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# Hubbard operators approach to the transport in molecular junctions

Tomasz Kostyrko[1] and Bogdan R. Bułka[2]
[1]*Institute of Physics, A. Mickiewicz University, ul. Umultowska 85, 61-614 Poznań, Poland*
[2]*Institute of Molecular Physics, Polish Academy of Sciences, ul. M. Smoluchowskiego 17, 60-179 Poznań, Poland*

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We present a procedure for calculation of transport characteristics of molecular junctions. It is based on the nonequilibrium Green's functions and exploits the Hubbard operators, which allows us to treat formally exactly all electron correlations within the molecule. The procedure reproduces exact results in the limiting cases: for a weak molecule-lead coupling and for high temperatures (i.e., Coulomb blockade limit), and for the limit of vanishing electron interactions. Between these limits the method can be applied as an interpolating scheme. As an example of an application we present the results obtained for a two-atom molecule.

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## I. INTRODUCTION

A great effort is focused on electronic transport through a single molecule attached to metallic electrodes, which is the crucial issue for further progress in the molecular electronics.[1,2] The future of this new field depends, however, on solving some basic problems. From the experimental side the main issue is to achieve an unambiguous contacts between the molecule and the electrodes.[3] An important aspect of theory is to take into account a geometry of chemical bonds, a contribution of various molecular orbitals as well as Coulomb interactions between electrons at the molecule. The electronic spectra of a single molecule can be determined with a high precision by quantum chemical procedures. For the molecule connected to electrodes the problem is much more complex, because one has to apply methods known in solid state calculations of the electronic structures, for example, the density functional theory combined with an empirical or an *ab initio* tight-binding approach,[4] which can be extended for a nonequilibrium situation with the electric current flowing through the molecule. The commonly used codes, which are based on a one-electron approximation and use a mean-field-type approach, neglect many-body effects.[5]

Electron interactions can lead to new phenomena, for example, to the Coulomb blockade (CB). The effect was extensively studied in single quantum dots and in systems of coupled quantum dots (artificial atoms and molecules).[6–11] In order to study the CB effect in the coherent transport the nonequilibrium Green's function technique[12] within an approximation, which includes many-electron states[9,10,13] is being used. For simple cases, e.g., for a two-atomic molecule, one can determine the current treating exactly all many-electron states and the molecule-electrode coupling to the lowest order. These approximations correspond to high temperatures, when electrons at the molecule are weakly correlated with electrons in the electrodes. At a low temperature one has to include in calculations higher-order tunneling processes between the molecule and the electrodes, which can lead to the Kondo resonance.[14,15] These calculations of electronic transport were performed for simplified models, which are far from real molecules. The methods are complex and it will be difficult to incorporate them into ab initio codes.

In this work we apply the technique of the Hubbard operators,[16] for a determination of the transport characteristics of molecular systems. The elegant description of simple systems was performed by Kikoin and Avishai[14] and Kuzmenko *et al.*[15] Using the symmetry of the Hubbard operators (the symmetry of the many-electron space) they were able to study the Kondo resonance for various electron occupancies and geometries of the system. Since charge excitations were neglected in these studies, they are limited to electronic transport at low temperatures and low source-drain voltages (in the limit of the linear response). Fransson and Eriksson[17] used the Hubbard operator technique in the limit of the infinitely strong on-site electron repulsion. They studied the many-electron effects in the current-voltage characteristics, in particular asymmetries in the current-voltage curve and in negative differential conductance. The technique was applied also for magnetic devices to show a role of electronic correlations in electronic transport.[18] It is worth mentioning that the Hubbard operators were also implemented into the slave boson approach and satisfactorily described the Fano resonance for the correlated electron system.[19]

Our purpose in this work is to show how the Hubbard operator method can be used to take into account the charge fluctuations in an arbitrary molecular junction. The problem of the charge fluctuations is important for electronic transport and was studied for simple models.[8,10,13,20,21] For strong Coulomb interactions and a weak molecule-lead coupling one gets the Coulomb blockade effect[8,10] and the negative differential conductance,[20] when radiative relaxation processes are included. Our method is complementary to those used in the past[8,10,20,21] and can be applied in the Coulomb blockade limit (i.e., for the Coulomb interaction $U$ larger than the molecule-electrode coupling $\Gamma$) as well as for the strong molecule-electrode coupling ($\Gamma \gg U$) in the nonlinear transport regime. The method is simpler and more general one than the previous approaches using the decoupling procedure for the equation of motion[6,7,9,13] and therefore we hope that it can be easier implemented in the codes used in calculations for real molecules.

A general model of a molecular junction and a method of computation of the electric current is presented in Sect. II. In Sect. III we present the equation of motion for the Green's functions, which are approximately solved in Sect. IV. In Sect. V we exemplify the application of the method to the two-atom molecule. We show that various charge and spin correlation functions at the molecule can be determined, which allows a study of the influence of many-electron effects on electronic transport. The general conclusions are presented in Sect. VI.

## II. THE MODEL AND COMPUTATION OF THE CURRENT

The general considerations presented in this section hold for the system which can be described using a Hamiltonian defined as

$$\mathcal{H} = \sum_{\alpha} \mathcal{H}_{\alpha} + \mathcal{H}_{M} + \mathcal{H}_{T}. \tag{1}$$

The first part of the Hamiltonian describes noninteracting leads (where $\alpha = L$ for the left lead and $\alpha = R$ for the right lead),

$$\mathcal{H}_{\alpha} = \sum_{k\sigma} \epsilon_{k\alpha} c^{\dagger}_{k\alpha\sigma} c_{k\alpha\sigma}. \tag{2}$$

It is assumed that the one-particle energy in the both leads is uniformly shifted by the bias voltage $V = V_L - V_R$, $\epsilon_{k\alpha} \to \epsilon_{k\alpha}(0) + eV_{\alpha}$. The molecular Hamiltonian $\mathcal{H}_M$ is written quite generally using the diagonal Hubbard operators,[16] $X_{\lambda\lambda}$,

$$\mathcal{H}_{M} = \sum_{\lambda} E_{\lambda} X_{\lambda\lambda}. \tag{3}$$

The Hubbard operators are defined in terms of the exact eigenstates $|\lambda\rangle$ of the isolated molecule, $X_{\lambda\mu} = |\lambda\rangle\langle\mu|$. Both the eigenenergy values $E_{\lambda}$ and the eigenstates are voltage dependent, i.e., they take into account the effect of the external electric field created at the molecule by the bias (or gate) voltage.

The last term in Eq. (1) describes the tunneling of electrons between the molecule and the leads,

$$\mathcal{H}_{T} = \sum_{k\alpha\sigma} (v_{k\alpha} c^{\dagger}_{k\alpha\sigma} d_{\alpha\sigma} + \mathrm{H.c.}). \tag{4}$$

Above, we assumed single-atom contacts with the both leads, $d_{\alpha\sigma}$ is the electron operator for the atom of the molecule contacting with the left (for $\alpha = L$) or the right (for $\alpha = R$) electrode, and $v_{k\alpha}$ is the tunneling (hopping) parameter. In the present paper we restrict ourselves to the single orbital per atom, keeping in mind that the generalization to the multiorbital description is straightforward.

The computation of the current is based on the use of the formula valid generally for the interacting molecular junction with noninteracting leads,[22]

$$I = \frac{ie}{h} \sum_{\sigma} \int d\omega\, \Gamma_L [f_L (G^{r}_{LL\sigma} - G^{a}_{LL\sigma}) + G^{<}_{LL\sigma}]. \tag{5}$$

In Eq. (5), $\mathcal{G}^{r,a,<}$ denotes the retarded, advanced, and lesser Green's function in the site and frequency representation and $\Gamma_L$ stands for the coupling function,

$$\Gamma_{\alpha} = 2\pi \sum_{k} \delta(\omega - \epsilon_{k\alpha}) |v_{k\alpha}|^2, \quad \alpha = L, R, \tag{6}$$

and $f_L$ is the Fermi function for the left lead.

