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# Uniform electron gas under an external bias: The generalized Thomas-Fermi-Dirac model and the dual-mean-field theory

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**Abstract.** The uniform electron gas placed between two reservoirs is used as a model system for molecular junctions under an external bias. The energetics of the electron gas are calculated by generalizing the Thomas-Fermi-Dirac (TFD) model to nonequilibrium cases. We show that when the bias voltage is not zero, the first Hohenberg-Kohn (HK) theorem breaks down, and energies of the electron gas can be determined by the total electron density together with the density of nonequilibrium electrons, supporting the dual-mean-field (DMF) theory recently proposed by us [J. Chem. Phys. 139, (2013) 191103]. The generalization of TFD functionals to DMF ones is also discussed.

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**Key words**: molecular electronics, density functional theory (DFT), dual mean field theory, Thomas-Fermi-Dirac (TFD) model

## 1 Introduction

Building electronic devices on the basis of single molecules has drawn dramatic attention in past two decades. [1] On the theoretical side, the *ab initio* method that combines the density functional theory (DFT) and nonequilibrium Green's functions' (NEGF) techniques has proven to be powerful in describing electron quantum transport at molecular scale, [2] and has achieved great success in understanding and designing molecular-scale electronic devices. [3–10] In this method, the mean-field potential obtained from DFT is used to calculate electronic structures of molecular junctions with or without an external bias. In our recent paper [11], we have shown that when a finite external bias is

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present, the properties of a molecular junction can not be determined by the total electron density alone, and a dual-mean-field (DMF) theory is proposed to incorporate the bias-induced nonequilibrium effects. One of the key results of the DMF theory is that the current-carrying electrons experience a different effective mean-field potential from the equilibrium electrons do. In this paper, we present detailed analysis of energetics of the uniform electron gas (UEG) placed between two reservoirs. Our calculations clearly show that the first Hohenberg-Kohn (HK) theorem that is the basis of DFT breaks down for the system under study when the external bias is not zero, providing a strong support for the DMF theory [11].

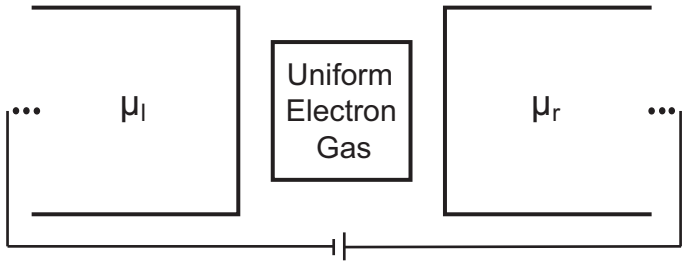


Figure 1: The uniform electron gas is sandwiched by two reservoirs. A battery maintains the chemical potentials, $\mu_l$ and $\mu_r$, in the left and right reservoirs, respectively. The bias voltage acrossing the uniform electron gas is defined by $(\mu_l-\mu_r)/e$. We assume $\mu_l>\mu_r$.

## 2 The generalized Thomas-Fermi-Dirac model

The model is shown in Fig. 1, where an uniform electron gas is placed between two reservoirs. A battery is connected to the system to maintain the chemical potentials $\mu_l$ and $\mu_r$ for the left and right reservoirs respectively. The bias voltage accrossing the system can then be defined as $V_b=(\mu_l-\mu_r)/e$. When $V_b$ is not zero, the uniform electron gas is in a nonequilibrium state. The nonequilibrium distribution is as follows: Electrons coming from the left reservoir obeys the distribution $f_{FD}(\mu_l)$, and electrons coming from the right reservoir obeys the distribution $f_{FD}(\mu_r)$, where $f_{FD}$ is the equilibrium Fermi-Dirac distribution function. In Fig. 2, we schematically show the distribution in momentum space. By defining two Fermi vectors, $\frac{\hbar^2k_{fr}^2}{2m_e}=\mu_r$ and $\frac{\hbar^2k_{fl}^2}{2m_e}=\mu_l$, the kinetic and exchange energies of the uniform electron gas can then be analytically calculated in terms of two Fermi vectors by generalizing the Thomas-Fermi-Dirac (TFD) model to nonequilibrium cases [12].

The kinetic energy density can be worked out as follows.

$$k(k_{fr},k_{fl})=\frac{1}{V}\sum_{\boldsymbol{k},s}\langle \boldsymbol{k},s|\,\hat{t}\,|\boldsymbol{k},s\rangle=\frac{1}{V}\sum_{\boldsymbol{k},s}\frac{|\boldsymbol{k}|^2}{2} \tag{1}$$