First-Principles Based Matrix-Green’s Function Approach to Molecular Electronic Devices: General Formalism

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Transport in molecular electronic devices is different from that in semiconductor mesoscopic devices in two important aspects: (1) the effect of the electronic structure and (2) the effect of the interface to the external contact. A rigorous treatment of molecular electronic devices will require the inclusion of these effects in the context of an open system exchanging particle and energy with the external environment. This calls for combining the theory of quantum transport with the theory of electronic structure starting from the first-principles. We present a rigorous yet tractable matrix Green’s function approach for studying transport in molecular electronic devices, based on the Non-Equilibrium Green’s Function Formalism of quantum transport and the density-functional theory of electronic structure using local orbital basis sets. By separating the device rigorously into the molecular region and the contact region, we can take full advantage of the natural spatial locality associated with the metallic screening in the electrodes and focus on the physical processes in the finite molecular region. This not only opens up the possibility of using the existing well-established technique of molecular electronic structure theory in transport calculations with little change, but also allows us to use the language of qualitative molecular orbital theory to interpret and rationalize the results of the computation. We emphasize the importance of the self-consistent charge transfer and voltage drop on the transport characteristics and describe the self-consistent formulation for both device at equilibrium and device out of equilibrium. For the device at equilibrium, our method provides an alternative approach for solving the molecular chemisorption problem. For the device out of equilibrium, we show that the calculation of elastic current transport through molecules, both conceptually and computationally, is no more difficult than solving the chemisorption problem.

I. INTRODUCTION

There has been significant progress in exploring the concept of molecular electronics in recent years, due to the advancement of techniques for characterizing and manipulating individual molecules. The fact that useful devices can be built on the basis of individual molecules, as demonstrated recently by several research groups, has generated wide-spread interest in this new technology. In order to fulfill the true promise of molecular electronics, it is essential to have a thorough understanding of the electronic and transport processes at the single molecule level. This paper represents an attempt to put our understanding of electronic transport through individual molecules on a firm theoretical basis starting from the first-principles.

Traditionally electron transport phenomena are studied in the context of bulk semiconductor devices, the theoretical description of which is largely built upon two premises: (1) the effective-mass equation and (2) the Boltzmann Transport Equation (BTE). The effective-mass equation subsumes the effect of the background periodic lattice potential into an effective Hamiltonian so that the electrons can be considered as particles of effective mass $m^*$ in some applied field. The semi-classical nature of the electronic motion in the bulk devices, on the other hand, allows us to describe the distribution of electrons in response to the applied fields and various scattering mechanisms through the solution of the BTE equation, in much the same way as that of classical point-like particles. Within this approach, the quantum-mechanical effect only comes in through the calculation of band structures and the various

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carrier scattering rates, which provides the input to the solution of the BTE or its approximate versions such as the drift-diffusion equation. As a result, the study of transport phenomena is effectively decoupled from the study of the electronic structures.

The investigation of quantum mechanical transport has begun to flourish during the past two decades, largely due to the advancement in lithographic techniques which has allowed routine fabrication of submicron features in artificially tailored semiconductor heterostructures. Two quantum mechanical effects distinguish such mesoscopic devices from bulk devices, reflecting the wave-particle duality of electron. One is the quantization of electronic charge which evidences itself in coulomb blockade and single-electron transistors. The other is the preservation of quantum phase coherence over a length with size comparable to one of the device dimensions and the resulting energy quantization of confined electrons, which leads to the observation of conductance quantization in transport through a narrow constriction (quantum point contact) and negative differential resistance in double-barrier tunneling structures (resonant-tunneling diode). Transport in these quantum semiconductor structures is now determined by the scattering property and occupation of the electronic eigenstates under an appropriate external potential. On the other hand, electrons in such quantum semiconductor structures are usually confined in one or two directions. The confinement potential, often the electrostatic potential due to a nearby gate or the band discontinuity across the heterostructure interface, varies slowly on the atomic scale. So the electrons can still be described satisfactorily as free carriers using the single-band effective mass approximation and most of the important phenomena in mesoscopic transport can be understood without worrying about the complex electronic structures.

The situation changes dramatically when we consider molecular electronic devices formed by sandwiching a chemically synthesized molecule between two large (on the molecular scale) metallic electrodes. At the molecular scale, the simplicity associated with the effective-mass approximation breaks down and the electronic structure of the system has to be taken explicitly into account. The quantum mechanical scattering problem involved is now the scattering of electrons under the potential of the atomic nuclei and the potential due to other electrons. Understanding transport in such molecular devices therefore requires a knowledge of the microscopic electronic structure of the electrode-molecule-electrode system under both zero and finite bias voltages.

The reduction to molecular scale also brings in another complication in transport study as compared to the mesoscopic systems: treatment of the interface to an external contact. In mesoscopic transport, the details of contact are often not important. The measuring electrodes, taken as infinite electron reservoirs, can either be simulated by reflectionless semi-infinite leads with simple confinement potential at the interface, or only come into the theoretical formulation as an appropriate boundary condition. This is no longer true when the device is of molecular dimension. Since the electrodes can have atomic structures on the surface whose dimensions can be comparable to the molecule, the usually well-defined boundary between the active device region and the contact region is blurred. The interface to the external contact becomes an integral part of the device and the measured electrical characteristics will depend on the details of the atomic arrangement of the contact. Moreover, the electronic and structural properties of the molecule could be modified by the bonding to the measuring contact, bringing in additional complications.

In summary, molecular electronic devices are different from their mesoscopic counterparts in two important aspects: (1) the effect of the electronic structure and (2) the effect of the interface to the external contact. Since the molecule can freely exchange energy and electrons with the electrodes, a rigorous treatment of molecular electronic device can only be achieved including these effects in the context of an open system. As a result, a successful modeling of molecular electronic devices in general calls for combining the theory of quantum transport and the theory of electronic structure starting from first-principles.

There have been numerous theoretical works on transport through individual molecules describing the electronic structure at different levels. Early works have focused on understanding the fundamental mechanisms of transport in the molecular-scale and developing simple theory for the explanation of experimental results. These works thus were centered on model Hamiltonian or semi-empirical theories (notably the Extended-Hückel-Theory of organic molecules and π-electron tight-binding theory of carbon nanotubes). Due to the interdisciplinary nature of molecular electronics, different methods have been used reflecting the authors’ own background which are essentially all equivalent to the Landauer formula of mesoscopic transport as used extensively in our previous works. Such works have provided useful insights into the factors governing transport through individual molecules. However, the usefulness of this approach is limited by its incapability of providing an accurate description of the electronic structure of the molecule and the metal surface involved. Even if a good parameterization exists for the molecule and the bulk separately, the charge transfer and the resulting self-consistent charge and potential relaxation upon the formation of surface and adsorption of the molecule is difficult to treat unless drastic assumptions are made or additional parameters are introduced. In addition, it is difficult to take into account coupling between electrons and molecular vibrational modes which is expected to play an increasingly important role as the molecular size increases.

More recently, Lang and coworkers have presented self-consistent studies of both the conductance and current-voltage characteristics of atomic and molecular wires using the jellium model of a metal surface and the local-
density-approximation (LDA) of density functional theory (DFT) with plane-wave basis set. The calculation proceeds by recasting the Kohn-Sham equation of the electrode-molecule-electrode system into a scattering form using the Lippmann-Schwinger equation and solving the wavefunctions of the scattering state self-consistently. The current is obtained by summing over the contribution of the scattering states which are occupied according to the Fermi distribution in each electrode, following the spirit of Landauer theory. Similar approaches have also been used by Tsukada and coworkers and Guo and coworkers.

The jellium model has an appealing, and physically reasonable, simplicity: all the complexities of the bulk band structure are simply ignored, the effect of the substrate persists only in providing a continuous energy spectrum and the only inhomogeneity left in the metal region is the essential one-dimensional inhomogeneity of the surface itself. However, the jellium model is known to be deficient in describing the electronic density of states and charge density in the region perturbed by the absorbed molecule even for sp-bonded simple metals for which it is more successful, and it cannot answer questions regarding the effect of adsorption geometry and surface relaxation. In addition, it is not applicable to semiconductors and gives serious quantitative error when applied to noble and transition metals where the bonding at the surface is more directional. The use of the plane-wave basis set and the wavefunction formulation also makes it difficult to treat larger molecular systems, to improve the description of the electronic structure and to include other scattering mechanisms.