## III. EQUATION OF MOTION FOR THE GREEN'S FUNCTION

In order to obtain the Green's function, we study the more general Green's function defined in terms of the Hubbard operators,

$$\mathcal{G}_{\lambda\lambda',m\sigma} = \langle\langle X^{F}_{\lambda\lambda'} | d^{\dagger}_{m\sigma} \rangle\rangle, \tag{7}$$

where superscript $F$ at the Hubbard operator means the operator reducing number of particles in the system by one (a fermioniclike operator). The Green's function in the site representation can be obtained from the above defined Green's function as

$$\langle\langle d_{j\sigma} | d^{\dagger}_{m\sigma} \rangle\rangle = \sum_{\lambda\lambda'} \langle\langle X^{F}_{\lambda\lambda'} | d^{\dagger}_{m\sigma} \rangle\rangle p^{\lambda\lambda'}_{j\sigma}, \quad p^{\lambda\lambda'}_{j\sigma} = \langle\lambda | d_{j\sigma} | \lambda'\rangle. \tag{8}$$

The retarded Green's function $\langle\langle X^{F}_{\lambda\lambda'} | d^{\dagger}_{m\sigma} \rangle\rangle$ fulfills the following equation of motion (EOM):

$$\begin{aligned}(\omega - E_{\lambda'} + E_{\lambda}) \langle\langle X^{F}_{\lambda\lambda'} | d^{\dagger}_{m\sigma} \rangle\rangle = {} & \langle\{X^{F}_{\lambda\lambda'}, d^{\dagger}_{m\sigma}\}\rangle - \sum_{k\alpha l\sigma'} v_{k\alpha,l} \sum_{\mu'} \langle\langle X^{B2}_{\lambda\mu'} c^{\dagger}_{k\alpha\sigma'} | d^{\dagger}_{m\sigma} \rangle\rangle\, p^{\lambda'\mu'}_{l\sigma'} - \sum_{k\alpha l\sigma'} v_{k\alpha,l} \sum_{\mu} \langle\langle X^{B2}_{\mu\lambda'} c^{\dagger}_{k\alpha\sigma'} | d^{\dagger}_{m\sigma} \rangle\rangle\, p^{\mu\lambda}_{l\sigma'} \\ & + \sum_{k\alpha l\sigma'} v^{*}_{k\alpha,l} \sum_{\mu} \langle\langle X^{B}_{\lambda\mu} c_{k\alpha\sigma'} | d^{\dagger}_{m\sigma} \rangle\rangle\, p^{\mu\lambda'*}_{l\sigma'} + \sum_{k\alpha l\sigma'} v^{*}_{k\alpha,l} \sum_{\mu'} \langle\langle X^{B}_{\mu'\lambda'} c_{k\alpha\sigma'} | d^{\dagger}_{m\sigma} \rangle\rangle\, p^{\lambda\mu'*}_{l\sigma'}. \end{aligned} \tag{9}$$

To obtain the above equation, we differentiated the two-time Green's function with respect to the left time argument and performed the Fourier frequency transform of the result. Here, the bosoniclike Hubbard operators $X^{B}_{\lambda\lambda'}$, $(X^{B2}_{\lambda\lambda'})$ do not change the number of electrons in the state $|\lambda'\rangle$ (reduce the number of electrons in the state $|\lambda'\rangle$ by two).

In order to compute the single particle Green's functions one needs the thermodynamic averages of the anticommutators $\langle\{X^{F}_{\lambda\lambda'}, d^{\dagger}_{m\sigma}\}\rangle$. These averages play a role of the residua of the Green's functions of the molecule in the limit $\Gamma \to 0$. They may be represented in terms of the linear combination of the "bosonic" Hubbard operators, which do not change the number of particles in the system,

$$\langle\{X^F_{\lambda\lambda'},d^\dagger_{m\sigma}\}\rangle=\sum_{\nu'}p^{\lambda\nu'*}_{m\sigma}\langle X^B_{\nu'\lambda'}\rangle+\sum_{\nu}p^{\nu\lambda'*}_{m\sigma}\langle X^B_{\lambda\nu}\rangle. \tag{10}$$

Using the Keldysh lesser Green's functions, $\mathcal{G}^<_{\lambda\lambda',m\sigma}=\langle\langle X^F_{\lambda\lambda'}|d^\dagger_{m\sigma}\rangle\rangle^<$, we can calculate the needed averages both in the equilibrium and nonequilibrium case. We first note that standard application of the lesser Green's function,

$$\langle d^\dagger_{m\sigma}X^F_{\lambda\lambda'}\rangle=\int\frac{d\omega}{2\pi i}\mathcal{G}^<_{\lambda\lambda',m\sigma}, \tag{11}$$

does not allow us directly to single out the needed bosonic averages. To proceed we follow the Hubbard original work[16] and use the fact that the molecular Hamiltonian $\mathcal{H}_M$ commutes with the electron number operator for the molecule. From the multiplication rules of the Hubbard operators we have

$$\sum_\lambda p^{\lambda\gamma}_{m\sigma}d^\dagger_{m\sigma}X^F_{\lambda\lambda'}=\sum_\lambda p^{\lambda\gamma}_{m\sigma}d^\dagger_{m\sigma}X^F_{\lambda\gamma}X^B_{\gamma\lambda'}=\sum_{\lambda\gamma'}p^{\lambda\gamma'}_{m\sigma}d^\dagger_{m\sigma}X^F_{\lambda\gamma'}X^B_{\gamma\lambda'}$$
$$=d^\dagger_{m\sigma}d_{m\sigma}X^B_{\gamma\lambda'}; \tag{12}$$

hence

$$\sum_{m\lambda\sigma}p^{\lambda\gamma}_{m\sigma}d^\dagger_{m\sigma}X^F_{\lambda\lambda'}=\sum_\sigma\hat{N}_\sigma X^B_{\gamma\lambda'}=N_\gamma X^B_{\gamma\lambda'}, \tag{13}$$

where $N_\gamma$ is the number of electrons in the molecular state $|\gamma\rangle$. The average of any bosonic Hubbard operator (except $\langle X_{00}\rangle$, where $|0\rangle$ denotes the empty state) can be obtained as

$$\langle X^B_{\gamma\lambda'}\rangle=\frac{1}{N_\gamma}\sum_{\lambda\sigma m}p^{\lambda\gamma}_{m\sigma}\int\frac{d\omega}{2\pi i}\mathcal{G}^<_{\lambda\lambda',m\sigma}. \tag{14}$$

The remaining average, $\langle X_{00}\rangle$, can be computed using the other ones with the completeness relation $\langle X_{00}\rangle=1-\Sigma_{\lambda\neq 0}\langle X_{\lambda\lambda}\rangle$.

