Electronic transport in DNA functionalized graphene sensors

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Abstract

A theoretical understanding of the experimental electronic transport phenomena in gas sensors based on DNA functionalized graphene is presented by quantitatively investigating the time-dependent electronic transport in these devices using the nonequilibrium Green’s function (NEGF) formalism and tight-binding approximation. The time-dependent zeroth and first order contributions to the current are calculated with derivations of the equation of motion and Dyson equation. The zeroth order contribution is identified as the time-dependent Landauer formula in terms of the slow time variable and the first order contribution is found to be small in this experiment. The current is explicitly calculated by deriving a formula for the transmission function and considering a form for the hopping integral which includes the effect of chemical vapors on the charge distribution of the carbon atoms and the nearest-neighbor carbon-carbon distance $a_{cc}$. Theoretical results are found in agreement with the experimental results. A shift in the Fermi level ($\varepsilon_f$) is calculated, which is a result of shift in the Dirac point due to adsorption of vapors on the DNA functionalized graphene. The work suggests that using the same values of change in $a_{cc}$ due to the four DNA bases for a specific target vapor, the theoretical values of the current response can be predicted for different DNA sequences leading to the application of the graphene sensors as a DNA analyser.

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I. INTRODUCTION

Graphene is a single atomic layer of graphite that is truly a two-dimensional structure. Graphene was first isolated in 2004 by micromechanical cleavage of graphite [1]. The exceptional and fascinating mechanical, structural and electronic properties of graphene make it a promising building block for next-generation electronics. The most remarkable property of graphene originates from its unusual electronic structure. Graphene has a unique electronic band structure where the valence and conduction bands meet at the Dirac points, giving rise to conical sections of the energy spectrum. Hence, charge carriers in graphene possess a linear dispersion relation similar to that described by the massless Dirac equation and thus behave in a unique manner. They move as if they have zero effective mass and a velocity which is about 300 times slower than the speed of light [2, 3, 4, 5, 8, 9, 10]. Graphene reveals ambipolar electric field-effect where the charge carriers can be electrons or holes with their density proportional to gate voltage [1, 2, 10]. By changing the gate voltage one can modify the charge carrier density in graphene and therefore the Fermi level can be tuned. In pristine graphene, the Fermi level lies at the Dirac point and generates zero density of states, that is, there are no states to occupy and hence there are no charge carriers which contribute to the electronic transport, resulting in a large resistivity. The Dirac point separates the region of conduction by electrons from the region where the transport is governed by holes. When the Fermi level shifts away from the Dirac point (into hole or electron conduction regime) on application of the gate voltage, the resistance decreases with increasing gate voltage. As a result, the carrier concentration increases which contributes to the transport. Graphene possesses extremely high carrier mobility, a measure of how fast charges travel [1, 2, 9, 10, 11, 12, 13, 14], leading to ballistic transport [1, 2, 12], and also exhibits quantum hall effect [3, 10, 15, 16, 17, 18, 19].

Graphene has a large surface area [20] with every carbon atom on its surface in direct contact with surrounding atmosphere, making its electronic and mechanical properties extremely sensitive to small changes in the environment. Hence, enabling the fabrication of miniaturized sensors capable of detecting a number of molecular species [21, 22, 23, 24, 25, 26, 27, 28, 29] with high sensitivity, excellent selectivity, and fast response and recovery time. Substantial progress in carbon nanotube (CNT) based chemical sensors has already been achieved as addressed in the literatures [30, 31, 32, 33, 34, 35, 36].
But a major difficulty in such sensors is the separation of semiconducting carbon nanotubes from metallic ones, while the more consistent electronic structure of graphene generally makes it more suitable as compared to CNTs for use in such devices. The sensing properties of graphene are found to be promising for gases such as NH$_3$, CO, H$_2$O, O$_2$, NO$_2$ and 2,4-dinitrotoluene (DNT) \[21, 22, 23, 24, 25, 26, 27, 28, 29\]. The gas sensing characteristics of graphene have been attributed to its two-dimensional structure and the extraordinary mobility of charge carriers \[21, 24\]. Since graphene is all surface, no bulk, thus there is a huge scope for studying the surface dependent gas sensing phenomenon on its surface. The large surface area gives very high sensitivity and the high electron mobility gives ultra fast response times. Graphene is superior because of its high electrical conductivity (even if there are few carriers) as well as low noise properties \[2, 3, 11, 21\] which make the local change in its electrical properties, due to adsorption of gas molecules on its surface acting as donors or acceptors, detectable.

Graphene has shown its potential for detection of various molecular species with high sensitivity in ambient conditions. However, its performance is limited to those molecular species that get adsorbed on the surface causing a detectable sensor response. But a weak or no observable response of intrinsic graphene (without resist residue on the surface) is found for water vapor, TMA, octanoic acid \[23\] and for DMMP and PA \[37\]. To overcome this limitation of intrinsic graphene, functionalization is a promising approach to tune its electronic properties. The effect of functionalization of graphene with metal nanoparticles and bio-molecules on their sensing properties in terms of enhanced reactivity and sensitivity towards molecular species has already been reported \[37, 38, 39, 40, 41, 42\].

Despite tremendous experimental progress in gas sensing applications of graphene the underlying mechanism of gas adsorption and detection is not very clear and needs an in-depth understanding. The path breaking experimental results on functionalized graphene have raised challenging issues for theory and modeling, especially, on how to describe the dynamics in the presence of dopants for electronic transport measurements. To address this issue a quantitative and detailed understanding of the electronic transport in such nanohybrids is needed.

This paper reports on the theoretical understanding of the experiment where the electronic transport properties (sensing response) of devices based on graphene monolayer FETs decorated with single stranded DNA (ssDNA) strands were measured in the presence of
chemical vapors [37] for which the clean device does not show any response. The electronic transport through the system is modeled using the tight-binding Hamiltonian and the nonequilibrium Green’s function (NEGF) formalism. In the experiment reported in Ref. [37], the ssDNA oligomers were applied to the surface of the graphene by putting a small drop of dilute solution of ssDNA in deionized water (700 µg/mL) onto the chip surface with the graphene device [37]. The device was then immediately placed into a chamber held at 100% relative humidity by a steam bath to prevent the solution from evaporating off the surface. The sample was left in the humid chamber for 45 minutes, after which the ssDNA solution was blown off with nitrogen gas. This process enabled the self-assembly of a nanoscale ssDNA layer on the graphene surface. Two ssDNA sequences, sequence 1: 5′ GAG TCT GTG GAG GAG GTA GTC 3′ and sequence 2: 5′ CTT CTG TCT TGA TGT TTG TCA AAC 3′ were selected to functionalize the graphene device.