The objective of this paper is to present a rigorous yet tractable self-consistent matrix Green’s function (MGF) approach for studying transport in molecular electronic devices, through which many limitations of the previous works can be overcome rather conveniently using existing computational techniques. In particular, this allows us to study quantum transport phenomena in nanodevices, where the devices can be characterized as a small active device region connected to electron reservoirs via non-interacting leads. Arbitrary interactions in the device can be included. For non-interacting electron systems in the coherent limit, it reduces to the familiar Landauer theory of mesoscopic transport. The formalism is fairly complete, and it has been applied successfully to studying quantum-mechanical transport phenomena in semiconductor mesoscopic systems such as resonant-tunneling diode and single-electron transistors, usually in combination with a model Hamiltonian and more recently using semi-empirical tight-binding formulations. For molecular electronic devices, within the Born-Oppenheimer approximation, the problem is to calculate the Green’s function of the interacting electron system under the potential of the given configuration of atomic nuclei and external fields.

The study of molecular electronic devices is greatly facilitated by recognizing the fact that due to the metallic screening in the electrodes, the charge and potential perturbation induced by the adsorption of the molecule extends over only a finite region into the electrodes, practically the region enclosing the surface metal atoms closest to the molecule. The charge and potential distributions beyond this region are the same as that of the bimetallic interfaces without the molecules. By expanding the wavefunction in terms of the finite set of local orbital functions, the matrix Green’s function approach allows us to take full advantage of this spatial locality by separating the device into the “extended-molecule” (which includes the molecule itself and the surface atoms perturbed by the molecule) and the electrode region, the description of which can be treated and systematically improved independent of each other. The effect of the external contact can be included rigorously as a self-energy operator, which depends only on the charge and potential distribution outside the “extended molecule” and needs to be computed only once, thereby the computation can be focused on the physical processes occurring in the finite “extended molecule” region. This not only opens up the possibility of using the full repertoire of molecular electronic structure calculation for studying transport in molecular electronic devices, but also allows us to interpret the result of computation using the simple picture of bonding and orbital interactions in molecules, which is necessary for the computation to be useful in terms of understanding rather than pure numbers. Although we will focus on the density-functional theory of the interacting electron system, the formalism doesn’t depend on the particular description of the electronic structure.

In matrix form, the present formulation is equivalent to previous works using semi-empirical tight-binding formulations. The tight-binding formulation provides a conceptually and computationally simple framework for studying transport in systems where a quantum mechanical description of the electronic structure is necessary but the characteristic length scale is much larger than inter-atomic spacing so atomic-scale details are not needed. Example systems include layered semiconductor devices and long carbon nanotubes. The present formulation keeps the simplicity of the tight-binding approach while putting it on a firm theoretical basis. The explicit use of the local basis function in the real space also allows much more detailed understanding of the physical processes through quantities such as the spatial distribution of charge and current densities, which play the fundamental role in density-functional theory and its time-dependent extension. In addition, the ambiguities associated with the semi-empirical formulation, such as the orthogonality of the basis functions used in such formulation and the treatment of self-consistent charge-transfer
many-body perturbation theory following the same procedure as their equilibrium counterpart.

The remainder of this paper is organized as follows: We discuss briefly the use of Non-Equilibrium Green’s Function and density-functional theory for modeling transport in molecular devices in Sec. II. The matrix Green’s function method is described in Sec. III. The self-consistent formulation for device at equilibrium is given in Sec. IV, where we show that our method provides an alternative and generalizing approach to the familiar chemisorption problem in surface physics. The self-consistent formulation for a device out of equilibrium is given in Sec. V. Finally, we devote Sec. VI to conclusions. We use atomic-units throughout this paper unless otherwise noted.

II. NON-EQUILIBRIUM GREEN’S FUNCTION APPROACH FOR MODELING MOLECULAR ELECTRONIC DEVICES

A. Non-Equilibrium Green’s Function Formalism

As current flows, the device is driven out of equilibrium. For systems out of equilibrium, the Green’s function approach can be developed following the same procedure as the equilibrium case, by defining the contour-ordered Green’s function, which we assume that the non-equilibrium term in the Hamiltonian is incorporated into a one-body external potential or its equivalent integral formulation:

\[ G(1,1') = -i \langle T_C [\psi_H(1) \psi^\dagger(1')] \rangle \] (for details, see Haug and Jauho[24]). The Green’s functions involved, besides the retarded and advanced Green’s function,

\[ G^R(1,1') = -i \Theta(t_1 - t_1') \langle \{ \psi_H(1), \psi_H^\dagger(1') \} \rangle, \]
\[ G^A(1,1') = i \Theta(t_1' - t_1) \langle \{ \psi_H(1), \psi_H^\dagger(1') \} \rangle, \] (2.1)

include the correlation function (or the “lesser” Green’s function) which is the central quantity in this formalism

\[ G^<(\vec{r}, t; \vec{r}', t') = +i \langle \psi^\dagger(\vec{r}, t) \psi(\vec{r}', t') \rangle \] (2.2)

Any physical observable can be obtained from \( G^< (\vec{r}, t; \vec{r}', t') \) and its transformations. For example, the quantities of most interest to us, the charge density \( n(\vec{r}, t) \) and the current density \( j(\vec{r}, t) \), are determined as following:

\[ n(\vec{r}, t) = \langle \psi^\dagger(\vec{r}, t) \psi(\vec{r}, t) \rangle = -i G^<(\vec{r}, t; \vec{r}', t') \] (2.3)

and

\[ j(\vec{r}, t) = \frac{1}{2i} \lim_{\vec{r}' \to \vec{r}} (\nabla - \nabla') \langle \psi^\dagger(\vec{r}, t) \psi(\vec{r}', t') \rangle = \frac{1}{2} \frac{\delta \sqrt{\Sigma}(\vec{r}, t; \vec{r}', t')}{\delta \vec{r} - \vec{r}'} \] (2.4)

For steady state, which we consider here, the Green’s functions depend only on the time difference \( t - t' \), which we can Fourier transform to energy. The resulting equations of motion (EOM) of the Non-Equilibrium Green’s function are the Keldysh-Kadanoff-Baym equations[25 26],

\[ \{ E - [-\frac{1}{2} \nabla^2 + V_{ext}(\vec{r})] \} G^R(\vec{r}, \vec{r}'; E) - \int d\vec{r}'' \Sigma^R(\vec{r}, \vec{r}''; E) G^R(\vec{r}'', \vec{r}; E) = \delta(\vec{r} - \vec{r}'), \] (2.5)

and

\[ \{ E - [-\frac{1}{2} \nabla^2 + V_{ext}(\vec{r})] \} G^<(\vec{r}, \vec{r}; E) - \int d\vec{r}'' \Sigma^R(\vec{r}, \vec{r}''; E) G^<(\vec{r}'', \vec{r}; E) = \int d\vec{r}'' \Sigma^< (\vec{r}, \vec{r}''; E) G^A (\vec{r}'', \vec{r}; E) \] (2.6)

or its equivalent integral formulation:

\[ G^<(\vec{r}, \vec{r}; E) = \int d\vec{r}'' \int d\vec{r}''' G^R (\vec{r}, \vec{r}'; E) \Sigma^<(\vec{r}'', \vec{r}'''; E) G^A (\vec{r}''', \vec{r}; E) \] (2.7)

where we assume that the non-equilibrium term in the Hamiltonian is incorporated into a one-body external potential \( V_{ext} \). The interactions are contained in the self-energy operators \( \Sigma[G] \) which can be obtained systematically from many-body perturbation theory following the same procedure as their equilibrium counterpart[27].
By solving the KKB equation for $G^<$, we will be able to calculate the current distribution within the device given the Hamiltonian of the system. However, in general, they involve the evaluation of the full correlation function and the retarded Green’s function in the presence of tunneling into the leads. The usefulness of the above expressions then depends on whether we can devise practical calculation schemes for the single-particle Green’s functions. For molecular-scale devices, the problem is to determine the state of the interacting electron system under the potential of the given atomic nuclei. By separating the term describing the electron interactions into the classical Coulomb part and the exchange-correlation part, we can write down the Keldysh-Kadanoff-Baym equation in the following form:

$$\{E - \frac{1}{2} \nabla^2 + V_{ext}(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}\} G^R(\vec{r}, \vec{r}'; E)$$
$$- \int d\vec{r}'' \Sigma^R(\vec{r}, \vec{r}''; E) G^R(\vec{r}'', \vec{r}''; E) = \delta(\vec{r} - \vec{r}''),$$

$$G^>(\vec{r}, \vec{r}'; E) = \int d\vec{r}'' \int d\vec{r}''' G^R(\vec{r}, \vec{r}''; E) \Sigma^<(\vec{r}'', \vec{r}'''; E) G^<(\vec{r}'', \vec{r}'''; E)$$

(2.8)

where the external potential $V_{ext}$ is the summation of the ionic potential and the potential that drives the system out of equilibrium (see the discussion in sections IV and V later).

