1}\right)_{ij}\langle\Psi_j|, \tag{18.7}$$

F is Fock operator,

$$F|\psi(1)\rangle = h(1)|\psi(1)\rangle + \int \rho(2|2)g(1,2)|\psi(1)\rangle d2 - \\ - \int \rho(1|2)g(1,2)|\psi(2)\rangle d2. \tag{18.8}$$

Equations 18.6 are obtained by substituting expression (18.4) in the formula (18.3) and formula (18.3) in the expression (18.2) for the total energy variation, taking into account that variation of exchange-correlation energy is given in formula (18.5) and the requirement is that the total energy variation δE is zero for arbitrary variations of the cluster wave functions.

Variational equations (18.6) may be further transformed to eigenvalue and eigenvector problem equations, following the procedure described in our works [15, 16]. As a result, we get the following equations:

$$(1-P_r)F(1-P_r)^{+}|\psi_i\rangle = E_i|\psi_i\rangle, \quad i \in \mathrm{c}, \tag{18.9}$$

where operator P_r is defined in the following way:

$$P_r = \sum_{i\in r}\sum_{j\in c+r}|\varphi_i\rangle\left(S^{-1}\right)_{ij}\langle\Psi_j|. \tag{18.10}$$

Equations 18.9 present not the general, but still, very important case of equations for mutually orthogonal cluster wave functions staying to be non-orthogonal to the rest of the system. Using cluster embedding equations (18.9) and the HF calculation method we have developed a modified cluster embedding scheme and have demonstrated that the consistent implementation of this scheme may radically reduce boundary effects in EMC model [15, 19].

18.2.3 DFT Kohn-Sham Approach

Let us consider what our variation procedure will give us when we use DFT Kohn-Sham approach. The electron gas kinetic energy and the energy of Coulomb interaction among electrons and electrons with the nuclei are the same for HF and Kohn-Sham methods. The only difference is due to the exchange-correlation energy E_{XC}. If we express the variation of the exchange-correlation energy in the local form:

$$\delta E_{XC} = \int V_{XC}(1)\delta(\rho(1|2))|_{2=1}d1, \tag{18.11}$$

where $V_{XC}(1)$ is the hermitean operator, then, considering that the total energy variation (18.2) is zero for arbitrary variations of the cluster wave functions, and taking into account that one-electron density variation is given by formula (18.3) and $\delta(S^{-1})$ is given by formula (18.4), we get equations of the form (18.6), where operator F is expressed in the following way:

$$F(1) = h(1) + \int \rho(2|2)g(1,2)d2 + V_{XC}(1). \tag{18.12}$$

Looking at formula (18.12) it is easy to see that operator F is Kohn-Sham one-electron Hamiltonian [20, 21].

There is no need to restrict ourselves by the local form of exchange-correlation functional and by formula (18.11) for its variation. We may consider non-local functionals, too. In this case variation of the exchange-correlation energy can be written in the following way:

$$\delta E_{XC} = \int w(1,2)\delta(\rho(2|1))d1d2. \tag{18.13}$$

If after permutation of coordinates in $w(1,2)$ we get hermitean conjugate: $w(2,1) = w^{+}(1,2)$, then for the non-local exchange-correlation functional our variation procedure will also give Eq. 18.6 with Kohn-Sham Hamiltonian (18.12), where exchange-correlation operator $V_{XC}(1)$ is non-local:

$$V_{XC}(1)|\psi(1)\rangle = \int w(1,2)|\psi(2)\rangle d2. \tag{18.14}$$

It is easy to see that the exchange operator in HF equations is a special case of non-local exchange-correlation operator (18.14) with $w(1,2) = -g(1,2)\rho(1|2)$.

Thus, on both HF and DFT Kohn-Sham levels, variational equations look the same. The only difference is in the form of one-electron effective Hamiltonian F. For the HF method we have Fock operator (18.8). For Kohn-Sham method we have

Kohn-Sham Hamiltonian (18.12), where the exchange-correlation operator may contain both a local part and a non-local part (18.14). Like in the HF case, transformation of variational equations into eigenvalue equations will give Eq. 18.9, because the transformation procedure does not depend on the form of one-electron Hamiltonian F.

We see that cluster embedding equations are the same for HF and DFT Kohn-Sham methods. It means that being developed for the HF method, our embedding scheme is also compatible with DFT Kohn-Sham approach and can be combined with time-dependent DFT.

18.3 Quantum Transport Theory and Cluster Model

In the previous section we have demonstrated that our embedding scheme is compatible with DFT Kohn-Sham approach. Therefore, we can apply EMC model for theoretical study of transport phenomena in quantum systems combining our cluster embedding method with TDDFT, following the ideas of Gross et al. [1, 2]. Our goal is the method for theoretical treatment of processes in nanodevices including calculations of electrical current and other properties significant for electronics.