The vapor response measurements were recorded at 1 mV applied bias voltage and zero gate voltage with varying concentrations. Initially, the carrier gas (N₂) was passed through the chamber at a rate of 1 slm and then chemical vapor dimethylmethylphosphonate (DMMP) was substituted for a small percentage of the N₂ flow with the total flow rate held constant [37]. Figure 2(a) of Ref. [37] shows the responses to DMMP vapor of devices based on pristine graphene, graphene functionalized with ssDNA sequence 1, and ssDNA sequence 2 at different concentrations. The sensor responses are presented as changes in the device current normalized to the current measured when pure N₂ flowed. The current response of clean graphene to DMMP vapor is very weak and barely detectable above the noise level, at all concentrations, although a response $\Delta I/I_0 \sim 1\%$ was recorded at the highest concentration. Functionalization of graphene with ssDNA enhanced the responses on the scale of 5% to 50%. The sensor responses were reproducible with nearly perfect recovery to baseline upon purging [37]. Because of the negatively charged backbone of ssDNA, its role is to make more hydrophilic environment around the chemically inert and hydrophobic conduction channel of graphene which facilitates the adsorption of more analytes on the device [37]. As a result, the sensor response increases compared to the response of clean graphene. The measured sensor responses of functionalized graphene device for DMMP with sequence 1 and 2 are given in Table 1 of Ref. [37].
II. TIGHT-BINDING MODEL AND nonequilibrium green’s function

To study the electronic transport in the DNA-decorated graphene-FET, a simplified theoretical model of the complex gas-DNA-graphene-FET system is presented. The model consists of a graphene monolayer, acting as the channel, connected to two metallic contact electrodes source (S) and drain (D) with a single strand of ssDNA sequence 1 applied on its surface as shown in Fig. 1. The model represents a graphene sheet with carbon atoms labeled as $A_1, B_1, A_2, B_2, \ldots, X_i$, where $X$ can be either carbon atom $A$ or $B$ and the index $i = 1, 2, \ldots, M/2$ or $(M+1)/2$ denotes the number of the carbon atoms, and $M$ is the total number of carbon atoms involved in the transport. Since graphene is decorated with two ss-DNA sequences, sequence 1 with 21 bases and sequence 2 with 24 bases. Therefore the value of $M$ can be odd or even depending on the type of the sequence. For ssDNA sequence 1, $M$ is odd and is equal to 23, while $M$ is even and equal to 26 for sequence 2 including the first $A_1$ and the last $X_{M/2}(X_{(M+1)/2})$ carbon atoms which are connected to S and D electrodes. In the present model, the decoration of graphene is shown for ssDNA sequence 1 with bases guanine (G), adenine (A), thymine (T) and cytosine (C), in the order of arrangement GAG TCT GTG GAG GAG GTA GTC, and denoted by green ovals interacting with different carbon atoms and the pink and purple circles represent the DMMP vapor and $N_2$ gas, Fig. 1.

In a graphene sheet, the carbon atoms are held together by $sp^2$ hybridized covalent bonds, while the electronic transport takes place by hopping along $\pi$ orbitals which can participate in some kind of bonding with adsorbates [43]. Here, it is assumed that the bonding is a kind of van der Waals (vdW) bonding ($\pi - \pi$ stacking) between the DNA bases and the carbon atoms.

The electrical properties of the graphene device changes as a result of adsorption of the DNA bases and vapor molecules on the graphene surface. The experimental sensor response is found to be sequence sensitive. Therefore, initially, when the graphene is decorated with ssDNA sequence 1, the base guanine (G) interacts with the carbon atom $B_1$ and the adenine (A) base interacts with $A_2$ and the rest of the bases keep on interacting with other carbon atoms. Upon DMMP exposure, the vapor molecule interacts with G base at an instant of time $t_1$ through vdW forces, Fig. 1(a). As a result, the electron hops from the $\pi$ orbital of the carbon atom $A_1$ to the neighboring carbon atom $B_1$ and the tunneling of the electron from
A\textsubscript{1} to B\textsubscript{1} is an elastic process with the corresponding integral called the hopping integral $\gamma\textsubscript{11}(t_1)$. Then, the electron hops from B\textsubscript{1} to A\textsubscript{2} with the hopping integral $\gamma\textsubscript{12}(t_1)$, and from A\textsubscript{2} to B\textsubscript{2} with $\gamma\textsubscript{22}(t_1) = \gamma_0$, where $\gamma_0$ is the hopping integral of the ssDNA coated graphene when exposed to N\textsubscript{2} (without the vapor). Hence, the hopping integrals between the rest of the carbon atoms $\gamma\textsubscript{ij}(t_1)$ are also $\gamma_0$ as shown in Fig. 1(a). The indices i(j)=1,2,···p(q), where p = q = M/2 for even M and p= (M-1)/2 and q=(M+1)/2 for odd M. In a similar manner, at time $t_{(M+1)/2}$ (for odd M) the time at which the vapor molecule interacts with the last base cytosine (C) of the DNA sequence 1 attached to the carbon atom, the hopping integrals are $\gamma\textsubscript{11}(t_{(M+1)/2}), \gamma\textsubscript{12}(t_{(M+1)/2}), \cdots \gamma\textsubscript{pq}(t_{(M+1)/2})$, Fig. 1(b). Hence, as a result of time-dependent interaction of vapor molecules with the DNA-decorated graphene, the hopping integrals as well as the on-site energy change with the time $t$ at which the vapor molecules trigger the different bases of the DNA sequence attached to the graphene. This time-dependent hopping integral and on-site energy give rise to time-dependent Hamiltonian and Green’s function for the functionalized graphene. Thus, to study the time-dependent electronic transport through the model system the time-dependent NEGF formalism is well suited.

FIG. 1: Adsorption of DMMP vapor on graphene decorated with ssDNA sequence 1 which is connected to S and D electrodes. The DNA bases are represented by green ovals, DMMP and N\textsubscript{2} molecules are indicated by pink and purple spheres. The arrow indicates the path of transmission. $\gamma\textsubscript{ij}(t)$ are the hopping integrals between different carbon atoms A\textsubscript{i} and B\textsubscript{i} at time $t$. Here, $t = \bar{t}_1, \cdots, \bar{t}_{(M+1)/2}$ after applying the adiabatic approximation (subsection IIB) and $\gamma_0$ represents the hopping integral in the absence of DMMP.
In order to understand the sensor response of the graphene device a simple model and its working is presented because the actual experimental picture of the system is quiet complicated. Graphene device is functionalized with two ssDNA sequences 1 and 2. Both sequences consist of four types of nucleobases G, C, A and T, respectively, but with different order of arrangement of these four bases. In the experiment [37], there are many strands of the same ssDNA sequence either 1 or 2 applied on the surface of the graphene sheet. Hence one expects an average sequence-independent effect, but this is not observed in the experiment. Experimental responses of devices to DMMP vapor are found to be sequence-dependent, the response of devices for sequence 1 is different than that for sequence 2. Thus in order to show the sequence-dependent effect as observed in the experiment, the model simply assumes the effect to be due to different charge transfer by different bases of a single strand of ssDNA sequence of type either 1 or 2.

The Hamiltonian corresponding to the coupled Gas-DNA-graphene-FET system is given as

\[ H_{\text{total}} = H_{\text{graphene}} + H_{\text{contact}} + H_{\text{tunneling}}, \]

where the Hamiltonian of graphene is expressed as

\[ H_{\text{graphene}} = \sum_{m} \varepsilon_{m}(t) d_{m}^\dagger d_{m} + \sum_{<mn>} \gamma_{mn}(t) d_{m}^\dagger d_{n}, \]

where \( d_{m}^\dagger \) and \( d_{m} \) are creation and annihilation operators of an electron in graphene, \( \varepsilon_{m}(t) \) is the on-site energy of the carbon atom and \( \gamma_{mn}(t) \) is the nearest-neighbor hopping integral between the carbon atoms as a function of time.