B. Density-Functional Theory as the Compromise

For transport through molecular scale devices, the system is characterized by the highly non-equilibrium distribution in the device region, which is driven by contact to two large reservoirs with different electrochemical potential. A truly first-principles treatment of the electronic processes in such non-equilibrium system can only be based on the non-equilibrium version of the many-body perturbation theory such as the quasi-particle theory or perhaps the time-dependent density-functional theory. Such a first-principles theory doesn’t exist yet. Instead, we will work with density-functional theory.

The theory of DFT is based on the study of systems in their ground state or in thermodynamic equilibrium corresponding to the grand canonical ensemble, where the variational formulation of quantum mechanics can be used. For transport through non-interacting systems, the problem can be solved by working in the scattering state representation, since electrons coming from different electrodes are in separate thermodynamic equilibrium at different electrochemical potentials. This is the essence of the Landauer theory of quantum transport. In this case, it may be justified to use density-functional theory to calculate the scattering state wavefunctions which correspond to a two-component system, each characterized by a well-defined thermodynamic ensemble. However, we are not aware of any formal proof of this. In fact, this has been the basis for the use of DFT to calculate current and conductance in the past. For the interacting electron system which DFT attempts to describe, the nonlinear current-voltage characteristic can be obtained only by doing perturbation theory in the part of the Hamiltonian that drives the system out of equilibrium. For these reasons, the use of the DFT formalism, with probably the exception of its time-dependent extension, in transport calculations can only be taken as qualitative in principle, although this doesn’t preclude its quantitative success in practice.

From here on, we will work with density functional theory in our modeling of molecular devices, with the understanding that we approximate the true self-energy operator for exchange-correlation interaction with the DFT description of exchange-correlation potential. We will treat the usage of DFT in a more qualitative sense in that it has a well-defined physical basis, from which we know where it can be expected to succeed and where it may fail and why. Therefore we will put more emphasis on using the results of such calculation for qualitative understanding rather than quantitative. These results may serve as the basis for further improvement as our understanding of molecular devices progresses. The reason for this choice is therefore practical, rather than fundamental.

III. THE METHOD OF MATRIX GREEN’S FUNCTION

Our starting point is the Keldysh-Kadanoff-Baym equation (Eq. (2.8)). Remember that we approximate the self-energy operator $\Sigma$ by the DFT description of the exchange-correlation potential $V_{xc}(\vec{r}, \vec{r}')$ which is an energy independent real operator, but doesn’t need to be local. In particular, we will only assume $V_{xc}$ to be local in the electrode region. It can take any non-local form in the “extended molecule”. There is no “less” self-energy operator $\Sigma^<$ associated with $V_{xc}$. This is in contrast with the true quasi-particle theory where $\Sigma$ is in general non-Hermitian and the corresponding $\Sigma^<$ represents the scattering rates or “life-time” of the quasi-particle state.
Given the exchange-correlation potential \( V_{xc}(\mathbf{r}, \mathbf{r}') \), we can define the single-particle wavefunction \( \psi_\mu(\mathbf{r}) \):

\[
[-1/2 \nabla^2 + V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'] \psi_\mu(\mathbf{r}) + \int d\mathbf{r}' V_{xc}(\mathbf{r}, \mathbf{r}') \psi_\mu(\mathbf{r}') = \epsilon_\mu \psi_\mu(\mathbf{r})
\]  

(3.1)

The retarded Green’s function \( G^R \) is related to \( \psi_\mu(\mathbf{r}) \) through the spectral representation:

\[
G^R(\mathbf{r}, \mathbf{r}'; E) = \sum_\mu \frac{\psi_\mu(\mathbf{r}) \psi_\mu(\mathbf{r}')^*}{E^+ - \epsilon_\mu}
\]

(3.2)

where \( E^+ = \lim_{\delta \rightarrow 0^+} E + i\delta \). We expand the wavefunction in terms of a finite set of local orbital functions:

\[
\psi_\mu(\mathbf{r}) \equiv \sum_i N \ c_{\mu i} \phi_i(\mathbf{r})
\]

(3.3)

where \( \phi_i(\mathbf{r}) \) are atom-centered and decay rapidly to zero away from the corresponding atomic center. We use the symbol \( \equiv \) to indicate the above expansion is exact only for a basis set that is complete. Besides the approximation of single-particle theory, this is the only approximation involved in our matrix Green’s function method. Note the choice of the basis set can be different in different parts of the system, reflecting the different nature of the electronic states in each of them. The Schrödinger-type equation can be transformed into a generalized eigenvalue problem:

\[
\sum_j H_{ij} c_{\mu j} = \epsilon_\mu \sum_j S_{ij} c_{\mu j}
\]

(3.4)

where \( S_{ij} \) is the overlap matrix,

\[
S_{ij} = \int d^3r \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r})
\]

(3.5)

and

\[
H_{ij} = \int d^3r \phi_i^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_j(\mathbf{r}) + \int d^3r \int d^3r' \phi_i^*(\mathbf{r}) V_{xc}(\mathbf{r}, \mathbf{r}') \phi_j(\mathbf{r}')
\]

(3.6)

Instead of solving the above equation, we substitute Eq. (3.3) into Eq. (3.2) and write down the Green’s function in terms of basis function \( \phi_i \):

\[
G^R(\mathbf{r}, \mathbf{r}'; E) \equiv \sum_{\mu, i,j} \sum_{\epsilon_\mu} c_{\mu i} c_{\mu j}^* \frac{\phi_i(\mathbf{r}) \phi_j(\mathbf{r}')}{E^+ - \epsilon_\mu}
\]

(3.7)

where

\[
G_{ij}^R(E) = \sum_{\mu} \frac{c_{\mu i} c_{\mu j}^*}{E^+ - \epsilon_\mu}
\]

(3.8)

It is straightforward to prove that \( G_{ij}^R(E) \) satisfies the following matrix equation:

\[
\sum_k (E^+ S_{ik} - H_{ik}) G_{kj}^R(E) = \delta_{ij}
\]

(3.9)

The above equation is an infinite matrix equation involving orbital functions centered around every atom of the molecular device.

