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Full Length Article

# Density functional theory for field emission from carbon nano-structures

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ABSTRACT

Electron field emission is understood as a quantum mechanical many-body problem in which an electronic quasi-particle of the emitter is converted into an electron in vacuum. Fundamental concepts of field emission, such as the field enhancement factor, work-function, edge barrier and emission current density, will be investigated, using carbon nanotubes and graphene as examples. A multi-scale algorithm basing on density functional theory is introduced. We will argue that such a first principle approach is necessary and appropriate for field emission of nano-structures, not only for a more accurate quantitative description, but, more importantly, for deeper insight into field emission.



## 1. Introduction

Although considerable progress has been made in the first principle study of field emission of nano-structures since the pioneering works dating back 15 years ago, [1–3] a quantitative description still remains a challenge. The hard-core difficulty is the multi-scale characteristic of the problem in which degrees of freedom from atomic to macroscopic scales are all crucial. Yet, first principle approaches are needed to obtain a quantum many-body picture of electron field emission (FE). The present paper is not intended to give a review of this big subject by any mean. Our purpose is to highlight how interesting the physics of FE is and why first principle calculations are absolutely necessary.

A first principle approach necessitates the re-examination of some basic concepts and conventional parameters in FE of nano-structures. For instance, the field enhancement factor and the work-function which are constants in the conventional field emission model are in fact field-dependent. For these field emission features of nano-emitters, both the atomic and electronic structures are crucial. As many-electron correlations are involved, the traditional FE picture of a single electron tunneling through a given potential energy barrier is obviously not complete. The quasi-particle concept provides a more advanced picture for FE, which can be conveniently presented in the language of density functional theory (DFT) [4,5]. To estimate the emission image, besides the local density of states (LDOS) in the edge region the precise atomic structure of the emitter edge is also important. Atomic structure relaxation is needed. All this should be done with DFT.

After some more discussions of our motivation for this work (Section 2), we introduce concisely the concepts of quasi-particles and the local density of states (Section 3). This leads up to the introduction of multi-scale density functional theory (MSDFT) for carbon nanotube (CNT) field emission in Section 4. The MSDFT is then applied to the study of the emission potential energy barrier in Section 5, where the field enhancement factor, the work-function, and the edge polarization are investigated. The image potential and the exchange–correlation correction are also discussed in this section. Then in Section 6 DFT-based methods for emission current density calculations are introduced. Notably, the calculated FE image of CNT exhibits a spontaneous axial symmetry breaking. The last section is a brief summary and a perspective on first principle theory for FE.

## 2. Motivation

The standard theory of FE was set up in 1928 by Fowler and Nordheim [6] and completed in the following decades [7]. The Fowler–Nordheim theory (FNT) is based on the non-interacting electron model of a metal, incorporating the concepts of quantum

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tunneling, Fermi level, and spin degrees of the electron. The FNT predicts that the logarithm of the ratio of emission current density ($J$) over the applied macroscopic field square ($F_M^2$) is inversely proportional to the field ($F_M$),

$$\ln (J/F_M^2) = -\frac{s}{F_M} + c_0 \tag{1}$$

This prediction has been confirmed by many FE experiments and has been considered as the major characteristic feature of FE, though exceptions do exist in the FE of some nano-emitters. The FNT is very useful for applications where the emission current density is mainly of interest. It is not difficult to extract the two parameters $s$ and $c_0$ of FNT from the experiment. Also for flat metallic emitters, it is explicitly known that $s$ is a function of the work-function and $c_0$ is a function of the work-function and the temperature of the emitter. For an emitter with a smooth emission surface (we will call it the edge of the emitter) distinct from a plane, the effect of the aspect-ratio is usually accounted for by a field enhancement factor that is defined as the ratio of the edge field to the applied macroscopic field.

On the other hand, first principle calculations by definition are not based on any drastic assumption or model, and it may incorporate many-body effects without too many approximations. DFT as a representative first principle theory for many-electron systems is certainly more complicated and less transparent than FNT, but it provides an understanding of the important many-body aspects of the problem that are ignored in FNT. In particular, for nano-emitters, the physics of FE is a great challenge because a nano-emitter is (1) a quantum many-body system; (2) an open quantum system; (3) a non-equilibrium problem; (4) a tunneling process that is detail sensitive. In fact the particles are not just tunneling but converting from quasi-particles to elementary electrons in vacuum during the FE process. These quantum-mechanical many-body features of FE are far beyond the scope of the FNT and have not been fully explored by either experimental or theoretical study. DFT is the perfect theoretical tool just appropriate for this subject, allowing details to be explored, such as the parameterization of the edge barrier incorporating the properties of both the electronic structure and the atomic structure.