The contact Hamiltonian is written as

\[ H_{\text{contact}} = \sum_{k\alpha S,D} \varepsilon_{k\alpha} c_{k\alpha}^\dagger c_{k\alpha}, \]

where \( c_{k\alpha}^\dagger \) and \( c_{k\alpha} \) are creation and annihilation operators for electrons with momentum \( k \) in the contact, either S or D. In the experiment, there is no external time-dependent bias applied between the S and D contacts therefore the contact Hamiltonian is time-independent and electrons in the contacts are non-interacting. The tunneling Hamiltonian which describes the coupling between the contact electrodes and graphene in the absence of a time-dependent
gate voltage is expressed as

$$H_{\text{tunneling}} = H_T = \sum_{n, k\alpha S, D} (V_{k\alpha, n} \epsilon_{k\alpha} d_n + H.c.).$$  \hspace{1cm} (4)$$

In the matrix form, the total Hamiltonian is expressed as

$$H(t) = \begin{pmatrix} H_S & V_{\text{grp}} & 0 \\ V_{\text{grp}}^\dagger & H_{\text{grp}}(t) & V_{\text{grpD}} \\ 0 & V_{\text{grpD}}^\dagger & H_D \end{pmatrix},$$ \hspace{1cm} (5)$$

where \(H_{\{S, D\}}\) are the Hamiltonians of the S and D contact electrodes (Eq. (3)), and \(H_{\text{grp}}\) is the time-dependent tight-binding Hamiltonian for graphene (Eq. (2)) with matrix elements defined as \(H_{A_i A_i} = \epsilon_{A_i}(t)\), \(H_{B_i B_i} = \epsilon_{B_i}(t)\), the on-site energy and \(H_{A_i B_i} = H_{B_i A_i} = \gamma_{ii}(t)\) \[44\], \(H_{A_{i+1} A_i} = H_{A_{i+1} B_i} = \gamma_{i,i+1}(t)\), the hopping integrals and the rest of the off diagonal elements are zero. \(V_{\text{grp}}\) and \(V_{\text{grpD}}\) are the coupling (tunneling) matrices between the two electrodes and graphene (Eq. (4)). Hence, the time-dependent tight-binding Hamiltonian for graphene is expressed as

$$H_{\text{grp}}(t) =$$

$$\begin{pmatrix} \epsilon_{A_1}(t) & \gamma_{11}(t) \\ \gamma_{11}(t) & \epsilon_{B_1}(t) & \gamma_{12}(t) \\ & \gamma_{12}(t) & \epsilon_{A_2}(t) \end{pmatrix} \cdots$$

$$\begin{pmatrix} \cdots & \epsilon_{B_4}(t) & \gamma_{pq}(t) \\ \gamma_{pq}(t) & \epsilon_{X_i}(t) \end{pmatrix}. \hspace{1cm} (6)$$

The effect of DMMP vapor and DNA is included in the graphene Hamiltonian in the form of time-dependent on-site energy and hopping integrals because as the time changes, the number of vapor molecules and hence their interaction with different DNA bases changes, which results in a change in the on-site energy and hopping integral leading to a change in sensor response. The reason for this tight-binding Hamiltonian can be understood with an example of a single adsorbate interacting with graphene as described in Ref. [43] where chemically adsorbed molecules are incorporated into the tight-binding model of graphene as laterally attached additional sites, where the on-site and coupling energies are extracted from the band structure of a graphene sheet with regularly placed adsorbates. But in the
In the present model system, the adsorbed molecules are included in the tight-binding Hamiltonian not as attached additional sites. Here, the effect of the molecules are incorporated into the change in the on-site energy and hopping between the adjacent carbon sites as a function of interaction time of DMMP molecules with the DNA coated graphene. Thus the effect of interaction of DMMP molecules on $\gamma_0$ and $\varepsilon_0$ of the pristine graphene is represented by taking a time-dependent Hamiltonian $H(t)$ with $\gamma_0 \rightarrow \gamma(t)$ and $\varepsilon_0 \rightarrow \varepsilon(t)$. This indicates that as the time changes, the number of adsorbates and hence the interaction changes, which results in a change in $\gamma_0$, $\varepsilon_0$ and the sensor response.

### A. Expression for the current

In the present model system, the time-dependence arises because of the interaction of DMMP molecules with the DNA-graphene system for a given vapor exposure time not because of externally applied time-dependent bias between the two electrodes, and a time-dependent gate voltage. Using the standard technique of the NEGF formalism [45, 46, 47, 48, 49, 50, 51, 52, 53] which is modified to fit the present model system, the equation of motion for the Greens function is derived and a general expression for the time-dependent current flowing from the source or drain contact into the graphene device is given as

$$I_{S/D}(t) = \frac{-2e}{\hbar} \int_{-\infty}^{t} dt' \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ e^{-i\varepsilon k_0 (t'-t)} \Gamma_{S/D}(\varepsilon) \left[ f_{S/D}(\varepsilon) G^{r}_{\text{grp}}(t, t') + G^{<}_{\text{grp}}(t, t') \right] \right\}, \quad (7)$$

where $G_{\text{grp}}$ denotes the Green’s function of graphene in the presence of the coupling with the contacts.

### B. Adiabatic approximation

In the adiabatic approximation, the time scale over which the system parameters change is large compared to the life time of an electron in the system (graphene) [55]. In the problem of electronic transport through the graphene-based sensor the experimental time scale of the gas flow is much longer ($\sim$ seconds) than the time scale of electron transport inside graphene ($\sim 10^{-15}$ s). Therefore the adiabatic approximation is applied to study the electronic transport in the gas sensor.
1. **Adiabatic expansion for the Green’s functions**

The best way to separate slow and fast time scales is to re-parameterize the Green’s functions. In other words the time variables of the Green’s functions are replaced by a fast time difference \( \delta t = t - t' \) and a slow mean time \( \bar{t} = \frac{t + t'}{2} \) as \[55\]

\[
G(t, t') = G\left(t - t', \frac{t + t'}{2}\right).
\]

The adiabatic approximation is applied to lowest order by expanding the Green’s functions about the slow time variable up to linear order in the fast time variables \[55\]

\[
G(t - t', \bar{t}) = G(t - t', \bar{t})|_{\bar{t}=t} + \left(\frac{t' - t}{2}\right) \frac{\partial G}{\partial \bar{t}} (t - t', \bar{t})|_{\bar{t}=t} \tag{9}
\]

which can be further written as

\[
G(t - t', \bar{t}) = G^{(0)}(t - t', \bar{t}) + G^{(1)}(t - t', \bar{t}), \tag{10}
\]

where \(G^{(0)}(t - t', \bar{t})\) and \(G^{(1)}(t - t', \bar{t})\) are the zeroth and first order Green’s functions which lead to the zeroth and first order contributions to the current.

Applying adiabatic expansion on \(G(t, t')\) in Eq. (7) the current becomes

\[
I_{S/D}(t - t', \bar{t}) = -\frac{2e}{\hbar} \int_{-\infty}^{t'} dt' \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ e^{-i\varepsilon_k(t - t')} \Gamma_{S/D}(\varepsilon) \left[ f_{S/D}(\varepsilon) G^{r}_{\text{grp}}(t - t', \bar{t}) + G^{<}_{\text{grp}}(t - t', \bar{t}) \right] \right\} + \frac{G^{r}_{\text{grp}}(t - t', \bar{t})}{2} + \frac{G^{<}_{\text{grp}}(t - t', \bar{t})}{2} \tag{11}
\]

Consider only the zeroth order contribution to the current \[12\]

\[
I_{S/D}^{(0)}(t - t', \bar{t}) = -\frac{2e}{\hbar} \int_{-\infty}^{t'} dt' \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ e^{-i\varepsilon_k(t' - t')} \Gamma_{S/D}(\varepsilon) \left[ G^{<}_{\text{grp}}(t - t', \bar{t}) + f_{S/D}(\varepsilon) G^{r}_{\text{grp}}(t - t', \bar{t}) \right] \right\} = I_{1}^{(0)}(t - t', \bar{t}) + I_{2}^{(0)}(t - t', \bar{t}).
\]
Solving for the first term

\[
I_1^{(0)}(t-t', \bar{t}) = -\frac{2e}{\hbar} \int_{-\infty}^{t'} dt' \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ e^{-i\varepsilon \kappa_0 (t'-t)} \Gamma_{S/D}(\varepsilon) G_{\text{grp}}^{(0)<}(t-t', \bar{t}) \right\}.
\]