Since we are interested only in the Green’s function in the “extended molecule”, we divide the system into three parts correspond to the left electrode, the right electrode and the “extended molecule” and write down the above equation in block matrix notation:

\[
\begin{pmatrix}
E^+ S_{LL} - H_{LL} & E^+ S_{LM} - H_{LM} & E^+ S_{LR} - H_{LR} \\
E^+ S_{ML} - H_{ML} & E^+ S_{MM} - H_{MM} & E^+ S_{MR} - H_{MR} \\
E^+ S_{RL} - H_{RL} & E^+ S_{RM} - H_{RM} & E^+ S_{RR} - H_{RR}
\end{pmatrix}
\times
\begin{pmatrix}
G_{LL}^R & G_{LM}^R & G_{LR}^R \\
G_{ML}^R & G_{MM}^R & G_{MR}^R \\
G_{RL}^R & G_{RM}^R & G_{RR}^R
\end{pmatrix}
= \begin{pmatrix}
I_{LL} & 0 & 0 \\
0 & I_{MM} & 0 \\
0 & 0 & I_{RR}
\end{pmatrix}
\]

(3.10)
The short-range of the local orbital basis means that for any reasonable molecule size and electrode spacing, we can neglect the inter-electrode block of the Hamiltonian and overlap matrix $H_{LR}(RL)$ or $S_{LR}(RL)$ (also means that we neglect the direct tunneling between the two electrodes) and it is straightforward to solve $G_{MM}^R$ as:

$$G_{MM}^R = \{ E^+ S_{MM} - H_{MM} - \Sigma_L^R(E) - \Sigma_R^L(E) \}^{-1}$$

$$\Sigma_L^R(E) = (E^+ S_{ML} - H_{ML}) G_{LM}^{0R} (E^+ S_{LM} - H_{LM})$$

$$\Sigma_R^L(E) = (E^+ S_{MR} - H_{MR}) G_{RR}^{0L} (E^+ S_{RM} - H_{RM})$$

$$G_{LL}^{0R} = (E^+ S_{LL} - H_{LL})^{-1}$$

$$G_{RR}^{0L} = (E^+ S_{RR} - H_{RR})^{-1}$$

(3.11)

Eq. (3.11) expresses the Green’s function in the molecule in terms of the Hamiltonian matrix element in the same region, with the coupling to the left and right electrode included rigorously in terms of the self-energy operators $\Sigma_L^R(E)$ and $\Sigma_R^L(E)$. Note again that due to the short-range nature of the basis set, only the finite block of $G_{LL(RR)}^R$ is needed for the calculation of $\Sigma_R^L(E)$ corresponding to the orbital basis in the left(right) electrode that have non-negligible overlap with the orbital basis in the extended molecule. So the calculation of $G_{MM}^R$ involves matrix operations only on finite matrices.

The matrix self-energy operator can be taken as the matrix elements of a non-local operator in real space:

$$\Sigma_{L;ij}^R(E) = \int \int d\vec{r} d\vec{r}' \phi_i^*(\vec{r}) \Sigma_{L}^R(\vec{r},\vec{r}') \phi_j(\vec{r}')$$

$$= \sum_{mn} (E^+ S_{ML;im} - H_{ML;im}) G_{LM;mn}^{0R} (E^+ S_{LM;nj} - H_{LM;nj})$$

$$= \sum_{mn} \int d\vec{r} \phi_i^*(\vec{r}) [E^+ - H] \phi_m(\vec{r}) G_{LM;mn}^{0R} \int d\vec{r}' \phi_n^*(\vec{r}') [E^+ - H] \phi_j(\vec{r}')$$

$$= \int d\vec{r} d\vec{r}' \phi_i^*(\vec{r}) \sum_{mn} [E^+ - H] G_{LM;mn}^{0R} \phi_m(\vec{r}) \phi_n^*(\vec{r}') [E^+ - H] \phi_j(\vec{r}')$$

$$= \int d\vec{r} d\vec{r}' \phi_i^*(\vec{r}) \left[ (E^+ - H) G_{LM;mn}^{0R} \phi_m(\vec{r}) \phi_n^*(\vec{r}') \right] [E^+ - H] \phi_j(\vec{r}')$$

with the equation for $\Sigma_L^R$ taking the same form.

Using the analytic continuation rules of Langreth, we can write down the corresponding “lesser” self-energy matrix as:

$$\Sigma_{L;ij}^<(E) = \int d\vec{r} d\vec{r}' \phi_i^*(\vec{r}) \Sigma_{L}^{<}(\vec{r},\vec{r}') \phi_j(\vec{r}')$$

$$= \sum_{mn} (E^+ S_{ML;im} - H_{ML;im}) G_{LM;mn}^{0<} (E^+ S_{LM;nj} - H_{LM;nj})$$

(3.13)

Since the left electrode in taken to be in thermodynamic equilibrium, we have $G_{LL}^{0<}(E) = i(G_{LL}^{0R}(E) - G_{LL}^{0A}(E)) f(E - \mu_L)$ and therefore:

$$\Sigma_{L;ij}^<(E) = i(\Sigma_{L;ij}^R - \Sigma_{L;ij}^A) f(E - \mu_L) = i \Gamma_{L;ij} f(E - \mu_L)$$

(3.14)

where $\Gamma_{L;ij} = \Sigma_{L;ij}^R - \Sigma_{L;ij}^A$ and $f(E - \mu_L) = \frac{1}{1 + e^{(E - \mu_L)/T}}$ is the Fermi distribution function. The equation for $\Sigma_L^<$ follows by replacing $L$ with $R$ in the above equation.

Similarly from the kinetic equation Eq. (2.9), we can write down the correlation function in the “extended molecule” in terms of the basis function $\phi_i$ as

$$G^<(\vec{r},\vec{r}'; E) = \sum_{ij} G_{ij}^E(\vec{r}) \phi_i(\vec{r}) \phi_j^*(\vec{r}') = \int d\vec{r}' \sum_{ij} G_{i}^E(\vec{r}) \phi_i(\vec{r}) \phi_j^*(\vec{r}') \sum_{n} \sum_{n} A_{ij}^G(\vec{r}) \phi_n(\vec{r}') \phi_n^*(\vec{r})$$

After rearranging the order of summation and integration and integrating over $\vec{r}'$ and $\vec{r}''$, we have

$$G^<(\vec{r},\vec{r}'; E) = \sum_{ij} \phi_i(\vec{r}) \phi_j^*(\vec{r}') \sum_{n} \sum_{n} A_{ij}^G(\vec{r}) \phi_n(\vec{r}') \phi_n^*(\vec{r})$$

Comparing the coefficients of $\phi_i(\vec{r}) \phi_j^*(\vec{r}')$, we obtain the following matrix equation:

$$G^<(E) = G^R(E) \Sigma^<(E) G^A(E)$$

(3.15)

If there is no inelastic scattering due to the electron-vibronic coupling, we get:
\[ \Sigma^<(E) = \Sigma^R_L(E) + \Sigma^R_R(E) = i\Gamma_L(E)f(E - \mu_L) + i\Gamma_R(E)f(E - \mu_R) \]  

(3.16) since there is no “lesser” self-energy operator associated with \( V_{xc} \). And we can express the correlation function in terms of the distribution in each electrode:

\[ G^<(E) = i[G^R(E)\Gamma_L(E)G^A(E)]f(E - \mu_L) + i[G^R(E)\Gamma_R(E)G^A(E)]f(E - \mu_R) \]  

(3.17) where the products within the brackets are matrix products. Every physical observable of interest can be computed from the matrix correlation function \( G^R_{ij} \). In particular, the current density is:

\[ J(\vec{r}) = \int dEJ(\vec{r};E) = 1/2 \sum_{ij} \int dEG^R_{ij}(E) \lim_{\vec{r}_0 \to \vec{r}} (\nabla' - \nabla)\phi_i(\vec{r})\phi_j^*(\vec{r}') \]  

(3.18)

The terminal current can be calculated numerically by integrating the current density \( J(\vec{r}) \) over the boundary surface between the molecule and the electrodes or any cross sectional area in the “extended molecule” due to the current continuity in the “extended molecule” region. But often it is more useful to compute the terminal current directly from the matrix Green’s function and the matrix self-energy operators. This can be achieved by defining a current operator, as in Caroli et al. and Datta:

\[ I(\vec{r}, \vec{r}'; E) = e/h[H(\vec{r})G^<(\vec{r}, \vec{r}'; E) - G^<(\vec{r}', \vec{r}; E)H(\vec{r})] \]  

(3.19) whose diagonal element gives the divergence of the current density:

\[ I(\vec{r}, \vec{r}; E) = \nabla \cdot J(\vec{r};E) \]  

(3.20)

The current over a surface enclosing the “extended molecule” is written as:

\[ I_{tot} = \int dE \int_S dS \nabla \cdot J(\vec{r};E) \]

\[ = \int dE \int d\vec{r}I(\vec{r}, \vec{r}; E) \]

\[ = e/h \int dE \int d\vec{r} \sum_{ij} [H(\vec{r})G^R_{ij}(E)\phi_i(\vec{r})\phi_j^*(\vec{r}) - G^R_{ij}(E)\phi_i(\vec{r})\phi_j^*(\vec{r})H(\vec{r})] \]

\[ = e/h \int dE \sum_{ij} [H_{ji}G^R_{ij}(E) - G^R_{ij}H_{ji}] \]

\[ = e/h \int dE Tr[HG^<(E) - G^<(E)H] \]  