In the framework of TDDFT, time-dependent one-electron density is constructed from Kohn-Sham one-electron wave functions:

$$\rho(r,t) = \sum_j \chi_j^*(r,t)\chi_j(r,t). \tag{18.15}$$

The wave functions satisfy time-dependent Schrödinger equation:

$$i\dot{\chi}(r,t) = H(t)\chi(r,t), \quad \text{where } \dot{\chi}(r,t) = \frac{\partial\chi(r,t)}{\partial t}. \tag{18.16}$$

Following notations of Gross et al., we consider that a nanodevice consist of the central part $\boldsymbol{C}$, the left electrode $\boldsymbol{L}$, and the right electrode $\boldsymbol{R}$. In EMC model [4] the central part $\boldsymbol{C}$ may be treated as a cluster while the electrodes $\boldsymbol{L}$ and $\boldsymbol{R}$ should be treated as the rest of the system. The time-dependent one-electron wave function may be expressed as a linear combination of the localized in the regions $\boldsymbol{C}$, $\boldsymbol{L}$ and $\boldsymbol{R}$ wave functions with time-dependent coefficients:

$$\chi(r,t) = \sum_n c_n(t)\Psi_n(r) = \sum_{n\in C} c_n(t)\psi_n(r) + \sum_{n\in L+R} c_n(t)\varphi_n(r). \tag{18.17}$$

Substituting this expansion in formula (18.16) and collecting coefficients $c_n(t)$ in column vector $|\chi\rangle$, we obtain the following matrix equations:

$$iS\,\dot{|\chi\rangle} = H|\chi\rangle, \tag{18.18}$$

where S is the overlap matrix, $S_{mn} = \langle \Psi_m \mid \Psi_n \rangle = \int \Psi_m^*(1)\Psi_n(1)d1$, and H is Hamiltonian matrix, $H_{mn} = \langle \Psi_m | H | \Psi_n \rangle$.

The equation system (18.18) can be transformed to the following form:

$$i\,\dot{|\chi\rangle} = \tilde{H}|\chi\rangle, \quad \text{where } \tilde{H} = S^{-1}H. \tag{18.19}$$

The method proposed by Gross et al. [1, 2] can be applied for Eq. 18.19 if non-diagonal parts of effective Hamiltonian matrix between the left and the right electrodes present zeroes: $\tilde{H}_{LR} = \tilde{H}_{RL} = 0$. Let us see whether it is true or not.

We may assume that the wave functions of the left electrode do not overlap with the wave functions of the right electrode, $S_{LR} = S_{RL} = 0$. It is good approximation for the localized wave functions. According to formulas (18.A5, 18.A6, 18.A7, 18.A8, 18.A9, and 18.A10) of the Appendix, under this assumption, inverse overlap matrix takes the following form:

$$S^{-1} = \begin{pmatrix} Q^C & -Q^C S_{CL} S_L^{-1} & -Q^C S_{CR} S_R^{-1} \\ -S_L^{-1} S_{LC} Q^C & S_L^{-1} + S_L^{-1} S_{LC} Q^C S_{CL} S_L^{-1} & S_L^{-1} S_{LC} Q^C S_{CR} S_R^{-1} \\ -S_R^{-1} S_{RC} Q^C & S_R^{-1} S_{RC} Q^C S_{CL} S_L^{-1} & S_R^{-1} + S_R^{-1} S_{RC} Q^C S_{CR} S_R^{-1} \end{pmatrix}. \tag{18.20}$$

Starting from the proposed by Gross Hamiltonian

$$H = \begin{pmatrix} H_C & H_{CL} & H_{CR} \\ H_{LC} & H_L & 0 \\ H_{RC} & 0 & H_R \end{pmatrix}$$

for the non-diagonal part of our effective Hamiltonian $\tilde{H}$ we get

$$\tilde{H}_{CL} = Q^C(H_{CL} - S_{CL} S_L^{-1} H_L), \tag{18.21}$$

$$\tilde{H}_{RL} = -S_R^{-1} S_{RC} Q^C (H_{CL} - S_{CL} S_L^{-1} H_L), \tag{18.22}$$

$$\tilde{H}_{CR} = Q^C(H_{CR} - S_{CR} S_R^{-1} H_R), \tag{18.23}$$

$$\tilde{H}_{LR} = -S_L^{-1} S_{LC} Q^C (H_{CR} - S_{CR} S_R^{-1} H_R). \tag{18.24}$$

We consider that the wave functions of the left electrode do not overlap with the wave functions of the right electrode. Hence, $H_{LR} = H_{RL} = 0$ is a good approximation in our case. The question arises: will $\tilde{H}_{LR} = \tilde{H}_{RL} = 0$ be as good too?

If we assume that the overlaps of the wave functions in the nanodevice central part with the electrodes S_{LC} and S_{RC} are small ($S^2 \ll S$), then, comparing formula (18.21) with (18.22) and formula (18.23) with (18.24) we may conclude that $\tilde{H}_{RL} \ll \tilde{H}_{CL}$ and $\tilde{H}_{LR} \ll \tilde{H}_{CR}$. It means that $\tilde{H}_{LR} = \tilde{H}_{RL} = 0$ is a good approximation. Therefore, for Eq. 18.19 we may apply the method proposed by Gross et al. [1, 2]. It means that using this method we may get the formula for electric current in a nanodevice treating the nanodevice in the framework of our cluster model with non-orthogonal wave functions.

