Optimal control of the local electromagnetic response of nanostructured materials: optimal detectors and quantum disguises

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We consider the problem of optimization of an effective trapping potential in a nanostructure with a quasi-one-dimensional geometry. The optimization is performed to achieve certain target optical properties of the system. We formulate and solve the optimization problem for a nanostructure that serves either as a single molecule detector or as a “quantum disguise” for a single molecule.

The rapid advance in fabrication techniques makes it possible to control the composition and geometry of nanostructured systems and materials on atomic scales [1]. One of the most interesting and challenging problems in modern nanoscience is how to utilize these fabrication capabilities to control the interaction of electromagnetic fields with nanostructured media. A successful solution to this problem would make possible the design of, for example, high energy density storage applications, or multifunctional nanophotonic materials with predefined properties [2].

There is, in general, a complex relationship between the effective electron trapping potential in a nanostructure and the nanostructure’s optical properties. One can usually solve this problem for a chosen geometry and structure of the system, thus for a given trapping potential. However, the inverse problem to find an optimal geometry of the nanostructure to attain desired optical properties seems much more complicated. In particular, the matter-field interaction becomes complex in the quantum limit of very small nanostructures, containing only a few electrons. Quantum mechanical corrections and the non-locality of the electromagnetic response become significant for system sizes comparable to a typical electron wavelength. This condition may be satisfied for such small objects as quantum dots, or for the next generation of microchips [3]. For example, for the semiconductor GaAs with a doping level of $10^{18}$cm$^{-3}$ and effective electron mass $m_e^* = 0.07 \times m_e$, the Fermi wavelength $\lambda_F \approx 20$nm is on the length scale currently available in microchip design. Thus, the problem has both fundamental and applied significance, and there is a strong demand for methods to efficiently explore the optimal design of quantum nanoscale devices.

A systematic approach to the theoretical analysis of optimal design of potentials in quantum scattering in semiconductor nanodevices was first developed in [4]. Twelve years later, an optimal design problem with similar objectives was considered in [5]. In [6] a simple tight-binding model was considered in two dimensions with the aim of fitting a target density of states, and as a result, also describing the basic response properties of the system. Another interesting example of inverse band structure engineering was considered for nitrogen impurities in GaP [7].

One of the potential applications of optimal design of nanostructures is to the engineering of efficient single molecule detectors. Single molecule sensing by means of optical excitation is receiving increasing attention [8]. In this work we will demonstrate that with the help of quantum design it is possible to control and manipulate induced local fields in the nanostructure on a very fine scale. We formulate and solve the optimal design problem for nanostructures, which may serve as single molecule detectors. We consider electrons trapped in the effective potential of the nanostructure. The presence of a polar molecule in close vicinity of the nanostructure may slightly modify the electron trapping potential, and as a result, its optical response. If a monochromatic electromagnetic field of frequency $\omega$ is used to excite the nanostructure followed by a measurement of the molecular induced changes, then it is possible to use this nanostructure (or, better, an array of identical nanostructures) as a single molecule detector. The optimal design goal is to find a nanostructure with an effective trapping potential that results in maximum contrast between the optical response either with or without a particular molecule at a given excitation frequency. Note, that the opposite optimization problem, to find the effective trapping potential that minimizes the contrast, can also be formulated. We also consider this problem, and refer to this type of nanostructure as providing quantum disguise.

We assume that there are $N_d$ electrons trapped in a nanostructure. The system is described by the Hamiltonian $H_n = \nabla^2 + V_{trap}(r)$, with the eigenenergies and eigenfunctions $E_i$ and $\psi_i$, respectively. Since inhomogeneous systems with a few electrons can have an electromagnetic response very different from the bulk, in our simulations we use the non-local density-density response function within the coordinate-space representa-
\[ \chi(r, r', \omega) = \sum_{i,j} \frac{f(E_i) - f(E_j)}{E_i - E_j - \hbar \omega - i\gamma} \times \psi_i^*(r) \psi_j^*(r') \psi_i(r') \psi_j(r), \]  

(1)

where \( f(E_i) \) is the Fermi filling factor and the small constant \( \gamma \) describes level broadening. \( \omega \) is the frequency of the external electromagnetic field. The electron eigenenergies \( E_i \) and eigenfunctions \( \psi_i \) are obtained numerically using real-space discretization of the Schrödinger equation. Using Eq. (1) we calculate the induced electric field \( E_{\text{ind}}(r, \omega) \) in the system within linear response theory [3].