(3.21)

Now again we have transformed the integral over the coordinates to the matrix equation involving the Hamiltonian and correlation function matrices. From here on the usual derivation using the matrix notation, often used in the second-quantized form or with the semi-empirical Hamiltonian matrix, can be carried through without change and we get the familiar final form for the terminal current in the matrix notation as:

\[ I_{L(R)} = e/h \int dE Tr[\Gamma_L(R)f(E - \mu_{L(R)})A(E) + iG^<(E)]] \]  

(3.22) where \( A(E) = i(G^R(E) - G^A(E)) \) and

\[ I = e/h \int dE Tr[\Gamma_L(E)G^R(E)\Gamma_R(E)G^A(E)][f(E - \mu_L) - f(E - \mu_R)] \]  

(3.23) where

\[ \Gamma_L(E) = i(\Sigma^R_L(E) - [\Sigma^R_L(E)]^\dagger), \]  

(3.24) \[ \Gamma_R(E) = i(\Sigma^R_R(E) - [\Sigma^R_R(E)]^\dagger) \]  

(3.25) Note that in order to represent the coupling to the electrodes as self-energy operators, it is essential that the “extended molecule” can be described by an effective single-particle theory. In other words, the Hamiltonian of the “extended molecule” in its second-quantized form can be diagonalized. If the Hamiltonian describing the the “extended molecule” contains product over four creation/annihilation operators, the simplified description of the electrodes using self-energy operator breaks down and more complicated expressions are needed.

The above formulae are powerful formal results. Its practical application will depend on the existence of efficient algorithms for accurate evaluation of the Hamiltonian matrix elements over local orbital functions. In practice, a Gaussian-type orbital basis is often used.
IV. SELF-CONSISTENT FORMULATION: DEVICE AT EQUILIBRIUM

A. Model of the molecular device

The present study considers a single molecule sandwiched between two semi-infinite metallic electrodes. In addition, there can be atomic-scale features on the metal surface. In the above formulation of our matrix Green’s function approach, we have not specified the form of the Hamiltonian operator. The specific form of the Hamiltonian comes into play as we consider the self-consistent formulation.

The analysis presented here is based on the spin-extension of Kohn-Sham density-functional (DF) theory [5], which requires the solution of effective single-particle, Schrödinger-like equations with spin-dependent potentials:

\[ H^\sigma \psi^\sigma_i(\vec{r}) = [-\frac{1}{2} \nabla^2 + V_{\text{ion}}(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}^\sigma(\vec{r})] \psi^\sigma_i(\vec{r}) = \varepsilon^\sigma_i \psi^\sigma_i(\vec{r}), \]

where \( \sigma = \alpha, \beta \) and

\[ \rho(\vec{r}) = \rho^\alpha + \rho^\beta, \]
\[ \rho^\alpha(\vec{r}) = \sum_i n_i^\alpha |\psi_i^\alpha(\vec{r})|^2, \]
\[ \rho^\beta(\vec{r}) = \sum_i n_i^\beta |\psi_i^\beta(\vec{r})|^2. \]

Here \( n_i^\sigma \) is the occupation number of the spin orbital \( \psi_i^\sigma \). For our system, the occupation of the eigenstate is governed by the metal Fermi-level \( E_F \), so at low temperature, \( n_i^\sigma = \Theta(\varepsilon_i^\sigma - E_F) \). In the valence-only calculations, the ionic potential \( V_{\text{ion}}(\vec{r}) \) is represented by the non-local pseudopotential \( V_{\text{ps}}(\vec{r}, \vec{r}') \), and the wavefunctions considered are the valence pseudo-orbitals.

The spin-density functional theory (SDF) is the necessary generalization in the presence of magnetic field. If the external potential is only of electrostatic nature, as in our case due to the atomic nuclei, the DF formalism shows that it is possible to determine the system property using a functional that depends on the density alone and not the spin-densities. The main advantage of the SDF over the DF formalism is that the greater flexibility of the SDF formalism introduced by the spin dependence allows us to build more of the physics into the approximate functional. For example, the SDF formalism can give a reasonable description of the bond-breaking in molecules by allowing electrons of different spins to have different spatial density distribution. It also provides a better description of the open-shell molecules in satisfying the requirement (Hund’s rule) that a state with a larger spin tends to be favored energetically. In addition, spin-orbit coupling effects can be included. As a result, the SDF formalism yields significantly better results for molecules and solids than the spin-unpolarized counterpart.

Our use of the SDF formalism here follows that of the unrestricted Hartree-Fock method in molecular calculations [6]. In that we neglect the off-diagonal part of the spin density matrix, so the wavefunctions of the \( \alpha \) and \( \beta \) electrons are decoupled from each other except for the spin-dependence in the exchange-correlation potential [7] for molecules with even number of electrons and singlet spin states, the spin-unrestricted procedure usually leads to the same result as the spin-restricted one. This breaks the rotational invariance in the spin space, and therefore cannot handle situations where the correlation between different spin channels are important, e.g., the formation of a local magnetic moment at the molecule (the Kondo effect) [8]. These effects don’t seem to be important, at least when the coupling between the molecule and the metal is strong.

We will consider both the local spin-density approximation (LSDA) and its generalized-gradient approximation (GGA), the exchange-correlation energy of which takes the following form:

\[ E_{xc}[n_\alpha, n_\beta] = \int d^3 r f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}), \]

\[ \gamma_{\alpha\alpha} = |\nabla n_\alpha|^2, \]
\[ \gamma_{\alpha\beta} = \nabla n_\alpha \cdot \nabla n_\beta, \]
\[ \gamma_{\beta\beta} = |\nabla n_\beta|^2 \]

(4.3)
B. The self-consistent formulation

The starting point of computing the nonlinear transport characteristics of the molecular device, is then to compute the self-consistent charge and potential distribution of the device at equilibrium. This problem is equivalent to calculating the electronic structure of the metal-molecule-metal junction, which is the generalization of the familiar chemisorption problem where we consider the adsorption of a single isolated molecule onto one metal surface. Chemisorption is an important part of surface physics/chemistry and substantial theoretical studies exist in the literature, using the wavefunction or Green’s function formulation, and working in real space or in finite basis expansion or combinations of the two. Our method is similar to these methods in many details. However, the uniqueness of our approach is that we use the finite basis expansion from the beginning, which allows us to separate the entire system naturally into different parts according to their geometrical arrangement, the treatment of which can then be improved independent of each other. This allows us to use existing, well-established techniques for treating the component systems—the molecules and the surface or the bulk—directly in the study of molecular devices with little change.

As explained in the above, instead of solving the Kohn-Sham equation directly, we approximate the single-particle wavefunction by an expansion in a finite set of local orbital basis functions and solve the matrix Green’s function $G_{ij}^\sigma(Z)$ as the solution of the matrix equation:

$$\sum_k (ZS_{ik} - H_{ik}^\sigma) G_{kj}^\sigma(Z) = \delta_{ij} \quad (4.4)$$

Here $Z$ is an arbitrary complex energy. From the spectral representation relation:

$$G_{ij}^\sigma(Z) = \sum_\mu \frac{c_\mu^i c_\mu^* j}{Z - \epsilon_\mu}, \quad (4.5)$$

we can obtain the density matrix $\rho_{ij}^\sigma$, which is defined as

$$\rho_{ij}^\sigma = \sum_\mu n_\mu^i c_\mu c_\mu^* j \quad (4.6)$$

by performing the following contour integration in the complex energy plane:

$$\rho_{ij}^\sigma = \frac{1}{2\pi i} \int_C dZ G_{ij}^\sigma(Z), \quad (4.7)$$

where the integration contour encloses the real energy axis from the energy of the lowest occupied state up to the Fermi energy $E_F$. A typical integration contour is shown in Fig. 2. The advantage of integrating along the complex energy contour is that by moving away from the real energy axis, the sharp features in the density-of-states are smoothed, therefore allowing for accurate integration with a small integration mesh.