## IV. APPROXIMATE SOLUTION OF THE EOM FOR THE GREEN'S FUNCTION

Below we discuss a decoupling scheme which, although still valid only above the Kondo temperature $T_K$, correctly reproduces both the limit of the Coulomb blockade as well as the results for the noninteracting case. In the simplest MFA-like approximation scheme,[6] the higher-order Green's functions from the rhs of Eq. (9) are decoupled in a mean-field-like manner and the system of equations for the Green's functions is closed. Here we write EOM for all the higher-order Green's functions which appear on the rhs of Eq. (9) rather than just decoupling them,

$$(\omega-E_{\zeta'}+E_\zeta+\epsilon_{k\alpha})\langle\langle X^{B2}_{\zeta\zeta'}c^\dagger_{k\alpha\sigma'}|d^\dagger_{m\sigma}\rangle\rangle=\langle\{X^{B2}_{\zeta\zeta'}c^\dagger_{k\alpha\sigma'},d^\dagger_{m\sigma}\}\rangle$$
$$+\sum_{p\beta\sigma''j}v_{p\beta,j}\langle\langle[X^{B2}_{\zeta\zeta'}c^\dagger_{k\alpha\sigma'},c^\dagger_{p\beta\sigma''}d_{j\sigma''}]|d^\dagger_{m\sigma}\rangle\rangle$$
$$+\sum_{p\beta\sigma''j}v^*_{p\beta,j}\langle\langle[X^{B2}_{\zeta\zeta'}c^\dagger_{k\alpha\sigma'},d^\dagger_{j\sigma''}c_{p\beta\sigma''}]|d^\dagger_{m\sigma}\rangle\rangle, \tag{15}$$

$$(\omega-E_{\zeta'}+E_\zeta-\epsilon_{k\alpha})\langle\langle X^{B}_{\zeta\zeta'}c_{k\alpha\sigma'}|d^\dagger_{m\sigma}\rangle\rangle=\langle\{X^{B}_{\zeta\zeta'}c_{k\alpha\sigma'},d^\dagger_{m\sigma}\}\rangle$$
$$+\sum_{p\beta\sigma''j}v_{p\beta,j}\langle\langle[X^{B}_{\zeta\zeta'}c_{k\alpha\sigma'},c^\dagger_{p\beta\sigma''}d_{j\sigma''}]|d^\dagger_{m\sigma}\rangle\rangle$$
$$+\sum_{p\beta\sigma''j}v^*_{p\beta,j}\langle\langle[X^{B}_{\zeta\zeta'}c_{k\alpha\sigma'},d^\dagger_{j\sigma''}c_{p\beta\sigma''}]|d^\dagger_{m\sigma}\rangle\rangle. \tag{16}$$

To proceed, we first compute the commutators in the higher-order Green's functions on the rhs of Eqs. (15) and (16) and next we decouple the resulting operators in a MFA-like way, neglecting the correlations of fluctuations between the electrons from the leads and the molecule.[7] In this decoupling, the correlations of fluctuations within the molecule itself are still treated exactly. As a result of this procedure, the higher-order Green's functions are approximated by the products of the lowest-order Green's functions, $\mathcal{G}_{\lambda\lambda',m}$ and the Fermi occupation factors of the electrons from the leads. Note that this is just the point where the correlations leading to the Kondo effect are neglected, since certain averages omitted here (e.g., the averages of the anticommutators on the rhs of Eqs. (15) and (16)) develop the logarithmic singularities as $T\to T_K$.

After inserting the result of this approximation for the higher-order Green's functions into the EOM, Eq. (9), we obtain the set of *linear* equations for the lowest-order Green functions $\mathcal{G}_{\lambda\lambda',m}$,

$$(\omega-E_{\lambda'}+E_\lambda)\mathcal{G}_{\lambda\lambda',m}=\langle\{X^F_{\lambda\lambda'},d^\dagger_{m\sigma}\}\rangle-\sum_{\mu\nu\sigma'jl}R^h_{jl}(-\omega+E_\mu-E_\lambda)p^{\lambda'\mu}_{l\sigma'}p^{\lambda\nu*}_{j\sigma'}\mathcal{G}_{\nu\mu,m}-\sum_{\mu\nu\sigma'jl}R^e_{jl}(-\omega+E_\mu-E_\lambda)p^{\lambda'\mu}_{l\sigma'}p^{\nu\mu*}_{j\sigma'}\mathcal{G}_{\lambda\nu,m}$$
$$-\sum_{\mu\nu\sigma'jl}R^h_{jl}(-\omega+E_{\lambda'}-E_\mu)p^{\mu\lambda}_{l\sigma'}p^{\mu\nu*}_{j\sigma'}\mathcal{G}_{\nu\lambda',m}-\sum_{\mu\nu\sigma'jl}R^e_{jl}(-\omega+E_{\lambda'}-E_\mu)p^{\mu\lambda}_{l\sigma'}p^{\nu\lambda'*}_{j\sigma'}\mathcal{G}_{\mu\nu,m}$$
$$+\sum_{\mu\nu\sigma'jl}R^h_{lj}(\omega-E_\mu+E_\lambda)p^{\mu\lambda'*}_{l\sigma'}p^{\mu\nu}_{j\sigma'}\mathcal{G}_{\lambda\nu,m}+\sum_{\mu\nu\sigma'jl}R^e_{lj}(\omega-E_\mu+E_\lambda)p^{\mu\lambda'*}_{l\sigma'}p^{\nu\lambda}_{j\sigma'}\mathcal{G}_{\nu\mu,m}$$
$$+\sum_{\mu\nu\sigma'jl}R^h_{lj}(\omega-E_{\lambda'}+E_\mu)p^{\lambda\mu*}_{l\sigma'}p^{\lambda'\nu}_{j\sigma'}\mathcal{G}_{\mu\nu,m}+\sum_{\mu\nu\sigma'jl}R^e_{lj}(\omega-E_{\lambda'}+E_\mu)p^{\lambda\mu*}_{l\sigma'}p^{\nu\mu}_{j\sigma'}\mathcal{G}_{\nu\lambda',m}. \tag{17}$$

Above,

$$R^{x}_{lj}(z)=\sum_{k\alpha}\frac{v^{*}_{k\alpha,l}v_{k\alpha,j}}{z-\epsilon_{k\alpha}}f^{x}_{k\alpha},\quad \text{where } f^{e}_{k\alpha}=f_{k\alpha},\quad f^{h}_{k\alpha}=1-f_{k\alpha}, \tag{18}$$

play a role of the components of the self-energy functions in the present approximation. The functions defined by Eq. (18) become divergent at $z\rightarrow\varepsilon_F$ when $T\rightarrow 0$ K. This divergence is the same as the one that appears in the theory of the Kondo effect. It means that calculations based on Eqs. (17) are meaningful for temperatures above $T_K$ only. It can be shown that in the case of the single atom Eqs. (17) reproduce the results of the theory of Meir *et al.*[7] (see the Appendix A).

The advantage of the above set of the inhomogeneous linear equations is that the averages of the Hubbard operators appear in Eq. (17) only as the inhomogeneity factors and as such they modify the residua rather than the poles of the Green's function. The self-energy functions $R^{e,h}_{lj}(z)$ do not depend on the averages of the Hubbard operators and they characterize the spectral properties of the leads only. In result, the self-consistent equations for the averages are the linear equations that can be, in principle, solved easily for relatively large system, provided the self-energy functions $R^{e,h}_{lj}(z)$ are known. The solution of Eqs. (17) can be written formally as

$$\mathcal{G}^{r,a}_{\lambda\lambda',m}=\sum_{\mu\mu'}[(\omega\hat{1}-\hat{\Omega}-\hat{Q}^{r,a})^{-1}]_{\lambda\lambda',\mu\mu'}\langle\{X^{F}_{\mu\mu'},d^{\dagger}_{m\sigma}\}\rangle, \tag{19}$$

where $\hat{1}$ denotes the unit matrix,

$$\hat{\Omega}_{\lambda\lambda',\mu\mu'}=\delta_{\lambda\lambda',\mu\mu'}(E_{\lambda}-E_{\lambda'}), \tag{20}$$

