Theoretically choosing multifunctional materials

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Abstract. The aim of this paper is to discuss the possibility of theoretically engineering multifunctional nanomaterials. The calculations were performed for 1D and 2D nanomaterials by using results obtained within the Hubbard model (HM). The main results of the HM are briefly reviewed. The conclusion is that the approach taken in this paper is a distinct improvement over those in the literature. In the present paper results of applications of the HM are directly used in examples of engineering nanomaterials. On the other hand, in the literature calculations were performed by ab initio methods and then fitted to the form of the Hamiltonian of the HM.

1. Introduction
This paper is devoted to the problem of theoretically predicting values of parameters of multifunctional materials. It seems appropriate to start by defining these materials. Multifunctional materials can be defined as the materials which perform multiple functions in a system to which they belong [1]. They can exist naturally, but they can also be artificially synthetized. The probably best known natural multifunctional material is the human skin.

Multifunctional nanomaterials offer interesting possibilities for applications. A recent list [1] shows as much as 11 areas of human activity in which multifunctional materials have important impact.

Just as an illustration, note that applications of multifunctional nanomaterials in medicine are particularly interesting. A recent example is a drug called Kadcyla produced by the chemical industry Roche. In it, two materials in the form of nanoparticles which are separately known to be cancer-toxic (called transtuzumab and DM1) are joined together and sent to find and destroy HER2 positive cancer cells. Details are available at http://www.roche.com.

In the example just mentioned, and in principle in any attempt of applying nanomaterials, there arises a practical question: how does one choose parameters of a multifunctional material? Experimentally, one could proceed by the "trial and error" method until reaching a satisfactory result. There is also the theoretical approach of modeling a material within some particular model. The calculations to be presented in this paper will be performed within the Hubbard model (HM).

Before embarking on the calculations, there are two questions which should be tackled to some extent. In view of the fact that large calculational projects, such as NOMAD (Novel Materials Discovery) (http://nomad-coe.eu), exist is it useful to perform small scale calculations like those to be presented here? Another big material science project is the Materials Genome...
Concerning NOMAD, the answer is positive. It is true that NOMAD guarantees high precision in treatment of any problem in material science. However, attempting to achieve the same goal by using any particular model is certainly easier as it bypasses problems related to access to NOMAD. Therefore, calculations discussed here can be treated as a first approximation to work possible by using NOMAD. A similar conclusion applies to MGI, which also has a data repository.

A bibliographical search concerning the applicability of the Hubbard model to modelling materials gave encouraging results. A search with the keywords "hubbard model material" on http://prola.aps.org published "anytime" performed beginning October 2018 gave 9218 results. The clear implication is that this model can be applied to modelling materials. Classified as "most relevant" in this list is [2]. In this paper, the authors used ab initio electronic structure methods to design a material whose Hamiltonian matches as closely as possible that of the single band Hubbard model. Another interesting paper from this list is [3]. That paper is devoted to the computation of the ground-state phase diagram of the Hubbard model.

The next two sections contain a brief reminder of the main results of the HM needed in this paper, while the rest of the paper is devoted to the application of the HM in the choice of parameters of multifunctional nanomaterials.

2. The Hubbard model

This is a reminder of the main equations of the HM, while the reader interested in details is referred to [4,5]. See also [6].

The basic point for the study of any physical system is its Hamiltonian. For a 1D system, within the second quantisation formalism, the Hamiltonian has the following form

\[ H = -w \sum_{l,\sigma} (c^+_{l,\sigma}c_{l+1,\sigma} + c^+_{l+1,\sigma}c_{l,\sigma}) + U \sum_j n_{j,\uparrow}n_{j,\downarrow} \]  \hspace{1cm} (1)

The following symbols have been used: \( w \) denotes the hopping and \( U \) is the interaction energy of a pair of electrons having opposite spins on a lattice site \( j \). Symbols of the form \( c^+_{l,\sigma} \) denote a creation operator for an electron having spin \( \sigma \) on lattice site \( l \), while \( c_{l+1,\sigma} \) is the annihilation operator for an electron at lattice site \( l+1 \) with spin \( \sigma \). The current operator is

\[ j = -iw \sum_{l,\sigma} (c^+_{l,\sigma}c_{l+1,\sigma} - c^+_{l+1,\sigma}c_{l,\sigma}) \]  \hspace{1cm} (2)

Knowing the Hamiltonian of a system enables the calculation of its transport properties. One of the methods for such calculations is the so called "memory function" approximation (MFA), developed in the 1970s as a consequence of previous work of Kubo. The MFA is extensively discussed in the literature (some references are given in [4]). Without repeating this discussion, we shall just state the final result for the electrical conductivity of a 1D system [4].