The electronic charge density $\rho^\sigma(\vec{r})$, which is needed for the evaluation of $H_{ij}^\sigma$, can be computed according to

$$\rho^\sigma(\vec{r}) = \sum_{i,j} \rho_{ij}^\sigma \phi_i(\vec{r})\phi_j^*(\vec{r}) \quad (4.8)$$

We can also obtain the local density of states (DOS), defined as

$$n^\sigma(\vec{r}, E) = \sum_\mu |\psi_\mu^\sigma(\vec{r})|^2 \delta(E - \epsilon_\mu)$$

$$= \sum_\mu \sum_{i,j} c_\mu^i c_\mu^* j \phi_i(\vec{r})\phi_j^*(\vec{r}) \delta(E - \epsilon_\mu), \quad (4.9)$$

from the following equation:

$$n^\sigma(\vec{r}, E) = -\frac{1}{\pi} \lim_{\delta \to 0^+} \sum_{i,j} \text{Imag} \{G_{ij}^\sigma(E + i\delta)\} \phi_i(\vec{r})\phi_j^*(\vec{r}) \quad (4.10)$$

and the total density of states
\[ n^\sigma(E) = \int d^3r n^\sigma(\vec{r}, E) = -\frac{1}{\pi} \lim_{\delta \to 0^+} \sum_{i,j} \text{Imag}[G^\sigma_{i,j}(E + i\delta)]S_{ji} = -\frac{1}{\pi} \text{Tr}\{\text{Imag}[GS]\} \]  

(4.11)

We can also obtain the projection of the total density of states into the molecular region as

\[ n^\sigma_{Mol}(E) = -\frac{1}{\pi} \text{Tr}\{\text{Imag}[GS]_{Mol}\} \]  

(4.12)

where the trace is taken with respect to the orbital indices of the molecule. The transmission coefficient through the molecule is determined from:

\[ T(E) = \text{Tr}\{\Gamma_L G^R \Gamma_R G^A\}, \]
\[ \Gamma_L = i(\Sigma^R_L - (\Sigma^R_L)^\dagger), \]
\[ \Gamma_R = i(\Sigma^R_R - (\Sigma^R_R)^\dagger). \]  

(4.13)

From here on, we avoid writing down explicitly the spin indices unless otherwise noted, with the understanding that we need to solve the Green’s function corresponding to each spin direction and the total transmission is the summation over the two spin channels.

The self-consistent computation is greatly simplified by realizing that due to the metallic screening within the electrode, the charge and potential perturbation induced by the adsorption of the molecule extends over only a finite region into the electrodes, practically only the region including the surface metal atoms closest to the molecule.

The charge and potential distributions beyond this region are the same as that of the bimetallic interfaces without the molecules. It is this region—the molecule plus the perturbed surface atoms—that enters the above matrix Green’s formulation and is called the “extended molecule”. The computation of the Green’s function of the left and right electrodes then depends only on the charge and potential distribution of the bimetallic interfaces, which can be calculated separately and need to be calculated only once. Note that in this formulation we have neglected the long-range charge perturbation to the metal surface due to the presence of nonzero electric field in the “extended molecule”. This long-range charge perturbation could be important if we want to compute quantities that increase with distance such as the dipole moment associated with the adsorbed molecule. Since we are mostly interested in the electrostatic potential in the “extended molecule” region which is inversely proportional to distance, no significant error will be introduced by neglecting these long-range charge perturbations.

The device characteristic is determined only by the electronic processes in the finite “extended molecule” region. In the MGF formalism, the effects of the contacts enter in two different ways: (1) as the infinite electron source and drain, the contacts inject electrons into and absorb electrons from the molecule, the occupation of the single-particle states within which is set by the electrochemical potential of the contacts. The self-energy operators describe this interaction between the molecular states with the continuum of states in the contacts, which of course depends on the band structure of the metal. (2) as the boundary condition, the charge and potential distribution in the “extended molecule” must join the charge and potential distribution deep within the interior of the contacts. Since the metallic electrodes are described well by the local-density-approximation, we assume only the exchange-correlation term in the “extended molecule” region may have a nonlocal form. So only the determination of the electrostatic potential is constrained by the long-range coulomb interaction such that it joins to the bulk value at regions beyond the “extended molecule”. The exchange-correlation potential depends only on the charge distribution in the “extended molecule” region, so it is irrelevant when we discuss the constraint of the boundary condition on potential imposed by the presence of the electrodes.

Note that the unperturbed part of the contacts are the semi-infinite crystal with the perturbed surface atoms removed. Its Green’s function \( G_{LL(R)}^{0,R} \) can be calculated from that of the semi-infinite crystal using the “reduced space” idea of Williams, Feibelman and Lang, which is essentially a two-component version of our MGF equation (Eq. 3.10). In this approach, we deal with the following two-by-two block matrix equation:

\[
\begin{pmatrix}
E^+ S_{LL(R)} - H_{LL(R)} & E^+ S_{L(R)P} - H_{L(R)P} \\
E^+ S_{PL(R)} - H_{PL(R)} & E^+ S_{PP} - H_{PP}
\end{pmatrix} \times \begin{pmatrix}
G_{S;LL(R)}^R & G_{S;L(R)P}^R \\
G_{S;PL(R)}^R & G_{S;PP}^R
\end{pmatrix} = \begin{pmatrix}
I_{S;LL(R)} & 0 \\
0 & I_{S;PP}
\end{pmatrix}
\]

(4.14)

where we have separated the semi-infinite surface into two parts with \( P \) denoting the region of the semi-infinite surface that is included in the “extended molecule” and \( L(R) \) denoting the region of the semi-infinite surface corresponding to the unperturbed part of the left (right) electrode. From the above equation, we get:

\[ G_{LL(R)}^{0,R} = (E^+ S_{LL(R)} - H_{LL(R)})^{-1} \]
\[ = G_{S;LL(R)}^R - G_{S;L(R)P}^R(G_{S;PP}^R)^{-1}G_{S;PL(R)}^R \]

(4.15)
we note that satisfactory description of the charge and potential distribution in the bulk can be obtained without the calculation while allowing meaningful quantitative comparison between theory and experiments. In particular, electrodes will need to be added to the bulk values for electrostatic potential calculations. This greatly simplifies from different materials, an additional linear potential term corresponding to the work function difference across the "extended molecule", a good description of the contact can be obtained if we calculate the potential and the Green’s determined by the local interaction between the molecule and the neighbor surface atoms that are included in the region, .i.e., outside the "extended molecule". Since the exact nature of the contact is almost never known needs to be performed range of admolecule perturbation, from which we can also get the corresponding surface Green’s function.

In the above formulation, the “reference potential” \( V^0 \) and the “reference charge density” \( \rho^0 \) are those obtained from the self-consistent calculation of the bimetallic interfaces (without the molecule). In this way, \( \Delta V^{eff} \) is nonzero only within the “extended molecule”. \( \Delta V^{ion} \) is the ionic potential due to the atomic ions in the isolated molecule plus any changes in the ionic potential that may be caused by the surface reconstruction and/or the modification of the molecular structure upon the adsorption onto the surfaces (any such structural relaxation is taken as occurring only in the “extended molecule”).

Since the MGF formalism allows us to calculate the Green’s function of the “extended molecule” given the potential within the same region, we want to transform the above equation into a form that better suits our purpose. Since the exchange-correlation potential in the “extended molecule” doesn’t depend on the charge distribution outside this region, we don’t need to include it in the choice of \( V^0 \). This will also allow us to use different approximation schemes for the exchange-correlation potential in different part of the total system. Instead of calculating the change in the potential, we take a more constructive approach to get the potential directly and write down the Hamiltonian of the “extended molecule” as:

\[
H^\sigma = -\frac{1}{2} \nabla^2 + V^0(\vec{r}) + V^{ion}(\vec{r}) - V^{ion,0} + \int d^3\vec{r} \frac{\rho(\vec{r}) - \rho^0(\vec{r})}{|\vec{r} - \vec{r}'|} + V_xc(\vec{r}),
\]

where

\[
V^{ext,0}(\vec{r}) = V^0(\vec{r}) - V^{ion,0} - \int d^3\vec{r} \frac{\rho^0(\vec{r})}{|\vec{r} - \vec{r}'|}
\]
performed fully self-consistent calculations, for example, using the overlapping-atomic-potential model or tight-binding parameters. This approximate treatment of contacts can always be improved without affecting other parts of the calculation.