Rearranging the terms and changing variable \(t'\) to \((t-t')\) and the limits we get

\[
I_1^{(0)}(t-t', \bar{t}) = -\frac{2e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ \Gamma_{S/D}(\varepsilon) \int_0^\infty d(t-t')e^{i\varepsilon \kappa_0 (t'-t')} G_{\text{grp}}^{(0)<}(t-t', \bar{t}) \right\},
\]

\[
= -\frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ \Gamma_{S/D}(\varepsilon) \int_{-\infty}^\infty d(t-t')e^{i\varepsilon \kappa_0 (t'-t')} G_{\text{grp}}^{(0)<}(t-t', \bar{t}) \right\}.
\]

Taking the Fourier transform we obtain

\[
I_1^{(0)}(\bar{t}) = -\frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ \Gamma_{S/D}(\varepsilon) G_{\text{grp}}^{(0)<}(\varepsilon, \bar{t}) \right\},
\]

and using the definition of \(G_{nm}^{<}(t, t') = \frac{i}{\hbar} < d_n(t')d_n(t) >\) the first term is written as

\[
I_1^{(0)}(\bar{t}) = i \frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \Gamma_{S/D}(\varepsilon) G_{\text{grp}}^{(0)<}(\varepsilon, \bar{t}) \right\}. \tag{13}
\]

Now solving for the second term

\[
I_2^{(0)}(t-t', \bar{t}) = -\frac{2e}{\hbar} \int_{-\infty}^{t} dt' \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ e^{-i\varepsilon \kappa_0 (t'-t)} \Gamma_{S/D}(\varepsilon) f_{S/D}(\varepsilon) G_{\text{grp}}^{(0)r}(t-t', \bar{t}) \right\}
\]

\[
= -\frac{2e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ \int_0^\infty d(t-t')e^{i\varepsilon \kappa_0 (t'-t')} \Gamma_{S/D}(\varepsilon) f_{S/D}(\varepsilon) G_{\text{grp}}^{(0)r}(t-t', \bar{t}) \right\},
\]

since \(G_{\text{grp}}^{(0)r}(t-t', \bar{t})=0\) for \(t-t' < 0\) from the definition of \(G_{nm}^{<}(t, t') = \frac{i}{\hbar} \theta(t-t') < \{d_n(t), d_m(t')\} >\), therefore the second term becomes

\[
I_2^{(0)}(\bar{t}) = -\frac{2e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{ImTr} \left\{ \Gamma_{S/D}(\varepsilon) f_{S/D}(\varepsilon) G_{\text{grp}}^{(0)r}(\varepsilon, \bar{t}) \right\}
\]

\[
= i \frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \Gamma_{S/D}(\varepsilon) f_{S/D}(\varepsilon) \left[ G_{\text{grp}}^{(0)r}(\varepsilon, \bar{t}) - G_{\text{grp}}^{(0)a}(\varepsilon, \bar{t}) \right] \right\}. \tag{14}
\]

Putting Eqs. (13) and (14) in Eq. (12) we get

\[
I_{S/D}^{(0)}(\bar{t}) = i \frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \Gamma_{S/D}(\varepsilon) \left[ G_{\text{grp}}^{(0)<}(\varepsilon, \bar{t}) + f_{S/D}(\varepsilon) \left[ G_{\text{grp}}^{(0)r}(\varepsilon, \bar{t}) - G_{\text{grp}}^{(0)a}(\varepsilon, \bar{t}) \right] \right] \right\}. \tag{15}
\]
C.  Green’s function for graphene

The time-ordered Green’s function of graphene $G_{nm}(t, t')$ satisfies the equation of motion

$$\left[ i\hbar \frac{\partial}{\partial t} - \varepsilon_n(t) \delta_{nm} - \sum_{<nm'>} \gamma_{nn'}(t) \right] G_{nm}(t, t') = \delta(t-t')\delta_{nm} + \sum_{k'\alpha'} V_{k'\alpha',n}^* G_{k'\alpha',m}(t, t'), \quad (16)$$

where $G_{k'\alpha',m}(t, t') = g_{k'\alpha'}(t - t') \sum_{m'} V_{k'\alpha',m'} G_{m'm}(t, t')$ is the contact time-ordered Green’s function.

Equation (16) can be further written as

$$\left[ i\hbar \frac{\partial}{\partial t} - \varepsilon_n(t) \delta_{nm} - \sum_{<nm'>} \gamma_{nn'}(t) \right] G_{nm}(t, t') = \delta(t-t')\delta_{nm} + \sum_{m'} V_{k'\alpha',m'} g_{k'\alpha'}(t-t') G_{m'm}(t, t')$$

$$= \delta(t-t')\delta_{nm} + \sum_{m'} \Sigma_{nm'}(t-t') G_{m'm}(t, t'). \quad (17)$$

where

$$\Sigma_{nm'}(t-t') = \sum_{k'\alpha'D} V_{k'\alpha',n}^* g_{k'\alpha'}(t-t') V_{k'\alpha',m'}, \quad (18)$$

is the time-independent self-energy \[51\].

After replacing $m'$ with $n'$ Eq. (17) can be further written as

$$\left[ i\hbar \frac{\partial}{\partial t} - \varepsilon_n(t) \delta_{nn'} - \sum_{<nn'>} \gamma_{nn'}(t) \right] G_{nn'}(t, t') = \delta(t-t')\delta_{nn} + \Sigma_{nn'} G_{nn'}(t, t'). \quad (19)$$

Equation (19) can be rewritten in full matrix form as

$$\left[ i\hbar \frac{\partial}{\partial t} - H_{\text{grp}}(t) - \Sigma_S(t-t') - \Sigma_D(t-t') \right] G_{\text{grp}}(t, t') = \delta(t-t')\delta_{nm}. \quad (20)$$

Applying adiabatic expansion on $G_{\text{grp}}(t, t')$ one obtains

$$\left[ i\hbar \frac{\partial}{\partial t} - H_{\text{grp}}(t) - \Sigma_S(t-t') - \Sigma_D(t-t') \right] \left( G_{\text{grp}}^{(0)}(t-t', \bar{t}) + G_{\text{grp}}^{(1)}(t-t', \bar{t}) \right) = \delta(t-t')\delta_{nm}. \quad (21)$$

Expanding $H_{\text{grp}}(t)$ around $\frac{t+t'}{2} = \bar{t}$ \[55\] gives rise to

$$H_{\text{grp}}(t) = H_{\text{grp}}(\bar{t}) + \frac{\partial H_{\text{grp}}(\bar{t})}{\partial \bar{t}}(t-\bar{t}) = H_{\text{grp}}^{(0)}(\bar{t}) + H_{\text{grp}}^{(1)}(\bar{t}). \quad (22)$$
Substituting Eq. (22) in Eq. (21) to get

\[ \left[ i\hbar \frac{\partial}{\partial t} - H_{\text{grp}}^{(0)}(\bar{t}) - H_{\text{grp}}^{(1)}(\bar{t}) - \Sigma(t-t') - \Sigma_{D}(t-t') \right] \left( G_{\text{grp}}^{(0)}(t-t',\bar{t}) + G_{\text{grp}}^{(1)}(t-t',\bar{t}) \right) = \delta(t-t')\delta_{nm}. \]  

(23)