The final result for the electrical conductivity is given by

\[ \sigma_R(\omega_0) = (1/2\chi_0)(\omega_0^2/\pi)[\omega_0^2 - (bw)^2]^{-1}(Uw/N^2)^2S \]  \hspace{1cm} (3)

and the symbol \( S \) denotes the following function

\[ S = 42.49916(1 + \exp(\beta(-\mu - 2w)))^{-2} + 78.2557(1 + \exp(\beta(-\mu + 2w \cos(1 + \pi))))^{-2} \]
\[ + \frac{bw}{\omega_0 + bw}(4.53316 \times (1 + \exp(\beta(-\mu - 2w)))^{-2} \]
\[ + 24.6448(1 + \exp(\beta(-\mu + 2w \cos(1 + \pi))))^{-2}). \]  \hspace{1cm} (4)
The symbol $\mu$ denotes the chemical potential of the electron gas on a 1D lattice [6], $n$ is the filling factor of the lattice, $N$ the number of sites in the lattice, $b$ a numerical constant,

$$
\mu = \frac{(\beta\omega)^6(n_{s} - 1)|w|}{1.1029 + 0.1694(\beta\omega)^2 + 0.0654(\beta\omega)^4}
$$

### 3. Optics

Relations between the electrical conductivity and reflectivity of solids are known since the middle of the twenties of the last century. These are the so called Kramers-Kroning (KK) relations. Detailed considerations on the KK equations can be found, for example, in [6,10]. In the context of this paper, there is one logically arising question: can these relations be used in theoretically choosing a nano-material? The answer is, as the reader may suppose, positive.

Skipping the details of the calculation (see [6] for example) it can be shown that the reflectivity is given by

$$
R = (2\pi\sigma R)^2 - K\omega[4\pi\sigma R - K\omega(1 + K^2)]
$$

and

$$
K_{1,2}^2 = \frac{4\pi\omega\sigma I - \omega^2 \pm [(4\pi\omega\sigma R)^2 + (\omega^2 - 4\pi\omega\sigma I)^2]^{1/2}}{2\omega^2},
$$

where the symbols $\omega, \sigma R$ and $\sigma I$ denote the frequency, the real and imaginary components of the conductivity. These two expressions are applicable to 1D materials. Their applicability can be extended to 2D materials by a change of variables: $\sigma = [\sigma_x^2 + \sigma_y^2]^{1/2}$ [9].

The KK relations can be applied in several ways in engineering a nanomaterial. For example, what parameters a nanomaterial must have in order to have reflectivity close to zero? Or, if a material has a particular value of $t_x$ what value of $t_y$ must it have in order to have a particular value of the reflectivity?

### 4. Choosing multifunctional materials

Every part of any system performs a certain task within the domain of possibilities of the system as a whole. If a part of a system, or the system as a whole can perform multiple tasks, it is called a multifunctional system. Going a step further, a nanomaterial is called a multifunctional nanomaterial if its behavior can be controlled by the application of various external fields [8].

#### 4.1. 1D material under a thermal field

One of the parameters of a material is the chemical potential of the electron gas. In the 1D case, it is given by eq.(5), and discussed in more detail [4,6]. It was shown by Lieb and Wu [7] that the chemical potential is zero for half filling, regardless of the temperature. Speaking from the experimental point of view, the half-filled case means that the material is pure (not doped) and that it is not a conductor of electricity [6].

Taking into account the fact that in real experiments materials are at some non-zero temperature, the obvious question is: can the chemical potential become close to zero for the lattice filling factor $n$ different from one? A positive answer to that question would have some interesting consequences in the applications of the HM.

Take equation $(5)$ and arbitrarily normalize the chemical potential to $\mu = 1$ at the point $n = 1.1, T = 116K$ and $t = 0.02$. Repeating the same calculation for $n = 1.3$, and then plotting the two graphs, one gets figure 1. Figure 1. shows that for $T \geq 180 \, K$, the chemical potential tends approximately to zero.