Given the Hamiltonian of Eq. (4.19), the matrix elements entering the Fock matrix in Eq. (3.6) can then be separated into the core, Coulomb and exchange-correlation matrix as usual in the molecular density-functional calculations:

\[ H_{ij}^c = H_{ij}^{core} + J_{ij} + F_{xc,ij} \]

where \( H_{ij}^{core} \) is the summation of the kinetic-energy, the ionic potential and the “external potential” matrices, and \( J_{ij} \) is the Coulomb matrix:

\[
J_{ij} = \sum_{kl} \rho_{kl}(i|j|kl),
\]

\[
\rho_{kl} = \rho_{kl}^\alpha + \rho_{kl}^\beta
\]

where we have used the conventional notation for the electron repulsion integrals (ERI). For exchange-correlation energy of the functional form as Eq. (4.3), the exchange-correlation potential and their matrix elements are given by:

\[
V_{xc}^\alpha[\rho^\alpha, \rho^\beta] = \frac{\partial f}{\partial \rho^\alpha},
\]

\[
F_{xc,ij} = \int V_{xc}^\alpha(\bar{r})\phi_i(\bar{r})\phi_j(\bar{r})d^3\bar{r}
\]

and similarly for \( V_{xc}^\beta \) and \( F_{xc,ij}^\beta \).

At this point the outline of the calculation of the equilibrium property of molecular devices using the self-consistent matrix Green’s function method is complete:

1. A judgment is made as to the set of atomic sites on the electrode surfaces which are included into the “extended molecule”.
2. A judgment is made as to the set of atomic sites on the electrode surfaces which are considered to be coupled to the “extended molecule”.
3. A basis set \( \phi_i(\bar{r}) \) is chosen for the atoms within the “extended molecule”.
4. The Hamiltonian matrix of the unperturbed part of the electrodes and also the coupling between them and the “extended molecule” is determined from either the self-consistent bulk charge/potential distribution or from an approximate construction such as the tight-binding model. The corresponding surface Green’s function and self-energy matrix is then calculated at a preselected numerical energy integration mesh.
5. The “external potential” \( V_{ext,0} \) and its matrix elements \( V_{ij}^{ext,0} \) are calculated either from a self-consistent surface/bulk calculation or by approximate construction. Also calculated are the matrix elements of the kinetic energy operator and the ionic potentials. Together they give the core Hamiltonian matrix.
6. An initial guess is made for the spin density matrix \( \rho_{MM}^\alpha \) of the “extended molecule”. A natural choice for the initial guess is the density matrix of the free “extended molecule”. An even better one is the density matrix of the free “extended molecule” under the action of the “external potential” \( V_{ext,0} \).
7. Calculate the Coulomb and exchange-correlation part of the Fock matrix. For Gaussian-type orbital (GTO) basis, the Coulomb matrix elements can be calculated analytically. The existence of efficient algorithms for this operation is the main strength of GTO over other choices of local atomic orbital functions such as Slater-type orbitals (STO). The calculation of the exchange-correlation matrix elements must be performed numerically over the 3-d molecular volume due to the rather complicated form of the exchange-correlation potential (Eq. 13).
8. Eq. (14) is then solved to obtain \( G_{MM}(Z) \) for each \( Z \) of the numerical integration mesh. The corresponding density-matrix \( \rho_{MM}^\alpha \) is then recalculated via the numerical integration over the complex energy contour using Eq. (17).
9. Repeat step (7) and (8) until the input density or Fock matrix agrees with the output density or Fock matrix within a preset range. Due to the long-range nature of Coulomb interaction and the “heterogeneous” character of the “extended molecule”, strong oscillations often occur in the iteration process, therefore acceleration methods for self-consistent convergence are generally needed for the self-consistent process to converge.
10. The electronic density of states, charge transfer, electrostatic potential and transmission coefficients are then calculated and analyzed.

Note the above procedures are almost identical to that of calculating the electronic structure of the free “extended molecule” under some external potential \( V_{ext,0} \), the only exception being that at each iteration, instead of diagonalizing the Fock matrices, we integrate along the complex energy contour to obtain the density matrix \( \rho_{ij} \) for the next iteration.
V. SELF-CONSISTENT FORMULATION: DEVICE OUT OF EQUILIBRIUM

A. The meaning of the voltage drop

Given the charge $\rho^0$ and the electrostatic potential $V_{\text{ex}}^0$, the computation of the Hamiltonian matrix $H_{\text{ex}}^0$ is the same as that of the free “extended molecule” under the “external” potential $V_{\text{ext},0}(\vec{r})$. The self-energy operator, depending only on the charge and potential distributions obtained from the separate surface/bulk calculations and needs to be calculated only once. Since the above step is the computationally most demanding one, it allows us to take advantage of the full repertoire of molecular electronic structure calculations. In practice, this step can be replaced by call to any existing high-quality quantum-chemical software such as Gaussian 98.

The meaning of the voltage drop

To understand the voltage drop, we start by considering the electrostatic potential $V_{\text{ex}}(\vec{r})$ and the charge density $\rho(\vec{r})$. The electrostatic potential is related to the charge density through the Poisson equation:

$$\nabla^2 V_{\text{ex}}(\vec{r}) = \rho(\vec{r}),$$

where $\rho(\vec{r})$ is the charge density. In the symmetric case, since the charge neutrality is related through the Poisson equation:

$$V_{\text{bias}} = V_{\text{ex}} - V_{\text{bias}},$$

the computation of the Hamiltonian

$$H_{\text{ex}}^0 = $$

is the same as that of the free “extended molecule” under the “external” potential $V_{\text{ext},0}(\vec{r})$, which, like the self-energy operator, depends only on the charge and potential distributions obtained from the separate surface/bulk calculations and needs to be calculated only once. Since the above step is the computationally most demanding one in our self-consistent calculation, this allows us to take advantage of the full repertoire of molecular electronic structure calculations. In practice, this step can be replaced by call to any existing high-quality quantum-chemical software such as Gaussian 98.

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B. The self-consistent formulation

Note the equilibrium electrostatic potential \( V_{es}^0 \) is related to the equilibrium charge distribution \( \rho^0 \) through the following equation:

\[
V_{es}^0(\vec{r}) = V_{ext}^0(\vec{r}) + V_{ion}(\vec{r}) + \int d\vec{r}' \frac{\rho^0(\vec{r}')}{|\vec{r} - \vec{r}'|} \tag{5.8}
\]

From Eq. (5.7), the electrostatic potential at nonzero bias \( V_{es}^0 \) is thus:

\[
V_{es}(\vec{r}) = V_{bias}(\vec{r}) + V_{ext}^0(\vec{r}) + V_{ion}(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \tag{5.9}
\]

Defining \( V_{ext}(\vec{r}) = V_{bias}(\vec{r}) + V_{ext}^0(\vec{r}) \), we can write down the Hamiltonian of the molecular device at nonzero bias in the same form as that at equilibrium (Eq. (4.19)):

\[
H^\sigma = -\frac{1}{2} \nabla^2 + V_{ext}(\vec{r}) + V_{ion}(\vec{r}) + \int d^3r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{ext, \sigma}(\vec{r}), \tag{5.10}
\]

Again \( V_{ext} \) can be regarded as the electrostatic potential due to the charge distribution outside the “extended molecule”. The addition of \( V_{bias} \) reflects the change in the boundary condition in this electrostatic potential.\[88\]

For device out of equilibrium, the central quantity is the matrix correlation function \( G^<(E) \), which is computed using the KKB equation:

\[
G^<(E) = i[G^R(E)\Gamma_L(E)G^A(E)]f(E - \mu_L) + i[G^R(E)\Gamma_R(E)G^A(E)]f(E - \mu_R) \tag{5.11}
\]