and $\hat{Q}^{r,a}$ is a resonance-broadening matrix, defined by Eqs. (17). In general, the matrix $\hat{Q}$ is a frequency-dependent function, divergent at temperatures of order of $T_K$. In the present paper we neglect this divergence, which is justified as long as $T\gg T_K$ and put $f_{k\alpha}\sim 1/2$ in the functions $R^x$ from Eq. (18). As a result we obtain an explicit formula for the resonance broadening matrix in the following form:

$$\hat{Q}^{r}=-i\sum_{\alpha}\Gamma_{\alpha}q_{\alpha},\quad (q_{\alpha})_{\nu\nu',\zeta\zeta'}=\delta_{\nu\nu',\zeta\zeta'}+\frac{1}{2}\sum_{\sigma,\alpha=L,R}(p^{\nu\zeta}_{\alpha\sigma}p^{\nu'\zeta'}_{\alpha\sigma}+p^{\zeta\nu}_{\alpha\sigma}p^{\zeta'\nu'}_{\alpha\sigma}), \tag{21}$$

and $\hat{Q}^{r}=-\hat{Q}^{a}$. The great advantage of this approximation is that the matrix $\hat{Q}$ is independent of the frequency which considerably reduces the complexity of evaluation of the integrals from Eqs. (5) and (14). The same result can be obtained if we approximate the higher order Green functions on the r.h.s. of Eq. (17):[13]

$$\langle\langle c_{k\alpha\sigma'}X|d^{\dagger}_{m\sigma}\rangle\rangle^{r,a}\approx\frac{1}{2}v_{k\alpha}g^{r,a}_{\alpha}\langle\langle\{d_{\alpha\sigma'},X\}|d^{\dagger}_{m\sigma}\rangle\rangle^{r,a}. \tag{22}$$

Above, $g^{r,a}_{\alpha}$ denote the retarded and the advanced Green's function for the noninteracting leads.

In order to unambiguously determine the needed Green's functions one has to compute the values of the averages of the anticommutators that appear in Eq. (19). In the nonequilibrium phase this requires knowledge of the lesser Green's functions from Eq. (14). For the computation of the lesser Green function we repeat the procedure of the equation of the motion method. For the corresponding decoupling of the Green's function we assume that, by an analogy with Eq. (22),

$$\langle\langle c_{k\alpha\sigma'}X|d^{\dagger}_{m\sigma}\rangle\rangle^{<}\approx\frac{1}{2}v_{k\alpha}g^{r}_{\alpha}\langle\langle\{d_{\alpha\sigma'},X\}|d^{\dagger}_{m\sigma}\rangle\rangle^{<}+\frac{1}{2}v_{k\alpha}g^{<}_{\alpha}\langle\langle\{d_{\alpha\sigma'},X\}|d^{\dagger}_{m\sigma}\rangle\rangle^{a}, \tag{23}$$

where $g^{<}_{\alpha}$ denotes the lesser Green's function of the noninteracting leads. The approximations defined by Eqs. (22) and (23) reduce to the exact result in the limiting cases of the Coulomb blockade as well as the noninteracting limit, and in between they serve as the interpolating ansatz. Using Eq. (23) the lesser Green's function can be readily obtained as

$$G^{<}_{\lambda\lambda',m\sigma}=\sum_{\mu\mu'}[(\omega\hat{1}-\hat{\Omega}-\hat{Q}^{r})^{-1}\hat{Q}^{<}(\omega\hat{1}-\hat{\Omega}-\hat{Q}^{a})^{-1}]_{\lambda\lambda',\mu\mu'}\langle\{d^{\dagger}_{m\sigma},X^{F}_{\mu\mu'}\}\rangle, \tag{24}$$

where

$$\hat{Q}^{<}=2i\sum_{\alpha}\Gamma_{\alpha}q_{\alpha}f_{\alpha}. \tag{25}$$

In a similar way the expression for the greater Green's function can be derived. Using the results for the Green's functions in Eq. (5) we derive the explicit equation for the current,

$$I=\frac{2e\Gamma_L\Gamma_R}{h}\sum_{\lambda\lambda'\mu\mu'}p^{\lambda\lambda'}_{L\sigma}\langle\{d^{\dagger}_{L\sigma},X^{F}_{\mu\mu'}\}\rangle\times\int d\omega(f_L-f_R)[(\omega\hat{1}-\hat{\Omega}-\hat{Q}^{r})^{-1}q_R(\omega\hat{1}-\hat{\Omega}-\hat{Q}^{a})^{-1}]_{\lambda\lambda',\mu\mu'}. \tag{26}$$

The advantage of the last result is that it is independent of the form and size of the molecular junction. The approximations made above in obtaining Eq. (26) do not guarantee the current to fulfill the properties required from the stationary charge flow for all possible values of the physical parameters. To impose this condition we performed the transformation of the time arguments in the double-time representation of all the Green's functions,

$$\langle\langle a(t)|b(t')\rangle\rangle\rightarrow\langle\langle a(t_0+\tau/2)|b(t_0-\tau/2)\rangle\rangle, \tag{27}$$

requiring that the result be dependent on $\tau$ but not on $t_0$.[13] The final formula for current that fulfills this condition can be obtained from the previous one by the simple symmetrization of the prefactors in Eq. (26) with respect to the indexes: $\lambda$, $\lambda'$, $\mu$, $\mu'$,

$$
p_{L\sigma}^{\lambda\lambda'}\langle\{d_{L\sigma}^{\dagger},X_{\mu\mu'}^{F}\}\rangle \rightarrow \frac{1}{2}(p_{L\sigma}^{\lambda\lambda'}\langle\{d_{L\sigma}^{\dagger},X_{\mu\mu'}^{F}\}\rangle + p_{L\sigma}^{*\mu\mu'}\langle\{d_{L\sigma}^{\dagger},X_{\lambda\lambda'}^{F}\}\rangle^{*}). \tag{28}
$$

In order to use Eq. (26) we have to compute self-consistently the averages of the Hubbard operators that determine the averages of the anticommutators in Eq. (26). From Eq. (14) we obtain the self-consistent *linear* equations for the averages of the boson-like Hubbard operators,

$$
\langle X_{\alpha\alpha'}\rangle = \sum_{\beta\beta'} W_{\alpha\alpha',\beta\beta'}\langle X_{\beta\beta'}\rangle,
$$

$$
W_{\alpha\alpha',\beta\beta'} = \frac{1}{N_{\alpha'}}\sum_{\lambda\mu,m\sigma}(p_{m\sigma}^{\lambda\alpha'}p_{m\sigma}^{*\beta''\mu}J_{\lambda\alpha'',\beta'\mu} + p_{m\sigma}^{\lambda\alpha'}p_{m\sigma}^{*\mu\beta'}J_{\lambda\alpha'',\mu\beta''}), \tag{29}
$$

and

$$
J_{\lambda\lambda',\mu\mu'} = \int\frac{d\omega}{2\pi i}[(\omega\hat{1} - \hat{\Omega} - \hat{Q}^{r})^{-1}\hat{Q}^{<}(\omega\hat{1} - \hat{\Omega} - \hat{Q}^{a})^{-1}]_{\lambda\lambda',\mu\mu'}. \tag{30}
$$