The effect of the presence of a molecule is modeled by a contrast ratio. To characterize the response of the nanostructure. To optimize the potential which is added to the effective trapping potential in the nanostructure \( V_{\text{mod}}(r) = -A \exp(-B|x-r_0|^2) \), where \( r_0 \) is the position of the molecule. The Gaussian potential is chosen just for demonstration purposes. We also performed simulations using a \( r^{-6} \) potential with a cut-off, and obtained qualitatively similar results. A more realistic molecular potential could be deduced from \textit{ab initio} simulations.

As stated above, the presence of a molecule can modify the response of the nanostructure. To characterize the difference between state 1 without the molecule and state 2 with the molecule attached, we introduce the contrast ratio between the two responses:

\[ I_{\text{contr}} = \int_V |E_{\text{ind}}^1(r, \omega) - E_{\text{ind}}^2(r, \omega)|^2 d^3r/I_0, \]  

(2)

where the normalization intensity \( I_0 = \int_V |E_{\text{ind}}^1(r, \omega)|^2 d^3r \) and \( E_{\text{ind}}^1(r, \omega) \), \( E_{\text{ind}}^2(r, \omega) \) are the induced electric fields in state 1 and state 2, correspondingly. The choice of the normalization intensity \( I_0 \) is dictated by the aim of finding a nanostructure, whose response in the state 2 generates a local electric field with the largest intensity.

We assume that the effective trapping potential \( V_{\text{trap}}(r) \) can be represented as a sum of \( N_p \) model potentials \( V_{\text{mod}}(r) \) located at \( r_i \), \( i = 1, \ldots, N_p \), which can be controlled during the material fabrication procedure with sufficient precision:

\[ V_{\text{trap}}(r) = \sum_{i=1}^{N_p} V_{\text{mod}}(r - r_i), \]  

(3)

For simplicity we assume \( V_{\text{mod}}(r) \) to be the Coulomb potential of a charge \( Q \) with a cutoff \( a \):

\[ V_{\text{mod}}(r) = \begin{cases} Q/|r|, & |r| > a, \\ Q/a, & |r| \leq a. \end{cases} \]  

(4)

The optimization algorithm searches for the optimal parameters \( r_i \) to maximize or minimize the contrast ratio given by Eq. (2). The search for the optimal potential \( V_{\text{trap}}(r) \) is performed using Brent’s “principal axis” optimization algorithm [10] for a scalar function of several variables.

In order to reduce the computational complexity of the problem we perform the simulations considering a quasi-1D nanostructure geometry. We assume that spatial localization of electrons in the other two dimensions \((y, z)\) creates relatively large energy gaps in the sub-bands, so we can neglect excitation in these directions. The incoming field is linearly polarized, with the polarization along the \( x \) axis. Such systems can be created even on an atomic scale using STM techniques [11] by placing atoms of different species in a line. Let \( L \) be the length of the system. Then \( E_0 = \frac{e^2}{2m_e} \) is the unit of energy determined by the geometry of the system. Here \( m_e \) is the electron mass. We perform optimization of the trapping potential at the frequency of the external field \( \hbar \omega = 0.1E_0 \). We assume there are \( N_e = 15 \) electrons trapped within the nanostructure. We set the temperature to \( T = 0K \), and the level broadening \( \gamma = 10^{-2}E_0 \).

For the model potential in Eq. (1) we use the cut-off parameter \( a = 0.05L \) and \( Q = 15e/N_p \), where \( e \) is the electron charge. For our simulations we set the molecular position at \( x_0 = L/2 \). We set the parameters of the molecular potential \( V_{\text{mol}}(r) \) to \( A = 0.005e/L \) and \( B = 0.14L^{-2} \).