Consider only the zeroth order contribution gives

\[ \left[ i\hbar \frac{\partial}{\partial t} - H_{\text{grp}}^{(0)}(\bar{t}) - \Sigma(t-t') - \Sigma_{D}(t-t') \right] G_{\text{grp}}^{(0)}(t-t',\bar{t}) = \delta(t-t')\delta_{nm}. \]  

(24)

Taking the Fourier transform with respect to the fast time variable \((t - t')\) we get

\[ \left[ \varepsilon - H_{\text{grp}}^{(0)}(\bar{t}) - \Sigma_{S}(\varepsilon) - \Sigma_{D}(\varepsilon) \right] G_{\text{grp}}^{(0)}(\varepsilon,\bar{t}) = 1. \]  

(25)

This leads to the zeroth order Green’s function for graphene in the presence of the coupling with the contacts

\[ G_{\text{grp}}^{(0)}(\varepsilon,\bar{t}) = \frac{1}{\varepsilon - H_{\text{grp}}^{(0)}(\bar{t}) - \Sigma_{S}(\varepsilon) - \Sigma_{D}(\varepsilon)}. \]  

(26)

D. Dyson equation

Equation (19) in full matrix form is expressed as

\[ \left[ i\hbar \frac{\partial}{\partial t} - \varepsilon_{n}(t) - \sum_{<nn'>} \gamma_{nn'}(t) \right] G_{\text{grp}}(t,t') = \delta(t-t')\delta_{nm} + \Sigma(t-t')G_{\text{grp}}(t,t'). \]  

(27)

Define two auxiliary time-ordered Green’s functions \(g\) and \(\bar{g}\) that satisfy the equation of motions

\[ \left[ i\hbar \frac{\partial}{\partial t} - \varepsilon_{n}(t) \right] g(t,t') = \delta(t-t'), \]  

(28)

and

\[ \left[ i\hbar \frac{\partial}{\partial t} - \varepsilon_{n}(t) - \sum_{<nn'>} \gamma_{nn'}(t) \right] \bar{g}(t,t') = \delta(t-t'), \]  

(29)

which is rearranged to

\[ \left[ i\hbar \frac{\partial}{\partial t} - \varepsilon_{n}(t) \right] \bar{g}(t,t') = \delta(t-t') + \sum \gamma_{nn'}(t)\bar{g}(t,t'). \]  

(30)

Using Eq. (28), Eq. (30) can be further written as

\[ \bar{g}(t,t') = g(t,t') \left[ \delta(t-t') + \sum \gamma_{nn'}(t)\bar{g}(t,t') \right]. \]  

(31)
From Eqs. (27) and (29)

\[ G_{\text{grp}}(t, t') = \bar{g}(t, t') + \bar{g}(t, t')\Sigma(t - t')G_{\text{grp}}(t, t'), \]  

which is the Dyson equation for the system of gas sensor.

III. RESULTS AND DISCUSSIONS

A. Zeroth order time-dependent Green’s function

The zeroth order graphene Hamiltonian \( H^{(0)}_{\text{grp}}(\bar{t}) \) is calculated by expanding the Hamiltonian \( H_{\text{grp}}(t) \) given in Eq. (6) around \( \bar{t} \) using Eq. (22), and taking only the zeroth order contribution. Using Eq. (26) and the Hamiltonian \( H^{(0)}_{\text{grp}}(\bar{t}) \), the zeroth order time-dependent retarded Green’s function for graphene \( G^{(0)r}_{\text{grp}} \) is calculated for a \( 9 \times 9 \) matrix and is given by

\[
G^{(0)r}_{\text{grp}}(\varepsilon, \bar{t}) = \begin{pmatrix}
\varepsilon - \varepsilon_{A_1}(\bar{t}) - \Sigma^r(\varepsilon) & \gamma_{11}(\bar{t}) \\
\gamma_{11}(\bar{t}) & \varepsilon - \varepsilon_{B_1}(\bar{t}) & \gamma_{12}(\bar{t}) \\
\gamma_{12}(\bar{t}) & \varepsilon - \varepsilon_{A_2}(\bar{t}) & \ddots \\
& \ddots & \ddots \\
& & \ddots & \varepsilon - \varepsilon_{B_4}(\bar{t}) & \gamma_{45}(\bar{t}) \\
& & & \gamma_{45}(\bar{t}) & \varepsilon - \varepsilon_{A_5}(\bar{t}) - \Sigma^r(\varepsilon)
\end{pmatrix}^{-1}
\]

Using the Green’s function the density of states can be calculated by \( D(\varepsilon) = i[G^r - G^a]/2\pi \).

B. Time-dependent Landauer formula

Using Eq. (15) and assuming the source and drain coupling functions are proportional to each other (\( \Gamma^S(\varepsilon) = \lambda\Gamma^D(\varepsilon) \)), and writing the current as \( I^{(0)}(\bar{t}) = xI^{(0)}_S - (1 - x)I^{(0)}_D \) the expression for the total current is expressed as

\[
I^{(0)}(\bar{t}) = \frac{ie}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ x\lambda - 1 + x \right\} \Gamma^D(\varepsilon)G^{(0)c}_{\text{grp}}(\varepsilon, \bar{t}) + \left[ x\lambda f^S(\varepsilon) - f^D(\varepsilon) + xf^D(\varepsilon) \right] \\
\times \Gamma^D(\varepsilon) \left[ G^{(0)r}_{\text{grp}}(\varepsilon, \bar{t}) - G^{(0)a}_{\text{grp}}(\varepsilon, \bar{t}) \right].
\]
Now fixing the arbitrary parameter \( x = \frac{1}{(1+\lambda)} \), where \( \lambda \) is the constant of proportionality, a simple expression for the total current through graphene is derived as

\[
I^{(0)}(\bar{t}) = \frac{ie}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \frac{\Gamma_S(\varepsilon)\Gamma_D(\varepsilon)}{\Gamma_S(\varepsilon) + \Gamma_D(\varepsilon)} \left( \frac{\epsilon^{(0)}_{\text{grp}}(\varepsilon, \bar{t})}{\epsilon^{(0)}_{\text{grp}}(\varepsilon, \bar{t}) - \epsilon^{(0)}_{\text{grp}}(\varepsilon, \bar{t})} \right) \right\} \left[ f_S(\varepsilon) - f_D(\varepsilon) \right],
\]

(35)

Applying the adiabatic expansion and taking the Fourier transform of the Dyson equation (Eq. (32)) for the retarded Green’s function, one obtains

\[
G^{r}_{\text{grp}}(\varepsilon, \bar{t}) = \bar{g}^{r}(\varepsilon, \bar{t}) + \bar{g}^{r}(\varepsilon, \bar{t})\Sigma^{r}(\varepsilon)G^{r}_{\text{grp}}(\varepsilon, \bar{t}),
\]

(36)

where \( \Sigma^{r}(\varepsilon) \) is the self energy which can be expressed as

\[
\Sigma^{r}(\varepsilon) = \frac{G^{r}_{\text{grp}}(\varepsilon, \bar{t})}{\bar{g}^{r}(\varepsilon, \bar{t})} = \bar{g}^{r}(\varepsilon, \bar{t})^{-1} - G^{r}_{\text{grp}}(\varepsilon, \bar{t})^{-1}.
\]

(37)

In the present model system, the effect of vapor interaction with the DNA coated graphene is included in the Hamiltonian \( H_{\text{grp}}(\bar{t}) \) (as discussed before in section II) not in the self-energy which is time-independent and includes only the tunneling contributions with no interaction. The retarded and advanced self-energies are defined as

\[
\Sigma^{r,a}(\varepsilon) = \sum_{k\alpha} |V_{k\alpha}|^2 g^{r,a}_{k\alpha}(\varepsilon) = \Lambda(\varepsilon) \mp i\Gamma(\varepsilon)/2,
\]

(38)

where \( \Lambda(\varepsilon) \) and \( \Gamma(\varepsilon)/2 \) are the real and imaginary parts of the self energy with \( \Lambda(\varepsilon) = \Lambda_S(\varepsilon) + \Lambda_D(\varepsilon) \) and \( \Gamma(\varepsilon) = \Gamma_S(\varepsilon) + \Gamma_D(\varepsilon) \).