The set of Eqs. (29), supplemented with the completeness relation, determines the values of the relevant averages of the Hubbard operators. However, one should be aware that the above procedure is not unique at the level of the applied decoupling. If we studied instead the equations of motion for the Green's functions defined in terms of exclusively Hubbard operators, as $\mathcal{G}_{\lambda\lambda',\mu\mu'}=\langle\langle X_{\lambda\lambda'}^{F}|X_{\mu'\mu}^{F}\rangle\rangle$ rather than the "mixed" Green's function, $\mathcal{G}_{\lambda\lambda',m\sigma}$, we would obtain quite another and highly redundant set of equations to determine the averages. In the general case there is no guarantee, that the two approaches give the same results, except some limiting cases (zero interaction limit or zero coupling limit), where the applied decoupling becomes exact. The redundancy problem is well known in the theory of magnetism.[23,24] Although using the "mixed" Green's functions reduces the problem of the redundancy, it does not eliminate it completely. Indeed, one might compute the averages using the greater (Keldysh) Green's function, rather than the lesser ones. An application of the Hubbard procedure gives the result

$$
\langle X_{\lambda\mu}^{B}\rangle = \frac{1}{N_f - N_{\mu}}\sum_{\lambda'\sigma m} p_{m\sigma}^{\mu\lambda'}\int\frac{d\omega}{2\pi i}\mathcal{G}_{\lambda\lambda',m\sigma}^{>}, \tag{31}
$$

where $N_f$ is the number of electrons in the state $|f\rangle$ with the full occupation of the molecule (here $\mu \neq f$). Now it is the average $\langle X_{ff}\rangle$ rather than $\langle X_{00}\rangle$, that has to be computed from the completeness relation. The application of Eq. (31) in the linear response regime leads to another set of linear equations for the averages, with the matrix $\widetilde{W}$ substituting $W$ and defined as

$$
\widetilde{W}_{\alpha\alpha',\beta\beta'} = \frac{1}{N_f - N_{\alpha'}}\sum_{\lambda\mu,m\sigma}(p_{m\sigma}^{\alpha''\lambda}p_{m\sigma}^{*\beta''\mu}\widetilde{J}_{\alpha'\lambda,\beta'\mu} + p_{m\sigma}^{\alpha''\lambda}p_{m\sigma}^{*\mu\beta'}\widetilde{J}_{\alpha'\lambda,\mu\beta''}), \tag{32}
$$

where

$$
\widetilde{J}_{\lambda\lambda',\mu\mu'} = -\int\frac{d\omega}{2\pi i}[(\omega\hat{1} - \hat{\Omega} - \hat{Q}^{r})^{-1}\hat{Q}^{>}(\omega\hat{1} - \hat{\Omega} - \hat{Q}^{a})^{-1}]_{\lambda\lambda',\mu\mu'}. \tag{33}
$$

One may note that the two sets of the equations, (29) and (32), considered separately, are highly asymmetric in the treatment of different averages. This is not a problem in the limiting cases of our model where our results become exact, but in general it leads to different and at the same time unphysically asymmetric results for the averages. To alleviate this problem we form a symmetrized set of equations with the matrix $W_s$ being the arithmetic average of the matrices $W$ and $\widetilde{W}$. This approach guarantees that the obtained results are consistent with the exact electron-hole symmetry of our Hamiltonian.

## V. APPLICATION TO THE TWO-ATOM MOLECULE

In this section we exemplify the application of the method to the one-band model of the two-atom molecule described by the extended Hubbard Hamiltonian:

$$
\mathcal{H}_M = t\sum_{\sigma}(d_{L\sigma}^{\dagger}d_{R\sigma} + \text{H.c.}) + \sum_{i=L,R;\sigma}\varepsilon_i n_{i\sigma}^{d} + U_0\sum_{i=L,R} n_{i\sigma}^{d}n_{i-\sigma}^{d} + U_1\sum_{\sigma\sigma'} n_{L\sigma}^{d}n_{R\sigma'}^{d}. \tag{34}
$$

Above, $t$ is the interatom hopping; $U_0(U_1)$ denotes on-site (intersite) Coulomb repulsion. Hamiltonian (34) was extensively studied in the context of the Coulomb blockade in lithographically defined dots in semiconducting materials.[11] Such the model can also be relevant for the $H_2$ molecule trapped between the Pt electrodes, as studied by Smit *et al.*[25]

A computation of the *I*-*V* dependence of the junction requires taking into account the dependence of the molecular eigenstates and their energy levels on an external potential profile in the molecule. To obtain a detailed dependence of the potential one would need to include explicitly the Coulomb repulsion between the electrons from the molecule and the leads. In this paper we restrict ourselves to a simple phenomenological modeling of the potential profile, assuming that it drops linearly with the atom position $x$ (a potential ramp[27]):

$$
\mathrm{eV}_{\mathrm{mol}}(x) = \eta[\mathrm{eV}_L(1 - x) + \mathrm{eV}_R x], \tag{35}
$$

and $x$ is measured in units of the distance between the electrodes. The parameter $\eta$ defines the slope of the potential drop and in our numerical computations we put $\eta=1$, which leads to an upper estimate of the role of the external potential. The potential modifies the local energy $\varepsilon_i$ in the molecule: $\varepsilon_i=\varepsilon_i^{(0)}+\mathrm{eV}(1-2i/3)/2$, where $\varepsilon_i^{(0)}$ denotes the atomic level at the equilibrium $V=0$.

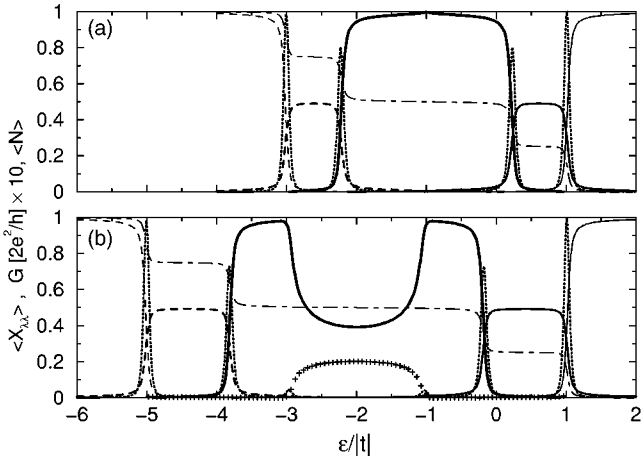

FIG. 1. Thermodynamic averages of the diagonal Hubbard operators as the functions of the local energy $\varepsilon$ for $\Gamma=0.01|t|$, $k_BT=2\Gamma$, $U_1=0$, and (a) $U_0=2|t|$, (b) $U_0=4|t|$. Here $\langle X_{0\,0}\rangle$—thin solid line, $\langle X_{1B\sigma\,1B\sigma}\rangle$—solid line, $\langle X_{2S_02S_0}\rangle$—thick solid line, $\langle X_{3B\sigma\,3B\sigma}\rangle$—broken line, $\langle X_{4\,4}\rangle$—thin broken line, $\langle X_{2T\,2T}\rangle$—crosses. The conductance (multiplied by a factor of 10) is shown with a dotted line, and the average of the total electron occupation $\langle\hat{N}\rangle$ (divided by 4) at the molecule is shown with the dash–dotted line.

In order to determine the transport characteristics of the system, we first compute all the eigenstates $|\lambda\rangle$ and the energy eigenvalues $E_\lambda$ of the isolated two-atom system described by the Hamiltonian (34) and determine the matrix elements of the fermion annihilation operators, $p_{j\sigma}^{\lambda\lambda'}$, defined in Eq. (8). The matrix elements are then used to obtain the resonance broadening matrices $\hat{Q}^{r,a,<,>}$ defined in Eqs. (21) and (25). The matrices $\hat{Q}^{r,a,<,>}$, the matrix elements $p_{j\sigma}^{\lambda\lambda'}$, and the eigenenergy values $E_\lambda$ are next used to find the parameters of the self-consistent equations (29) and (32), $W_{\alpha\alpha',\beta\beta'}$ and $\widetilde{W}_{\alpha\alpha',\beta\beta'}$, respectively. The linear system of self-consistent equations possesses a unambiguous solution which is used, together with matrices $\hat{Q}^{r,a}$ and the eigenvalues $E_\lambda$, in Eq. (26) to compute the current.