18.4 Summary and Conclusions

We have studied the applicability of our cluster embedding method with non-orthogonal wave functions for theoretical modeling of processes in nanodevices. The processes in nanodevices have been treated in the framework of time-dependent DFT. We have demonstrated that our cluster embedding method based on HF calculation scheme is compatible with DFT Kohn-Sham calculation scheme. Cluster embedding equations remain the same if instead of Fock operator we use Kohn-Sham Hamiltonian. Therefore, our cluster embedding model is compatible with the time-dependent DFT and the quantum transport theory based on TDDFT.

We have treated the possibility to combine our cluster embedding method with the approach for electric current calculation developed by Gross with co-workers [1, 2]. Gross' method implies that the wave functions of the central part of a nanodevice are orthogonal to the wave functions of the electrodes. We have demonstrated that the approach for the electric current calculation developed for orthogonal wave functions can be applied for non-orthogonal wave functions if we transform the initial equations, assuming that the overlaps between wave functions are small ($S^2 \ll S$). Therefore, using this assumption, we can combine our cluster embedding method with the approach of Gross et al. for calculations of the electric current in nanodevices.

Thus, we can conclude that the embedded cluster model with non-orthogonal wave functions is applicable for theoretical modeling of nanodevices.

Appendix

According to the results presented in the Appendices of our works [15–18], when we divide the quantum system into two subsystems and write the matrix of one-electron wave functions overlaps and its inverse matrix in a block form:

$$S = \begin{pmatrix} S_1 & S_{12} \\ S_{21} & S_2 \end{pmatrix}, \qquad S^{-1} = Q = \begin{pmatrix} Q^1 & Q^{12} \\ Q^{21} & Q^2 \end{pmatrix};$$

then, for the inverse matrix we get the following formulas:

$$Q^1 = \left(S_1 - S_{12}S_2^{-1}S_{21}\right)^{-1} = S_1^{-1} + S_1^{-1}S_{12}Q^2S_{21}S_1^{-1}; \tag{18.A1}$$

$$Q^{12} = -Q^1S_{12}S_2^{-1}, \qquad Q^{21} = -S_2^{-1}S_{21}Q^1; \tag{18.A2}$$

$$Q^2 = S_2^{-1} + S_2^{-1}S_{21}Q^1S_{12}S_2^{-1}. \tag{18.A3}$$

We apply these formulas to get S^{-1} when we have three subsystems: $\boldsymbol{C}$ (the cluster with a nanodevice), $\boldsymbol{L}$ (the left electrode), and $\boldsymbol{R}$ (the right electrode). If we choose that subsystem 1 is cluster $\boldsymbol{C}$ then subsystem 2 is the electrodes $\boldsymbol{L}$ + $\boldsymbol{R}$. Therefore, according to our notations,

$$S_1 = S_C, \quad Q^1 = Q^C; \qquad S_2 = \begin{pmatrix} S_L & S_{LR} \\ S_{RL} & S_R \end{pmatrix}, \quad Q^2 = \begin{pmatrix} Q^L & Q^{LR} \\ Q^{RL} & Q^R \end{pmatrix}.$$

Assuming that the wave functions of the left electrode do not overlap with the wave functions of the right electrode, $S_{LR} = S_{RL} = 0$, we have

$$S_2 = \begin{pmatrix} S_L & 0 \\ 0 & S_R \end{pmatrix}, \quad S_2^{-1} = \begin{pmatrix} S_L^{-1} & 0 \\ 0 & S_R^{-1} \end{pmatrix}. \tag{18.A4}$$

According to formula (18.A3),

$$Q^2_{mn} = \left(S_2^{-1}\right)_{mn} + \sum_{i,j\in L+R} \left(S_2^{-1}\right)_{mi} \left(S_{21}Q^1S_{12}\right)_{ij} \left(S_2^{-1}\right)_{jn}.$$

Substituting (18.A4) in the last formula, we get the following results:

$$Q^L = S_L^{-1} + S_L^{-1}S_{LC}Q^CS_{CL}S_L^{-1}, \tag{18.A5}$$

$$Q^R = S_R^{-1} + S_R^{-1}S_{RC}Q^CS_{CR}S_R^{-1}; \tag{18.A6}$$

$$Q^{LR} = S_L^{-1}S_{LC}Q^CS_{CR}S_R^{-1}, \tag{18.A7}$$

$$Q^{RL} = S_R^{-1}S_{RC}Q^CS_{CL}S_L^{-1}. \tag{18.A8}$$

According to formulas (18.A2),

$$Q^{12}_{mn} = -\sum_{i\in L+R} \left(Q^1S_{12}\right)_{mi} \left(S_2^{-1}\right)_{in}.$$

Substituting (18.A4) in the last formula, we obtain the following results:

$$Q^{CL} = -Q^C S_{CL} S_L^{-1}, \quad Q^{CR} = -Q^C S_{CR} S_R^{-1}. \tag{18.A9}$$

In the same way we can get

$$Q^{LC} = -S_L^{-1} S_{LC} Q^C, \quad Q^{RC} = -S_R^{-1} S_{RC} Q^C. \tag{18.A10}$$

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