Equation (38) leads to the self-energy difference as

\[
\Sigma(\varepsilon) = \Sigma^{r}(\varepsilon) - \Sigma^{a}(\varepsilon) = -i\Gamma(\varepsilon).
\]

(39)

Using Eq. (38) the zeroth order retarded and advanced Green’s functions for graphene from Eq. (26) are

\[
G^{(0)r,a}_{\text{grp}}(\varepsilon, \bar{t}) = \left[ \varepsilon - H^{(0)}_{\text{grp}}(\bar{t}) - \Lambda(\varepsilon) \pm i\Gamma(\varepsilon)/2 \right]^{-1}.
\]

(40)

This equation gives rise to

\[
G^{(0)r}_{\text{grp}}(\varepsilon, \bar{t}) - G^{(0)a}_{\text{grp}}(\varepsilon, \bar{t}) = \frac{-i\Gamma(\varepsilon)}{(\varepsilon - H^{(0)}_{\text{grp}}(\bar{t}) - \Lambda(\varepsilon))^2 + (\Gamma(\varepsilon)/2)^2},
\]

(41)
\[
G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})G_{\text{grp}}^{(0)a}(\epsilon, \bar{t}) = \frac{1}{(\epsilon - H_{\text{grp}}^{(0)}(\bar{t}) - \Lambda(\epsilon))^2 + (\Gamma(\epsilon)/2)^2}.
\] (42)

From Eqs. (41) and (42)
\[
G_{\text{grp}}^{(0)r}(\epsilon, \bar{t}) - G_{\text{grp}}^{(0)a}(\epsilon, \bar{t}) = G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})G_{\text{grp}}^{(0)a}(\epsilon, \bar{t})(-i\Gamma(\epsilon))
= G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})(-i\Gamma(\epsilon))G_{\text{grp}}^{(0)a}(\epsilon, \bar{t}).
\] (43)

Using Eq. (39), Eq. (43) becomes
\[
G_{\text{grp}}^{(0)r}(\epsilon, \bar{t}) - G_{\text{grp}}^{(0)a}(\epsilon, \bar{t}) = G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})(-i\Gamma(\epsilon))G_{\text{grp}}^{(0)a}(\epsilon, \bar{t})
= G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})\Sigma(\epsilon)G_{\text{grp}}^{(0)a}(\epsilon, \bar{t}).
\] (44)

Substituting Eq. (44) in Eq. (35)
\[
I^{(0)}(\bar{t}) = \frac{e}{\hbar} \int \frac{d\epsilon}{2\pi} \text{Tr}\left\{ \frac{i\Sigma(\epsilon)}{\Gamma_S(\epsilon) + \Gamma_D(\epsilon)} G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})\Sigma(\epsilon)G_{\text{grp}}^{(0)a}(\epsilon, \bar{t}) \right\}[f_S(\epsilon) - f_D(\epsilon)].
\]

In this equation, the quantity \(-i(\Gamma_S(\epsilon) + \Gamma_D(\epsilon)) = -i\Gamma(\epsilon)\) is just the self-energy \(\Sigma(\epsilon)\) (Eq. (39)). Hence the current becomes
\[
I^{(0)}(\bar{t}) = \frac{e}{\hbar} \int \frac{d\epsilon}{2\pi} \text{Tr}\left\{ \Gamma_S(\epsilon)G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})\Gamma_D(\epsilon)G_{\text{grp}}^{(0)a}(\epsilon, \bar{t})\Sigma(\epsilon)\Sigma^{-1}(\epsilon) \right\}[f_S(\epsilon) - f_D(\epsilon)],
\] (45)

which leads to
\[
I^{(0)}(\bar{t}) = \frac{e}{\hbar} \int \frac{d\epsilon}{2\pi} \text{Tr}\left\{ \Gamma_S(\epsilon)G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})\Gamma_D(\epsilon)G_{\text{grp}}^{(0)a}(\epsilon, \bar{t}) \right\}[f_S(\epsilon) - f_D(\epsilon)].
\] (46)

This is the time-dependent Landauer formula derived in terms of the slow time variable \(\bar{t}\), where \(f_{(S,D)}(\epsilon)\) are the Fermi distribution functions in the source and drain contacts, and \(\Gamma_{(S,D)} = i[\Sigma_{(S,D)}^{r} - \Sigma_{(S,D)}^{a}]\) describe the contact-graphene coupling.

C. The transmission function

From equation (46) the transmission function of the graphene system is identified as
\[
T(\epsilon, \bar{t}) = \text{Tr}(\Gamma_S(\epsilon)G_{\text{grp}}^{(0)r}(\epsilon, \bar{t})\Gamma_D(\epsilon)G_{\text{grp}}^{(0)a}(\epsilon, \bar{t})),
\] (47)

Considering the first element of the \(\Gamma_S(\epsilon)(\Sigma_S(\epsilon))\) matrix and the last element of the \(\Gamma_D(\epsilon)(\Sigma_D(\epsilon))\) matrix the transmission function can be rewritten as
\[
T(\epsilon, \bar{t}) = \Gamma_{S,11}(\epsilon)G_{\text{grp19}}^{(0)r}(\epsilon, \bar{t})\Gamma_{D,99}(\epsilon)G_{\text{grp19}}^{(0)r}(\epsilon, \bar{t}),
\] (48)
where $G^{(0)rr} = G^{(0)a}$.

To calculate the current explicitly, an expression for the transmission function is derived in the linear response regime as the experiment is performed with low bias. In linear response, the expression for the current (Eq. (46)) becomes

$$I^{(0)}(\bar{t}) \approx \frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} T(\varepsilon, \bar{t}) \delta [f_{S}(\varepsilon) - f_{D}(\varepsilon)].$$

(49)

Equation (49) can be further written as

$$I^{(0)}(\bar{t}) \sim \frac{e}{\hbar} T(\varepsilon_{f}, \bar{t}) [\mu_{S} - \mu_{D}],$$

(50)

where $\mu_{\{S,D\}}$ are the chemical potentials associated with the S and D contacts. Equation (50) is obtained by using $\delta [f_{S}(\varepsilon) - f_{D}(\varepsilon)] = (\mu_{S} - \mu_{D})(-\frac{\partial f_{0}}{\partial \varepsilon})$ and $(-\frac{\partial f_{0}}{\partial \varepsilon}) = \delta (\varepsilon_{f} - \varepsilon)$ where $f_{0}(\varepsilon) = 1/[1 + \exp((\varepsilon - \mu)/k_{B}T)]$ is the equilibrium Fermi function and $\varepsilon_{f}$ is the Fermi energy of graphene.