The self-consistent averages of the diagonal Hubbard operators, $\langle X_{\lambda\lambda}\rangle$ have the meaning of the probability of occupation of the molecular states in the presence of coupling to the leads. They are presented in Fig. 1, as the functions of the local energy $\varepsilon_1=\varepsilon_2\equiv\varepsilon$ for zero applied voltage. With decreasing $\varepsilon$ (i.e., for increasing the gate voltage) the average of the total electron occupation at the molecule, $\langle\hat{N}\rangle=\Sigma_{\lambda\neq 0}\langle X_{\lambda\lambda}\rangle$, increases in a stepwise manner. For the moderate values of the Coulomb repulsion $U_0$ and small $\Gamma$ (see Fig. 1(a)), the ground state of isolated molecule is by far the most preferably occupied one for each value of $\langle\hat{N}\rangle$. In effect the molecule goes through the sequence of states: $|0\rangle\rightarrow|1B\sigma\rangle\rightarrow|2S_0\rangle\rightarrow|3B\sigma\rangle\rightarrow|4\rangle$. Here $|0\rangle$ denotes the empty state, $|1B\sigma\rangle$—single occupied bonding state, $|2S_0\rangle$—double occupied lowest energy singlet, $|3B\sigma\rangle$—triple occupied bonding state, and $|4\rangle$—fully occupied state. Each jump of the average electron occupancy $\langle\hat{N}\rangle$ is accompanied by a sharp peak of the linear conductance.

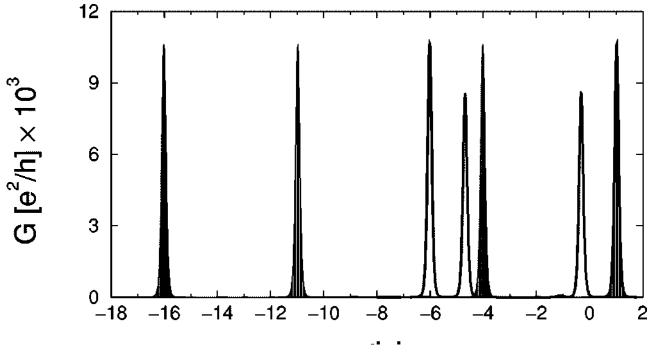

FIG. 2. Zero-voltage conductance as a function of the local energy $\varepsilon$ for $\Gamma=10^{-3}|t|$, $k_BT=0.05|t|$ (Coulomb blockade limit). Solid line: $U_0=5|t|$, $U_1=0$, shaded peaks: $U_0=5|t|$, $U_1=5|t|$. These results compare very well with the ones of the Coulomb blockade theory of Ref. 8 for the same parameter values.

In Fig. 1(b) we show that transitions between excited states also can be important. For this case the energy splitting between the double occupied ground-state singlet $|2S_0\rangle$ and the triplet states, $|2T\sigma\rangle$ and $|2T0\rangle$, is small enough and the both states can overlap. As a result, the occupancy of the triplet state $\langle X_{2T,2T}\rangle$ is enhanced and the occupancy of the singlet state $\langle X_{2S0,2S0}\rangle$ is reduced. Knowing these averages, one can determine the correlation functions,

$$\langle n_{1\sigma}n_{2\sigma'}\rangle=\sum_{\lambda,\lambda'}\langle\lambda'|n_{1\sigma}n_{2\sigma'}|\lambda\rangle\langle X^B_{\lambda\lambda'}\rangle, \tag{36}$$

and the spin-spin correlation function,

$$\langle\mathbf{S}_1\cdot\mathbf{S}_2\rangle=-\frac{3}{4}\sum_{\sigma\sigma'}(-1)^{\delta_{\sigma\sigma'}}\langle n_{1\sigma}n_{2\sigma'}\rangle. \tag{37}$$

The analysis of $\langle\mathbf{S}_1\cdot\mathbf{S}_2\rangle$ shows strong antiferromagnetic correlations for $\epsilon$ located between the singlet and the triplet state. If $\epsilon$ lies in the middle of the electronic band and the occupancy $\langle X_{2T,2T}\rangle$ is enhanced, the antiferromagnetic correlations are suppressed and the total magnetic moment at the molecule $\langle(\mathbf{S}_1+\mathbf{S}_2)^2\rangle$ increases (see also Ref. 13). It is interesting to note that the linear conductance in Fig. 1(b) also shows small peaks at the points of the rapid changes of the triplet state occupancy, despite the fact that the total electron occupancy $\langle\hat{N}\rangle$ is hardly changed there.

The zero-voltage conductance as the function of local energy $\varepsilon$ is presented in Figs. 2–4. For $\Gamma\ll k_BT\ll U_0$ the system is in the Coulomb blockade limit (Fig. 2), and the conductance shows a sequence of four peaks, with a widths (heights) quickly increasing (decreasing) with increase of temperature. The ratio of heights of the peaks depend on the nearest neighbors repulsion $U_1$, and for $U_0=U_1$ all four peaks have the same height. Our results are in this limit in a good quantitative agreement with the ones obtained earlier by Klimeck *et al.*[8] by means of the master equation approach.

In Fig. 3 we show the evolution of the conductance with the on-site repulsion $U_0$ for the large coupling $\Gamma$. At $U_0=0$ the conductance exhibits two peaks, centered at the positions

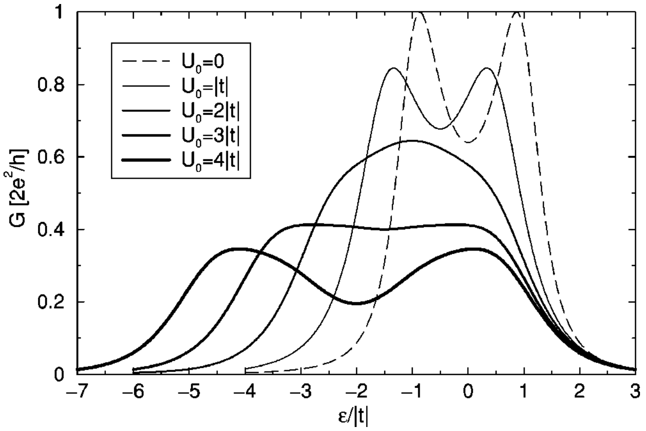

FIG. 3. Zero-voltage conductance as a function of the local energy $\varepsilon$ for $\Gamma=|t|$ for $k_BT=0$, $U_1=0$, $k_BT=0$ and several values of $U_0$ (in units of $|t|$).

of the bonding and the antibonding states, with the maximum value of the conductance equal to $2e^2/h$. In this limiting case our calculations reproduce the exact result for the conductance. With growing repulsion the peaks become shifted, increase in width, and decrease in height. For intermediate $U_0$ both peaks merge in a single, very wide feature. With a further increase of $U_0$, the two peak structure is formed again, resembling the formation of the upper Hubbard and the lower Hubbard band at the metal-insulator transition in the bulk systems.[8] The conductance for an intermediate value of $\Gamma$ is presented in Fig. 4. Again, the widths of the conductance peaks increases considerably with $U_0$. Unlike the strong $\Gamma$ case, however, we now note the formation of the system of four to six conductance peaks, depending on the value of $U_0$. The central pair of the peaks is related to the enhanced occupancy of the triplet states and is more pronounced as compared to the weak-$\Gamma$ case of Fig. 1(b). This is due to coupling-enhanced contribution from the virtual transitions to the excited states of triplet, $|2T0\rangle$ and $|2T\sigma\rangle$. The six-peak structure is best observed for the intermediate $\Gamma$ and $U_0$ values. In the limit of very weak $\Gamma$ we return to the four-peak structure known from the Coulomb blockade limit (compare Figs. 1(b) and 2).