This is a difference with the standard results of the HM, which state that the chemical potential and the electrical conductivity are zero for $n = 1$. In fact, this means that the...
material becomes electrically neutral at values of temperature above some limiting value of the temperature. In the context of choosing a nano-material this can be taken to imply that designing an electrically neutral material can be achieved by heating it above a limiting value of the temperature.

4.2. the conductivity of a 1D material under a thermal field

As described in the preceding section, a prerequisite for the calculation of the electrical conductivity of any physical system is the knowledge of its Hamiltonian. A frequent choice for such calculations is the memory function method. Applying this approach to the 1D Hubbard model, and using the formalism of second quantisation, one gets expressions (3)-(4) for the electrical conductivity.

The chemical potential, which contains the dependence on the doping and temperature, is given by equation (5). It is generally agreed that equations (3)-(5) can be applied to 1D systems of correlated electrons, such as low dimensional organic conductors and/or superconductors. The following two figures illustrate the behavior of systems of 1D correlated electrons under the control of a thermal field (i.e., under variable temperature).

Figure 2 shows the characteristic shape of the \( \sigma(T) \) curve. As the position of the maximum is sharp, this result opens up (in principle) the possibility of theoretically choosing a nanomaterial which will have a predetermined position of the maximum conductivity in the \( (\sigma, T) \) plane.

Experimentally speaking, the filling factor \( n \) denotes the doping of a material. Figure 3 shows that exposing a material to a varying doping field changes its conductivity in a characteristic manner, and thus opens up the possibility of designing a material with a specified value of the couple \( \sigma, n \).

Figure 4 is even more interesting, because it shows the behavior of the conductivity of a material under the influence of two variable fields: the thermal field, and (what could be called) the hopping field, under constant doping \( n \). In the region \( T < 180 \, K \) the relative differences of the conductivities for the largest and smallest values of the hopping \( t \) amount to as much as 50 per cent. Using calculations like those which led to this figure, one can theoretically design

![Figure 1](image-url)
Figure 2. The normalized elect. conduct. of 1D electron gas for $n = 0.9$

Figure 3. The normalized conductivity for three values of $n$ for a 1D material

materials with predetermined values of the conductivity for certain values of the doping and/or hopping. Practically, one would have to choose pairs of $(n, t)$ values, or fix $n$ and vary $t$ and then calculate the conductivity.

4.3. The two dimensional materials
The HM is at present solved only for the case of 1D [7]. In the special case of a 2D rectangular lattice where the conductivities along the axes are mutually independent and denoted by $\sigma_x$ and
Figure 4. The normalized conduct. of a 2D rectang. lattice for 3 values of $t$

$\sigma_y$, the conductivity of the lattice can be expressed as

$$\sigma = [\sigma_x^2 + \sigma_y^2]^{1/2}. \quad (8)$$

Theoretically choosing the parameters of a system having such a link between the conductivities of its parts may seem complicated. In fact, this 2D problem reduces to two 1D problems along the two lattice axes.

Figure 5. The normalized reflectivity of a 2D rectangular lattice for 2 values of $T$
Figure 5 taken from [6] is an example of the influence of external fields on a rectangular 2D lattice which is moderately useful for theoretically choosing a nanomaterial. It represents the dependence of the normalized electrical conductivity of a 2D lattice on the ratio of the filling factors along the two lattice axes. This ratio is symbolized by \( n_y/n_x = \theta \) and the parameters for which this figure was calculated are available in [6]. The point which could be useful in choosing a nanomaterial is here the turning point of one of the curves.

4.4. designing the optical properties of nano materials
An interesting, but complicated way of engineering a nano material is to predict theoretically the value of its reflectivity and link it to the values of various material parameters. It can be shown ([6] and references given there) that the reflectivity can be expressed as the following sum

\[
R \approx 1 - 2 \left( \frac{K \omega_0}{\pi \sigma_R} \right) + 2 \left( \frac{K \omega_0}{\pi \sigma_R} \right)^2 - ..
\]

(9)

This expression for the reflectivity implicitly depends on the dimensionality of the system through \( \sigma_R \) and \( K \). An illustrative example of the temperature dependence of the reflectivity is presented on fig.6.

Note an interesting detail on this figure, useful for theoretically choosing a nano material. The derivative \( dR/dT \) drastically changes at the temperature of approximately \( T \approx 70K \). The position of this point can be theoretically predicted, and it depends on the values of the hopping \( t \) and the filling factor \( n \). This means that fixing the temperature and which \( R \) changes, one can theoretically determine the values of \( t \) and \( n \).