Figs. (a)-(b) show the results of calculations for a non-optimized nanostructure. Fig. (a) gives the ground state electron density and the trapping potential without and with a molecule. Note, that in all the figures the trapping potential is scaled down by a factor of 10. Fig. (b) shows the induced field intensity \( |E_{\text{ind}}|^2 \) for the trapping potentials given in Fig. (a). Note, that the addition of the potential \( V_{\text{mol}}(x) \) just slightly modifies the induced field intensity.

Figs. (c)-(d) are the same as (a)-(b), but for an optimized potential. The optimization is performed to maximize the contrast ratio given by Eq. (2). Note, that in the optimized case, the difference in the induced field intensity with and without the molecule is so big, that we have to employ a logarithmic scale. The explanation of this effect is that the potential \( V_{\text{trap}} + V_{\text{mod}} \) produces an energy difference between the highest occupied and lowest unoccupied states that very well matches the frequency of the probe field \( \hbar \omega = 0.1E_0 \).

Now let us consider the opposite problem of searching for the trapping potential that minimizes the contrast ratio in Eq. (2). During the search for the quantum disguise trapping potential, the optimization procedure has a tendency to converge to a trivial solution, with the optimized parameters \( x_i \) diverging from the molecule position \( x_0 \). In this case, if there is a negligible probability of electrons occupying \( V_{\text{mol}} \), the presence or absence of the molecule does not change the response of the nanostructure. To avoid such solutions, we introduce a renormalized contrast ratio \( I_{\text{contr}}/\delta \rho_g^2 \), where \( \delta \rho_g = \int_V |\rho_1(r) - \rho_2(r)|^2 d^3r \).
where $\rho_1$ and $\rho_2$ are the electron ground state density with and without a molecule, respectively.

In Figs. 2 (a)-(c) we present the calculations in the same order, as in Figs. 1 (a)-(c), but for the “quantum disguise” potential. For the “quantum disguise” problem we set the parameters of the molecular potential $V_{\text{mol}}(r)$ to $A = 0.06e/L$ and $B = 0.14L^{-2}$, so the perturbation due to the presence of the molecule becomes comparable to the original trapping potential $V_{\text{trap}}$. Note, while the trapping potentials with and without the molecule, and the corresponding electron densities shown in Fig. 2 (c) are rather different, the optical responses of both systems at frequency $\omega = 0.1E_0$ is very close to each other (see Fig. 4 (d)).

The effect of quantum interference can be explained in terms of quantum interference between transitions in the combined system $H_n + V_{\text{mol}}$, which cancel each other to give approximately the response of $H_n$. We checked this assumption by plotting the induced charge densities $\rho_{ij}(x)$, corresponding to the transitions between states $i$ and $j$. We found that all these densities are quite different for the potentials shown in Figs. 2 (a) and 2 (c). However, they are all sum up to almost identical total induced charge densities $\rho_{\text{ind}}(x) = \sum_{i,j} \rho_{ij}(x)$.

We also studied the dependence of the nanostructure response on the frequency of the external field. Fig. 3 (a) shows the contrast ratio as a function of the frequency $\omega_i$. The dashed line shows $I_{\text{contr}}(\omega)$ for the initial, non-optimized trapping potential in Fig. 1 (a), and the solid line corresponds to the optimized trapping potential in Fig. 1 (c). Note, that the solid curve has a maximum at the frequency $\hbar \omega = 0.1E_0$, at which the optimization was performed. In Fig. 3 (b) we plot the contrast ratio $I_{\text{contr}}(\omega)$ for the potentials shown in Figs. 2 (a), (c). Again, the dashed line corresponds to the initial, non-optimized trapping potential, and the solid line corresponds to the optimized one. Note the dip near the target frequency $\hbar \omega = 0.1E_0$, at which the optimization was performed. In both figures the improvement of the target functionality $I_{\text{contr}}(\omega)$ is of two-three orders of magnitude.