The self-consistent calculation then proceeds by computing the input density matrix to the next iteration from the correlation function computed in the current iteration:

\[
\rho(\vec{r}) = \sum_{ij} \rho_{ij}\phi_i(\vec{r})\phi_j^*(\vec{r}) = \int \frac{dE}{2\pi i} G^<(\vec{r}, \vec{r}; E) = \sum_{ij} \int \frac{dE}{2\pi i} G_{ij}^<(E)\phi_i(\vec{r})\phi_j^*(\vec{r}) \tag{5.12}
\]

or in the matrix formulation:

\[
\rho_{ij} = \int \frac{dE}{2\pi i} G_{ij}^<(E) \tag{5.13}
\]

The density matrix is nothing but the energy integration of the matrix correlation function. To see better the physical meaning of this, we divide both sides of Eq. (5.13) by:

\[
A(E) = i[G^R(E) - G^A(E)] = G^R(E)(\Gamma_L(E) + \Gamma_R(E))G^A(E) \tag{5.14}
\]

and get:

\[
-\frac{iG^<(E)}{A(E)} = f(E - \mu_L)\gamma_L + f(E - \mu_R)\gamma_R, \tag{5.15}
\]

where the division of matrices is defined such that \( [\frac{A}{B}]_{ij} = \frac{A_{ij}}{B} \). Since the correlation function \(-iG^<\) describes the number of electrons at energy \( E \) and the spectral function \( A \) describes the density of states at energy \( E \), the above equation essentially says that the probability of the states at energy \( E \) being occupied in the molecule equals the probability of it being occupied in the left electrode multiplying the escape rate \( \gamma_L \) from the left electrode to the

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molecule plus the probability of it being occupied in the right electrode multiplying the escape rate $\gamma_R$ from the right electrode to the molecule.

Note the integration contour appearing in Eq. (5.13) is along the real energy axis rather than in the complex energy plane. Unlike the retarded Green’s function, the correlation Green’s function $G^< (E)$ is not analytic away from the real energy axis. This would have increased significantly the computational cost of the energy integration. However, for energy sufficiently lower than both $\mu_L$ and $\mu_R$, say $E < \mu_{L(R)} - 10kT$, we have $f(E - \mu_{L(R)}) \approx 1$ and Eq. (5.11) reduces to:

$$G^< (E) = i[G^R(E)\Gamma_L(E)G^A(E)] + i[G^R(E)\Gamma_R(E)G^A(E)]$$  \hspace{1cm} (5.16)

Comparing with Eq. (5.14), we have:

$$G^< (E) = iA(E) = -2i\text{Imag}[G^R(E)]$$  \hspace{1cm} (5.17)

Consequently the integration over the energy in Eq. (5.13) can be split into two parts:

$$\rho_{ij} = \frac{1}{2\pi i} \int_C dZ G_{ij}(Z) + \frac{1}{2\pi i} \int_{E_{\text{min}}}^{E_{\text{max}}} dE G^<_{ij}(E)$$  \hspace{1cm} (5.18)

where the first term represents integration along the same complex contour as that in Fig. (2) with the upper energy cutoff replaced by $E_{\text{min}}$ and the second term represents integration along real energy axis from $E_{\text{min}}$ to $E_{\text{max}}$. Here $E_{\text{min(max)}}$ is chosen such that for $E < E_{\text{min}}$, $f(E - \mu_{L(R)}) \approx 1$ and for $E > E_{\text{max}}$, $f(E - \mu_{L(R)}) \approx 0$. The integration along the real energy axis can be performed using fine integration grids since the range of integration is not much larger than $eV$.

It is clear from the above discussion that the only difference between the self-consistent formulation for device out of equilibrium and for device at equilibrium lies in the way of calculating the density matrix (Eq. (5.18)). At nonzero bias, the retarded Green’s function alone is no longer adequate for describing the observable property of the system. Instead, at each iteration, we need to calculate the correlation function from the retarded Green’s function, the energy integration of which gives the input density matrix for the next iteration. *All other procedures remain the same.* After self-consistency is achieved, we can calculate the terminal current using Eq. (3.21) or Eq. (3.22) and also the current density using Eq. (5.18). As a result, calculating current transport in molecular electronic devices is no more difficult than solving a molecular chemisorption problem, both conceptually and computationally.

VI. CONCLUSION

Modeling transport at the molecular scale requires a microscopic knowledge of the electronic structure of both the molecule and the surface which has to be considered in the context of an open system exchanging particles and energy with the external contacts. This complicates substantially the computational procedure and raises new questions about the theoretical basis. Although a first-principles theory of transport at the molecular scale doesn’t yet exist, we have shown that the Non-equilibrium Green’s Function Formalism of quantum transport combined with the density-functional theory of electronic structure provides a sound basis on which further works may be based.

Since the electronic process in such molecular devices is mainly determined by the interaction between the molecule and the surface atoms closest to it, it is highly desirable to separate the treatment of the physical processes in this “extended molecule” region from that in the rest of the system since in general the exact atomic geometry of the contact is not known. In addition, as we have described, the treatment of the contact is best chosen to make the description of the physical processes in the “extended molecule” consistent. This is conveniently dealt with within the matrix Green’s function approach using expansion in finite set of local orbital functions, where the effect of the contacts is taken into account using self-energy operators $\Sigma_{L(R)}$. In addition, by introducing an “external potential” $V^{ext}$ which describes the electrostatic potential due to the charge distribution outside the “extended molecule”, we have shown rigorously that the electronic and transport property of the molecular device can be determined from the electronic processes in the “extended molecule” alone, given the knowledge of $V^{ext}$ and $\Sigma_{L(R)}$. This allows the highly accurate and efficient techniques developed for molecular electronic structure computation to be used for studying transport through molecules with little change. We believe such an approach will greatly accelerate theoretical/computational research on molecular electronic devices.

Besides the computational advantage, the use of the local orbital basis sets and the techniques of molecular electronic structure theory will also greatly facilitate the interpretation of the result of computation using the language of qualitative molecular orbital theory which has provided the rationalization of the intuitive picture of bonding and
orbital interactions in molecules. Traditionally such discussion has relied on semi-empirical theories such as the Extended Hückel type of theory. The advancement of density-functional theory in quantum chemistry has made the use of self-consistent Kohn-Sham orbitals in such molecular orbital theory highly desirable. For molecular electronic devices, the orbitals involved are those of the molecule and the surface atoms closest to it. Much of the physics can then be understood in terms of the orbital interactions after the effect of self-consistent charge transfer and potential distribution has been included. Such an approach has been taken recently by the present authors to study the equilibrium property of the molecular device formed by the phenyldithiolate molecule bridging two gold contacts. Further work on nonlinear transport through molecules is under investigation.

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FIG. 1. Illustration of typical molecular devices.

FIG. 2. Integration contour in the complex energy plane. The cutoff energy $E_0$ should be below the lowest occupied states of the system considered.
FIG. 3. Program flow chart of the self-consistent Matrix Green’s function (MGF) approach to molecular device calculation. Note that besides the introduction of $V_{ext}$ and the self-energy operator $\Sigma_{L(R)}$, the only difference with the conventional molecular electronic structure calculation lies in the calculation of the density-matrix given the molecular Fock matrix. See the discussion in the main text.
FIG. 4. (a) Schematic illustration of the electrostatic potential profile $V_0^{es}$ in the absence of applied bias. $V_0^{es}$ joins to the bulk values in the interior of the contacts. The exact value of $V_0^{es}$ should be obtained from the self-consistent calculation of the metal-molecule-metal junction as described in the main text. (b) Schematic illustration of the electrostatic potential profile $V_{es}$ in the presence of applied bias $V$. Note the changes in the boundary condition of $V_{es}$ under bias. (c) Difference in the electrostatic potential $\delta V_{es} = V_{es} - V_0^{es}$ in the presence and absence of applied bias $V$. Full line shows the linear “applied bias” $V_{bias}$ while dotted line shows the true $\delta V_{es}$ including the effect of the self-consistent charge redistribution $\delta \rho$ under bias (see Eq. (5.5) and discussions thereon).