![Figure 6. The reflectivity of 1D HM for \( n = 0.8 \) \( t = 0.01 \)](image)

The first step was the calculation of the electrical conductivity. It was normalized to \( \sigma_R = 1 \) for \( n = 0.8 \), \( t = 0.005 \) eV and \( T = 116 \) K. In the case of a 2D material, two important ratios influence the results of calculations discussed here. These are the ratio of the conductivities, denoted by \( \sigma_{Ry}/\sigma_{Rx} = \Gamma \), and the ratio of the filling factors along the two lattice axes, symbolized by \( n_y/n_x = \theta \). Note that all the 2D materials discussed here imply materials with a square lattice.
The dependence of the reflectivity under constant temperature of a 2D lattice on the parameter $\theta$ is shown on the following figure, taken from [6]. Note that the decrease of $\theta$ leads to a decrease of the value of $R$. In practical terms, this means that decreasing the ratio of filling factors along the two lattice axes leads to increasing difficulties in seeing the specimen. This conclusion could have implications in work on invisibility cloaks.

![Graph showing reflectivity as a function of $\theta$ for $T = 150K$.](image)

**Figure 7.** The reflectivity as a function of $\theta$ for $T = 150K$

5. **Piezoresistivity under strain**

In various situations, both in laboratory work and practical applications, the need may arise for a material which becomes better conductor of electricity when exposed to a strain $\epsilon$. Such a material can be chosen theoretically, but the situation is slightly more complex than in the cases discussed so far.

Namely, in such a situation one has to take into account the dependence of the hopping $t$ on the strain. Using results on the overlap of atomic wave functions, in [11], the dependence of the hopping $t$ on the interatomic distance $r$ was approximated as

$$t = t_0[1 + r + (1/3)r^2] \exp(-r)$$

where $r$ is measured in the units of Bohr radius.

As a practical application, in which theoretical choice of a material is needed, let us consider an instrument based on piezoresistivity [4]. In this case the problem we encounter can be stated as "At a given temperature $T$ what value of the hopping $t$ must the material have, in order to achieve some chosen value of the sensitivity $G$?"

The sensitivity of a sensor based on piezoresistivity is defined as

$$G = -\frac{1}{\sigma} \left( \frac{\partial \sigma}{\partial \epsilon} \right)$$

where $\sigma$ is the conductivity and $\epsilon$ the strain. The dependence of $G$ on the strain has been studied in [4]. Clearly, the lower the temperature the more pronounced this dependence becomes.
6. Compressibilities

What would be the result of attempting to engineer a nanomaterial under the influence of high pressure? To render the problem more complex, imagine that the nanomaterial in question is a compound, consisting of two specimen of nanomaterials with compressibilities of different signs. This combination is in principle possible [12]. Imagine an experiment in which two materials having different coefficients of thermal expansion are fixed together. If such a combination is heated, it will bend to one side. A similar situation will occur if the two nanomaterials are subdued to high pressure and have compressibilities of different signs [12].

The isothermal compressibility is defined as

$$\beta_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_T$$  \hspace{1cm} (12)

where all the symbols have their standard meanings. The pressure $P$ and volume $V$ of a material are linked through the equation of state. Choosing an appropriate equation of state for a given nanomaterial is a delicate research subject. See, for example, [13].

In the case of a nanomaterial distributed along a straight line, the problem returns to those discussed earlier. However, if the materials are distributed along a curved line, the solution is strongly dependent upon the compressibilities and their signs. A detailed consideration of this problem is in preparation.

7. Conclusions

This paper attempted to answer an apparently simple question - is it possible to choose parameters of a nano-material theoretically so that they have certain pre-selected values? This choice of parameters is dependent on the theoretical model chosen to describe the material under study.

The calculations discussed in the present paper were performed for 1D and 2D materials within the Hubbard model. Calculations reported here are more direct than those in [2,3]. For example, in [2] the calculations were performed by ab initio methods, and then the Hamiltonian was matched to the Hamiltonian of the HM. On the other hand, in the present paper results of direct applications of the HM and the memory function method were used to demonstrate possibilities of engineering nano-materials, which is a distinct advantage. It was shown on several examples that it is possible to engineer multifunctional nano-materials by calculating their conductivity, reflectivity and sensitivity for piezoresistivity, making calculations within the Hubbard model a viable way in theoretically modelling nanomaterials.

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