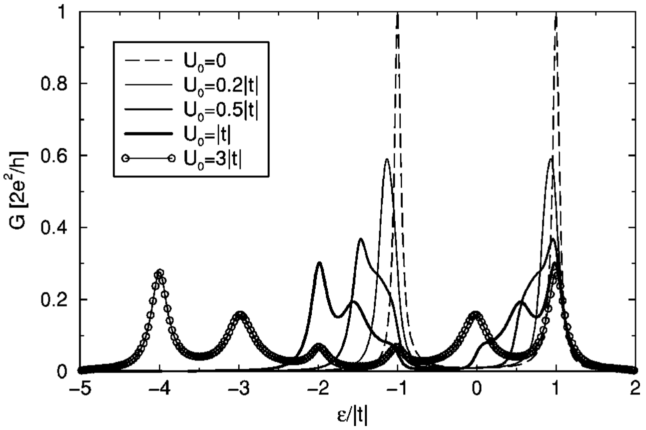

FIG. 4. Zero-voltage conductance as a function of the local energy $\varepsilon$ for $\Gamma=0.1|t|$ for $k_BT=0$, $U_1=0$, $k_BT=0$ and several values of $U_0$.

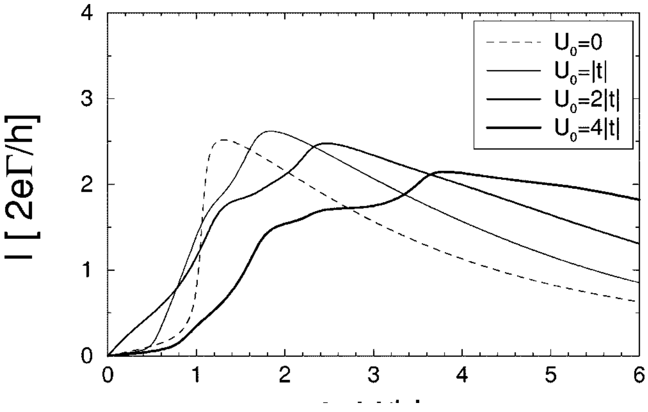

FIG. 5. The current-voltage dependence for several values of the Coulomb repulsion $U_0$, for the symmetric case: $U_0/2+\varepsilon=0$ and $\Gamma=0.1|t|$.

The current-voltage dependence is shown in Figs. 5 and 6 for several values of the repulsion $U_0$. Here again our computation becomes exact for the vanishing Coulomb repulsion. In the $U_0=0$ limit the stepwise increase of the current with the voltage corresponds to entering the single–electron molecular levels into the source-drain voltage window. For $U_0>0$ and $V>0$ the number of excited molecular levels participating in transport considerably increases as compared to the $V=0$ limit, since some of these states may enter directly in the source-drain voltage window. Because the Coulomb repulsion removes the degeneracy of many excited molecular states, the *I-V* dependence is much more involved than in the $U_0=0$ case. In the case of the intermediate value of $\Gamma$ (see Fig. 5) the *I-V* steps acquire substantial width, coming from the resonance broadening matrices $\hat{Q}^{r,a}$ which depend on the repulsion as well. In this case the contributions from the individual molecular excited states cannot be resolved and the *I-V* curve is fairly smooth. Note also that for the finite repulsion the current becomes a monotonously increasing function for much of the voltage range, unlike the reference limiting case of $U_0=0$, where the effect of the potential ramp leads to the negative differential conductance. This can be interpreted as an effect of screening of the

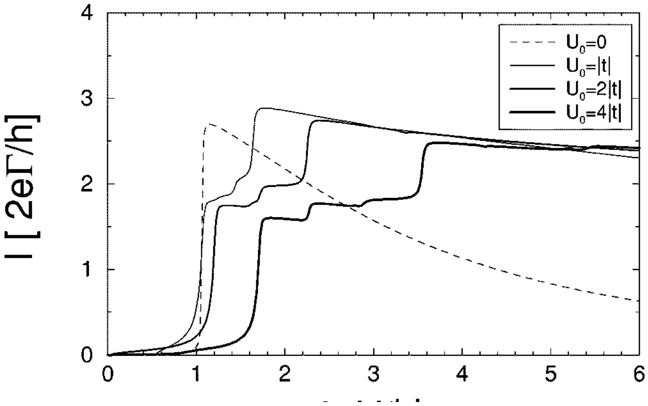

FIG. 6. The current-voltage dependence for several values of the Coulomb repulsion $U_0$, for the symmetric case: $U_0/2+\varepsilon=0$ and $\Gamma=0.01|t|$.

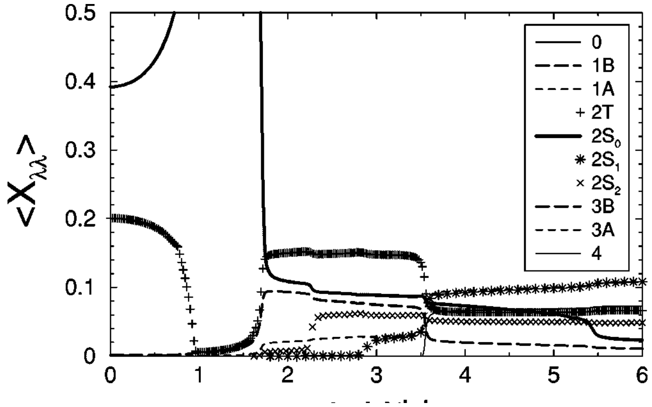

FIG. 7. The voltage dependence of the molecular state occupancy for $U_0=4|t|\varepsilon=-2|t|$ (symmetric case), and $\Gamma=0.01|t|$. The symbols in the legend refer to the molecular states of the isolated molecule: $|0\rangle$—the empty state, $|1B\sigma\rangle(|1A\sigma\rangle)$—the bonding (antibonding) state of the singly occupied molecule with spin $\sigma$, $|2T\sigma\rangle(|2T0\rangle)$—the triplet spin-1 (spin-0) state of the double occupied molecule, $|2S_\nu\rangle$, where $\nu=0$, 1, 2—the singlet states of the doubly occupied molecule, $|3B\sigma\rangle(|3A\sigma\rangle)$—the bonding (antibonding) state with spin $\sigma$ of the triply occupied molecule, and $|4\rangle$—the fully occupied state. Note that the solid line corresponding to the occupancy of the singlet ground state $|2S_0\rangle$ is close to 1 for $1<2$ eV$/|t|<1.5$.

external potential by the electron correlations within the molecule.