Transport is often dominated by states close to the Fermi level, and $\Gamma(\varepsilon)$ and $\Lambda(\varepsilon)$ the imaginary and real parts of the self-energy are generally slowly varying functions of energy, therefore the wide-band limit is considered in which the real part ($\Lambda$) of the self energy is neglected and the imaginary part ($\Gamma$) is considered to be energy independent. This approximation has the advantage of providing explicit analytic results. Hence, $\Lambda$ is neglected and $\Gamma$ is considered energy independent from now onwards. Taking $\Gamma_{S,11} = -2\text{Im}(\Sigma_{S,11}^{r}) = -2\text{Im} \Sigma_{S}^{r}$ and $\Gamma_{D,99} = -2\text{Im}(\Sigma_{D,99}^{r}) = -2\text{Im} \Sigma_{D}^{r}$ from the relationship $\Gamma_{\{S,D\}} = i[\Sigma_{\{S,D\}}^{r} - \Sigma_{\{S,D\}}^{a}]$, and using Eqs. (33) and (48) the expression for the transmission function for graphene coated with ssDNA sequence 1 in linear response regime is given by

$$T(\varepsilon_{f}, \bar{t}) = \frac{4 \text{Im} \Sigma_{S}^{r} \text{Im} \Sigma_{D}^{r}}{\text{Tr} \{ \gamma_{11}(\bar{t}) \gamma_{22}(\bar{t}) \gamma_{33}(\bar{t}) \gamma_{44}(\bar{t}) \} |G_{grp}^{(0)}(\varepsilon_{f}, \bar{t})|^{2}_{9 \times 9}.}$$

(51)

**D. The first order contribution to the current**

The first order contribution to the current is expressed as

$$I^{(1)}(\bar{t}) = \frac{ie}{\hbar} \int \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \frac{\Gamma_{S}(\varepsilon) \Gamma_{D}(\varepsilon)}{\Gamma_{S}(\varepsilon) + \Gamma_{D}(\varepsilon)} \left( G_{grp}^{(1)r}(\varepsilon, \bar{t}) - G_{grp}^{(1)a}(\varepsilon, \bar{t}) \right) \right\} [f_{S}(\varepsilon) - f_{D}(\varepsilon)].$$

(52)

The first order current $I^{(1)}(\bar{t})$ is found small as compared to the zeroth order current $I^{(0)}(\bar{t})$. The first order Green’s function $G^{(1)}(\bar{t})$ gives rise to the first order current $I^{(1)}(\bar{t})$,
and it is defined as \( G^{(1)r,a}(t-t', \bar{t}) = (\frac{t-t'}{2}) \frac{\partial G^{r,a}}{\partial \bar{t}}(t-t', \bar{t}) \bigg|_{\bar{t}=t} \) where the fast time variable \((t-t')\) is of the order of \( \sim 10^{-15} \) s. Therefore, the first order contribution being very small is not included in the final expression for the total current. There could be future experiments in which the first order term is enhanced (e.g., when \( \frac{\partial G^{r,a}}{\partial \bar{t}} \sim \frac{1}{t-t'} \)) and the first order contribution becomes significant.

IV. THEORY AND EXPERIMENT

To show that the theory and experiment are in a good agreement the sensor response, \( \Delta I(0)(\bar{t})/I_0 = 1 - I(0)(\text{vapor})/I_0(\text{air}) = 1 - T(\varepsilon_f, \bar{t})/T_0(\varepsilon'_f, \bar{t}_{\text{max}}) \) of the DNA coated graphene device is explicitly calculated using a 9 \times 9 matrix and a form for the hopping integral given as \( \gamma_{ij}(\Delta a_{cc}(\bar{t})) = \gamma_0 \exp(-\Delta a_{cc}(\bar{t})/a_0) \) \[57\]. This form for the hopping integral is derived from the definition of the hopping integral which is given as \( \gamma = \langle \varphi_{A(r-R_A)} | H_{\text{grp}} | \varphi_{B(r-R_B)} \rangle \), where \( \varphi_A \) and \( \varphi_B \) are the atomic wavefunctions of the carbon atoms A and B, and \( R_{A(B)} \) are their position vectors. Using the standard wavefunctions, this form for the hopping integral can be found. The parameter \( \gamma_0 \) is the hopping integral of the DNA coated graphene in the absence of DMMP vapor (only for N\(_2\)) which is chosen to be 3.3 eV with \( a_0 = 0.33 \) Å. The value of the hopping integral \( \gamma_{ij}(\Delta a_{cc}(\bar{t})) \) changes when the nearest-neighbor carbon-carbon distance \( a_{cc} \) changes by \( \Delta a_{cc} \) as a function of time \( \bar{t} \) due to the interaction of vapor molecules at each time \( \bar{t} \) s with the DNA-decorated graphene. The 9 \times 9 matrix consists of nine carbon atoms that are involved in the transport. Out of these nine carbon atoms the first (A\(_1\)) and the last (X\((M+1)/2\)) carbon atoms are connected to the source and drain electrodes. Seven ssDNA bases G, A, G, T, C, T, and G of sequence 1 interact with seven carbon atoms excepting the first and the last that are connected to S and D electrodes, Fig. 1. This is how the complex Gas-DNA-graphene system is modeled in a simplified way to explicitly calculate the sensor response.

The transmission function \( T(\varepsilon_f, \bar{t}) \) of the DNA-decorated graphene when exposed to DMMP vapor is calculated at different times \( \bar{t} \) with varying Fermi level \( \varepsilon_f \), whereas \( T_0(\varepsilon'_f, \bar{t}_{\text{max}}) = \frac{4 \text{ Im} \sum_{\alpha=1}^{9} \text{ Im} \sum_{\beta=1}^{9} \varphi_{\alpha}^{*} \varphi_{\beta} \langle G_{\text{grp}}(\varepsilon'_f, \bar{t}_{\text{max}}) \rangle_{\alpha,\beta}^{\alpha,\beta} }{\langle G_{\text{grp}}(\varepsilon'_f, \bar{t}_{\text{max}}) \rangle_{\alpha,\beta}^{\alpha,\beta}} \) is the transmission function of the device when exposed to N\(_2\) and calculated at the maximum time when all N\(_2\) molecules interact with the full DNA sequence, with a fixed value of the Fermi level \( \varepsilon'_f \). The best fitted value of \( \varepsilon'_f \) is found to be -0.7 eV as in this case the devices is hole doped due to N\(_2\) and the Fermi level
lies in the valence band.

To reproduce the experimental results, the model parameters $\Delta a_{cc}$ and $\varepsilon_f$ are fitted, and the best fitted values are given in Table I. These model parameters are found to be specific to the bases of the DNA sequence. The values of $a_{cc}(\bar{t})$ and $\varepsilon_f(\bar{t})$ are found to decrease (becomes more negative) and increase, respectively with time $\bar{t}$ leading to a decrease in sensor current. In the graphene channel, hole conduction dominates and DMMP is a strong electron donor. On interaction of DMMP vapor molecules, at a particular concentration, with ssDNA coated graphene a fractional charge transfer takes place from each DMMP-DNA-base complex to the graphene channel. This causes deformation in the carbon lattice of graphene and decreases the nearest-neighbor carbon-carbon distance $a_{cc}$ from its values when there is no vapor which affects the wavefunctions and enhances the hopping integral. As a result, the energy bands of graphene shift downward to lower energy which moves the Dirac point downward towards a lower energy position, resulting in a shift in the position of the Fermi level ($E_f$) via the relationship $\Delta E_f = E_f - E_{\text{Dirac}}$.