We now consider a molecule position sensitivity analysis. In Figs. 4 (a,b) we show the contrast ratio $I_{\text{contr}}$ as a function of the molecule position for the non-optimized trapping potential and the optimized one. In Fig. 4 (a) we show the results for the trapping potential parametrized using $N_p = 3$, and in Fig. 4 (b) $N_p = 5$. It is clear, that even without any localization mechanism an array consisting of the optimized nanostructures will outperform a similar array of non-optimized ones. Indeed, assuming that the molecule’s position $x_0$ is uniformly distributed on $[0, L]$, one can estimate the average enhancement by integrating the area under the curve. The integration over the curves shown in Fig. 4 (a) gives the average value of the contrast ratio of $S = 7.01$ with optimization, and $S' = 0.46$ for a nonoptimized nanostructure. Integration of the curves shown in Fig. 4 (b), gives $S = 8.43$ and $S'' = 0.053$ correspondingly. In the case of molecules localized near $x_0 = L/2$ the enhancement factor could reach up to three orders of magnitude, compared to the non-optimized nanostructures.

In conclusion, we demonstrated the feasibility of optimizing the trapping potential parameterized by just a few control parameters. Even in this limited case the target functionalities (such as detector sensitivity) can be enhanced by orders of magnitude.

Since the effects we consider are based on the resonance properties of the nanostructure, larger values of the level broadening $\gamma$ will result in reduced improvement of the design. From a simple analysis one can estimate that the intensity enhancement for the optimized design scales as $\propto (\gamma/E_0)^{-2}$. Thus, phonon, electron-electron scattering and other processes that lead to level broadening will reduce the optimization effect.

The results of optimal design for the quantum disguise problem show that although the real and imaginary parts of the nanostructure response are coupled through the Kramers-Kronig relations and are not completely independent, we succeeded to make the scattering and absorption properties of two significantly different quantum systems almost identical at a given frequency.

It is known that for the electron Hamiltonians there is a one-to-one correspondence (within an additive constant) between the non-degenerate ground state electron density $\rho(r)$ and the trapping potential $V_{\text{trap}}(r)$. This...
FIG. 2: Initial non-optimized trapping potential. (a) Trapping potential, no molecule (thin solid line) and with molecule (dotted line). The corresponding electron density, no molecule (thick solid line) and with a molecule (dotted line). (b) Induced field intensity, no molecule, (solid line), and with a molecule (dotted line). (c)-(d) Same as (a)-(b), but for an optimized potential that minimizes the contrast ratio \( I_{\text{contr}} \) at the frequency of the external field \( h\omega = 0.1E_0 \).

The relatively high sensitivity of the optical response of the optimized nanostructures to fabrication errors can potentially pose a serious problem. To address this problem we suggest that the optimal properties of the nanostructures could be controlled during the assembling phase using closed loop adaptive techniques similar to those used in optical field control [13].

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dependence is established through the Hohenberg-Kohn mapping [12]. Although some physical properties of the system can be deduced from its ground state, many characteristics, such as transport properties and optical response, strongly depend on the excitation spectrum of the system. The results suggest that there are situations, when the precision of the calculated excitation spectrum is crucial. In the case of the single molecule detector shown in Fig.1, two quantum systems with very close ground state densities could have very different responses. And the results for the quantum disguise problem show that two quantum systems with almost identical optical response at a given frequency could have rather different electron ground states.

FIG. 3: The contrast ratio \( I_{\text{contr}} \) between the induced field intensity, with and without the molecule, as a function of the frequency of the external field \( \omega \). (a) The dashed line refers to the non-optimized trapping potential shown in Fig. 1(a), and the solid line is for the optimized potential in Fig. 1(c). Note the local minimum near the target frequency \( h\omega = 0.1E_0 \). (b) Same as (a), but the contrast ratio is calculated for the potentials shown in Fig. 2(a) and (c), correspondingly.

FIG. 4: The contrast ratio \( I_{\text{contr}} \) between the induced field intensity, with and without the molecule, as a function of position \( x_0 \) of the molecule. (a) The dashed line refers to the non-optimized trapping potential shown in Fig. 1(a), and the solid line is for the optimized potential in Fig. 1(c). (b) Same as (a), but the contrast ratio is calculated for an optimized potential using \( \{x_i\}, i = 1, \ldots, 5 \) parameters.