For the weak $\Gamma$ (see Fig. 6), the steps reappear in the *I-V* dependence. In this case the *I-V* curve takes a form typical for the Coulomb blockade limit.[20,26] The details of the *I-V* dependence can be better understood from the corresponding plot of the occupancy of the molecular states with respect to the voltage for $U_0=4|t|$ for the symmetric case, which we present in Fig. 7. In the low voltage regime (for 2 eV$/|t|<1.6$), the occupancy of the triplet states, $\langle X_{2T\sigma\,2T\sigma}\rangle=\langle X_{2T0\,2T0}\rangle$, is reduced by the voltage at the expense of the growing occupancy of the ground state singlet state, $\langle X_{2S_02S_0}\rangle$. This is due to the fact that the energy of the bonding state $|2S_0\rangle$ decreases with the voltage, whereas the triplet states do not depend on the voltage. The current is still small in this region, and the occupancy of all the other states with the electron occupancy different from 2 is negligible. Near a threshold voltage, 2 eV$/|t|\sim 1.6$, the occupancy of the ground singlet state decreases rapidly, and at the same time the occupancy of the spin doublets, $\langle X_{1B\sigma\,1B\sigma}\rangle=\langle X_{3B\sigma\,3B\sigma}\rangle$ and $\langle X_{1A\sigma\,1A\sigma}\rangle=\langle X_{3A\sigma\,3A\sigma}\rangle$ as well as the occupancy of the triplet state begins to rise sharply. At the same threshold voltage the current rises rapidly, which is compatible with the fact that the charge at the molecule begins to fluctuate. A next, smaller current step can be noted near 2 eV$/|t|\sim 2.3$, where the excited state: $|2S_2\rangle$ enters the play. Another small current step is visible at 2 eV$/|t|\sim 2.8$, where the occupancy of the $|2S_1\rangle$ state begins to grow. Finally, the second big step in the *I-V* curve at 2 eV$/|t|\sim 3.6$ is accompanied by the rapid increase of the occupancy of the empty and the fully occupied state, $\langle X_{0\,0}\rangle$ and $\langle X_{4\,4}\rangle$, respectively.

The overall voltage dependence of the molecular state occupancy is complicated here by the effect of the potential ramp what is best seen for the very large voltage. Without the potential ramp, all the states are uniformly occupied and for each $|\lambda\rangle$, $\langle X_{\lambda\lambda}\rangle\to 1/16=0.0625$ for $V\to\infty$. The inhomogeneous potential promotes the occupancy of the excited states, $|2S_\nu\rangle$, $|1A\sigma\rangle$, and $|3A\sigma\rangle$, which for the growing voltage increasingly better couple to the electrodes than the corresponding ground states for the same number of electrons. On the other hand the triplet states, the empty, and the fully occupied state are hardly influenced by the ramp and their occupancy in the large voltage region does not depend much on the ramp.

## VI. CONCLUSIONS

In this paper we presented a Green's function approach for the computation of transport properties of molecular junctions, which uses the exact solutions for the isolated molecule. The approximations made in the equation of motion for the Green's functions, become accurate in the limiting cases of the Coulomb blockade on one hand and in the noninteracting case on the other one. In between the limits one can use the method as a kind of interpolative treatment.

Since we used the Hubbard operators to define the molecular Hamiltonian, our approach is formally independent of the size and geometry of the molecule. Using the Hubbard operators we are also able to easily compute the arbitrary correlation functions at the molecule and define the probabilities of occupation of many-particle molecular states, which is very helpful in the interpretation of the *I-V* dependence. In particular, we are able to determine the role of each excited state in the transport in the high voltage region.

An important technical advantage of the applied approximations is that the self-consistent equations for the necessary correlators are linear ones; hence we always obtain a unique solution. Another useful simplification is the absence of the energy dependence of the resonance broadening terms, matrices $\hat{Q}^{r,a}$, which allows us to obtain an explicit and general formula for the current, Eq. (26), which is the central result of this work. The last simplification allows us to reduce all the necessary integrations to the summations using the digamma function or its derivative and may be of practical importance in an application of the method for the larger molecules with a more complicated spectrum.

In our approach the interactions between the molecule and the leads are included in the mean-field-like way. In the decoupling of the Green's functions we omit the averages like $\langle c^\dagger_{k\alpha\sigma}X^F_{\lambda\lambda'}\rangle$, which are important in the Kondo limit.[7,9] In effect, our results can be reliable only for $T\gg T_K$. Also, the neglect of the energy dependence in the matrices $\hat{Q}^{r,a}$ does not allow to take into account the temperature changes of the resonance broadening terms, important in the low temperature, where the Kondo type divergence develops.

In this paper we exemplified the use of the method to the two-atom system with the relatively simple spectrum. An extension to more realistic models with several orbitals per atom is, in principle, straightforward and our general formulas for the current as well as the self-consistent equations can be then almost directly applied. For big molecules, a limitation may be the size of the molecular eigenspace and a resulting difficulty to determine the exact eigenstates of the isolated molecule. In such a case one can try to combine the method with a perturbative treatment to obtain an effective Hamiltonian valid in the restricted subspace of states for the limited range of voltage or the parameter values. The use of the Hubbard operators can be an advantage in such an application.[28]

## ACKNOWLEDGMENTS

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## APPENDIX A: SINGLE-DOT CASE

In this section we show that in the case of the single atom our approximation for the Green's function reduces to the results of Meir *et al.*[7] The one-particle Green's function $\langle\langle d_\sigma | d_\sigma^\dagger \rangle\rangle$ of the 1QD can be written as a linear combination of two Green's functions $\mathcal{G}_{\lambda\lambda'}$,

$$\langle\langle d_\sigma | d_\sigma^\dagger \rangle\rangle = \mathcal{G}_{0\sigma} + \sigma\, \mathcal{G}_{\bar{\sigma}2}. \tag{A1}$$

The structure of the approximate EOM, Eq. (17), can be represented for the 1QD as

$$(\omega - \varepsilon - \Sigma_{11})\mathcal{G}_{0\sigma} + \sigma\Sigma_{12}\mathcal{G}_{\bar{\sigma}2} = 1 - n_{\bar{\sigma}}, \tag{A2}$$

$$\sigma\Sigma_{21}\mathcal{G}_{0\sigma} + (\omega - \varepsilon - U - \Sigma_{22})\mathcal{G}_{\bar{\sigma}2} = \overline{\sigma} n_{\bar{\sigma}}.$$

The self-energy components, $\Sigma_{ij}$, can be obtained in terms of the functions $R^{e,h}(z)$ from Eq. (17) (see below). By the reasons of the electron-hole symmetry, one can expect that the following relations between the components of the self-energy is fulfilled:

$$\Sigma_{11} + \Sigma_{12} = \Sigma_{21} + \Sigma_{22} \equiv \tilde{\Sigma}, \tag{A3}$$

and we can define $\Sigma_0 = \Sigma_{11} - \Sigma_{21}$. The solution of Eqs. (A2) with the use of Eqs. (A1) and (A3) gives

$$\langle\langle d_\sigma | d_\sigma^\dagger \rangle\rangle = \frac{1 - n_{\bar{\sigma}}}{\omega - \varepsilon - \Sigma_0 + U\Sigma_{21}/(\omega - \varepsilon - U - \tilde{\Sigma})} + \frac{n_{\bar{\sigma}}}{\omega - \varepsilon - U - \Sigma_0 - U\Sigma_{12}/(\omega - \varepsilon - \tilde{\Sigma})}. \tag{A4}$$

The above result resembles closely the one obtained by the cited authors. Indeed, a careful examination of Eq. (17) using the fact that $p_{\sigma'}^{0\sigma} = \delta_{\sigma\sigma'}$ and $p_{\sigma'}^{\bar{\sigma}2} = \sigma\delta_{\sigma\sigma'}$ for the 1QD, gives

$$\Sigma = \begin{bmatrix} 2R^e(\omega) + R^h(\omega) - R^e(-\omega + U + 2\varepsilon) & -R^h(-\omega + U + 2\varepsilon) + R^h(\omega) \\ -R^e(-\omega + U + 2\varepsilon) + R^e(\omega) & 2R^h(\omega) + R^e(\omega) - R^h(-\omega + U + 2\varepsilon) \end{bmatrix}. \tag{A5}$$

Insertion of the self-energy components into Eq. (A4) reproduces the results of the earlier works.[7,9,12]

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