In the present paper we concentrate on CNT and graphene as examples. CNT is a promising emitter because of its large aspect-ratio as shown both experimentally and theoretically [8]. Graphene has an excellent electrical conductivity as an attractive FE emitter should be and does show promising FE properties [9]. A technical reason for choosing CNT and graphene is because their well-defined atomic structures can be studied by DFT. We recall that the tight-binding theory (TBT) can nicely describe the low energy (related to the Fermi level) electron behavior of both CNT and graphene [10,11]. It is helpful to have the DFT results compare with the TBT solutions. In this paper we will not mention other first principle approaches, such as time-dependent density functional theory [12,13] and non-equilibrium Green's function theory, [14,15] although they have their own merits and are promising also.

In earlier days DFT was applied to short segments of CNT with various tip structures, with results on the atomic and electronic structures [1–3,16–18]. Because of the short CNT segments used, the emission currents are too low compared to experiments so that a large field enhancement factor has to be assumed. Recently DFT calculations have been available for CNTs of microns in length. The multi-scale theory for FE was introduced by Zheng et al. [19] and further improved since then [20, 21], see Section 4.

## 3. Brief introduction for DFT

In most cases it is appropriate to calculate the emission current density as a function of the applied field by the time independent DFT because the emission will be steady in a few femtoseconds after the field applied [2,12,13].

The idea of DFT is to convert a many-electron problem into a one-particle problem at the cost of an unknown, but universal, exchange–correlation potential. The fundamental theorem was given by Hohenberg and Kohn: [4] (1) the Hamiltonian of a static many-electron closed system is uniquely determined by the electron density of the ground state; (2) the correct electron density of the ground state minimizes the energy functional of the electron density.

A practical way to calculate the ground state properties was provided by Kohn and Sham [5]. They introduced a fictional system of non-interacting "electrons" with orthogonal one-particle orbitals $\{\phi_i(\vec{r})\}$. The ground state of the non-interacting system is required to have the same electron density as the system of interacting electrons in the physical ground state. Consider a spin-neutral system with $2N$ electrons for simplicity. The electron density is given by

$$n(\vec{r}) = 2\sum_{i=1}^{N} |\phi_i(\vec{r})|^2 \tag{2}$$

The factor 2 accounts for the spin degrees of freedom (spin degeneracy is assumed). According to the theorem of Hohenberg–Kohn, the given $n(\vec{r})$ uniquely determines the Hamiltonian of the non-interacting system, so does the one-particle spectrum $\{\varepsilon_i\}$ and orbitals $\{\phi_i(\vec{r})\}$. In other words, $\{\varepsilon_i\}$ and $\{\phi_i(\vec{r})\}$ are functionals of $n(\vec{r})$. Therefore, the total kinetic energy of the non-interacting system $T_s = \sum_i \int |\nabla\phi_i(\vec{r})|^2 d\vec{r}$ is also a universal density functional.

On the other hand, the total energy $E[n]$ of the interacting system can be separated into two terms: a universal density functional $F[n]$ and the non-universal density functional $V[n] = \int v_{ex}(\vec{r}) n(\vec{r}) d\vec{r}$ with $v_{ex}$ the external potential from ions and other external fields [4]. Kohn and Sham defined another universal exchange–correlation density functional as $E_{XC}[n] = F[n] - T_s[n] - U[n]$, where $U[n] = \frac{1}{2}\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$ is the classical mutual Coulomb potential energy of electrons. Thus the total energy of the interacting many-body system is written as

$$E[n] = T_s[n] + V[n] + U[n] + E_{XC}[n] \tag{3}$$

The Hohenberg–Kohn theorem requires that the correct density should minimize $E[n]$, leading to the Kohn–Sham equation for the one-particle normalized orbitals,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{KS}(\vec{r}, [n])\right]\phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \tag{4}$$

The potential $v_{KS}$ is formally written as

$$\begin{aligned} v_{KS}(\vec{r}, [n]) &= \frac{\delta V}{\delta n(\vec{r})} + \frac{\delta U}{\delta n(\vec{r})} + \frac{\delta E_{XC}}{\delta n(\vec{r})} \\ &= v_{ex}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + v_{XC}(n(\vec{r}), [n]) \end{aligned} \tag{5}$$

The last term is called the exchange–correlation potential (XCP). It is a coordinate-depending functional of $n$ in general, thereby is nonlocal. If $v_{XC}$ was known, (2) and (5) form a closed set of self-consistent equations containing all information of the electronic structure of the interacting electron systems. Unfortunately, there is no way to obtain the exact functional $v_{XC}$ for interacting electron systems. All the complexity of many-electron systems is hidden in the XCP. Usually one finds $v_{XC}$ by a guess-and-check method.

For the cases of slowly varying density or high electron density, it is appropriate to assume that the XCP is simply a function of the

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