Referring to Fig. 1(a) and Table I, it is observed that at time $\bar{t}_1$ when the DMMP interacts with guanine base the change in C-C is $\Delta a_{A_1B_1}(\bar{t}_1) = -0.02$ and $\Delta a_{B_1A_2}(\bar{t}_1) = -0.018$. At time $\bar{t}_2$ DMMP interacts with another base adenine which causes a change $\Delta a_{B_1A_2}(\bar{t}_2) = -0.018 - 0.011 = -0.029$ and $\Delta a_{A_2B_2}(\bar{t}_2) = -0.009$, while $\Delta a_{A_1B_1}(\bar{t}_2)$ remain unchanged. At time $\bar{t}_3$ DMMP interacts with guanine again which causes a change $\Delta a_{A_2B_2}(\bar{t}_3) = -0.009 - 0.02 = -0.029$ and $\Delta a_{B_2A_3}(\bar{t}_3) = -0.018$. At time $\bar{t}_4$ DMMP interacts with thymine giving change $\Delta a_{B_2A_3}(\bar{t}_4) = -0.018 - 0.012 = -0.03$ and $\Delta a_{A_3B_3}(\bar{t}_4) = -0.01$. At time $\bar{t}_5$ DMMP interacts with cytosine and the change is $\Delta a_{A_3B_3}(\bar{t}_5) = -0.01 - 0.009 = -0.019$ and $\Delta a_{B_3A_4}(\bar{t}_5) = -0.007$. At time $\bar{t}_6$ DMMP interacts with thymine and the change is $\Delta a_{B_3A_4}(\bar{t}_6) = -0.007 - 0.012 = -0.019$ and $\Delta a_{A_4B_4}(\bar{t}_6) = -0.01$. At time $\bar{t}_7$ DMMP interacts with guanine and causing a change $\Delta a_{A_4B_4}(\bar{t}_7) = -0.01 - 0.02 = -0.03$ and $\Delta a_{B_4A_5}(\bar{t}_7) = -0.018$. Hence, the change in nearest-neighbor C-C distance due to interaction of DMMP with different bases, which changes the sensor response, is studied explicitly. Figure 2 shows a good match of the calculated sensor response and the experimentally measured sensor response of ssDNA sequence 1 coated graphene device as a function of the exposure time of DMMP vapor. When the device is exposed to pure N$_2$ gas the response is found in the opposite direction. In this case, the charge transfer takes place from graphene to the N$_2$-DNA-base complex causing an increase in $a_{cc}(\bar{t})$ from its
modified value due to vapor and a decrease in \( \varepsilon_f(t) \). This results in lowering the hopping integral and shifting the Fermi level closer to the valence band as shown by decreasing values of \( \varepsilon_f(t) \) in Table II. This increases the hole carrier concentration hence the device current which is in agreement with the experiment. Figure 3 shows the schematic of the interaction of \( N_2 \) with DNA coated graphene. When \( N_2 \) interacts with guanine at time \( \bar{t}_1 \) the change in \( a_{cc} \) is \( \Delta a_{A_1B_1}(\bar{t}_1) = -0.02 + 0.04 = 0.02 \) and \( \Delta a_{B_1A_2}(\bar{t}_1) = -0.029 + 0.02 = -0.009 \). At time \( \bar{t}_2 \) the change in \( a_{cc} \) due to adenine is \( \Delta a_{B_1A_2}(\bar{t}_2) = -0.009 + 0.013 = 0.004 \) and \( \Delta a_{A_2B_2}(\bar{t}_2) = -0.029 + 0.011 = -0.018 \). In a similar manner, the change in \( a_{cc} \) due to guanine base at \( \bar{t}_3 \) is \( \Delta a_{A_2B_2}(\bar{t}_3) = -0.018 + 0.04 = 0.022 \) and \( \Delta a_{B_2A_3}(\bar{t}_3) = -0.03 + 0.02 = -0.01 \). At time \( \bar{t}_4 \), the value of \( \Delta a_{cc} \) due to thymine at \( \bar{t}_4 \) is \( \Delta a_{B_2A_3}(\bar{t}_4) = -0.01 + 0.014 = 0.004 \) and \( \Delta a_{A_3B_3}(\bar{t}_4) = -0.019 + 0.012 = -0.007 \). At \( \bar{t}_5 \) the change in \( a_{cc} \) due to cytosine is \( \Delta a_{A_3B_3}(\bar{t}_5) = -0.007 + 0.011 = 0.004 \) and \( \Delta a_{B_3A_4}(\bar{t}_5) = -0.019 + 0.009 = -0.01 \). At \( \bar{t}_6 \) the change in \( a_{cc} \) due to thymine is \( \Delta a_{B_3A_4}(\bar{t}_6) = -0.01 + 0.014 = 0.004 \) and \( \Delta a_{A_4B_4}(\bar{t}_6) = -0.03 + 0.012 = -0.018 \). At \( \bar{t}_7 \) the change in \( a_{cc} \) due to guanine is \( \Delta a_{A_4B_4}(\bar{t}_7) = -0.018 + 0.04 = 0.022 \) and \( \Delta a_{B_4A_5}(\bar{t}_7) = -0.018 + 0.02 = 0.002 \). Figure 4 compares the theoretical and experimental results of the device with respect to exposure time of \( N_2 \). The values for different parameters used in the calculation of the current for \( N_2 \) are given in Table II. Detailed steps of the calculation of the sensor response are given in Appendix A. Similar calculations are also done for the graphene device when coated with ssDNA sequence 2 and exposed to DMMP and \( N_2 \). The values of the fitted parameters are given in Tables III and IV, and the sensor responses are shown in Figs. 5 and 6. Hence, the formula derived for the transmission function reproduces the sensor response of the experiment. The calculations show that the change in \( a_{cc} \) due to interaction of vapor with four bases G, A, T and C is in the order of \( G > T \sim A > C \) indicating the order of interaction energy of these bases towards graphene. The order of the interaction strength of these bases with graphene is also found in other theoretical and experimental studies where the predicted orders are different, e.g., (\( G > A \approx T \approx C \)), (\( G > A \sim T > C \)), (\( G > A > C < T \)) or (\( G > A > C > T \)) \cite{59, 60} and is not conclusive. These results are the prediction of the model which should be verified by experiments, ab-initio technique or density functional theory based calculations.

Experimental result (Fig. 2 of Ref. [37]) shows that the current response of devices to DMMP changes (decreases) drastically at progressively larger concentrations. The model
explains the reason for this change as the graphene device is functionalized with many strands of the same ssDNA sequence 1 or 2 more DNA bases are available for DMMP molecules to interact with. As the concentration increases the number of vapor molecules increases and they interact with more DNA strands (bases) causing more charge transfer to graphene. This results in more changes in C-C distance ($a_{cc}$ becomes more negative) with time which further moves the Dirac point downwards and shifts the Fermi level further away from the valence band of graphene. Hence reducing the carrier concentration and the current of the graphene device drastically.

V. CONCLUSIONS

A quantitative understanding of the experiment based on the DNA functionalized graphene gas sensor was presented. To study the electronic transport in the gas sensor a theoretical model of the DNA functionalized graphene was built, and a connection between the theoretical predictions and experimental observations was developed.

A time-dependent electronic transport through the graphene device was investigated based on a tight-binding model of the experimental system. The analytical calculations of electronic transport were performed using the method of the NEGF formalism and the adiabatic approximation. The detailed work included derivations of the Green’s function for graphene, and the expression for the time-dependent current by deriving the equation of motion and Dyson equation. The zeroth and the first order contributions to the current were derived. The contribution of the zeroth order current was significant and was identified as the Landauer formula which is time-dependent in terms of the slow time variable, whereas the first order contribution was found to be small and hence was not included in the total current when comparing with experiment. A transmission function formula was derived in terms of the time-dependent hopping integral and on-site energy. The sensor responses (change in current) of graphene coated with ssDNA sequence 1 and 2 for DMMP vapor and N$_2$ were then explicitly calculated using the transmission function formula and considering a form for the hopping integral which accounts for the effect of the DNA and DMMP molecules on the charge distribution of the carbon atoms and the nearest-neighbor carbon-carbon distance. The sensor response was found to be sensitive to the DNA bases as the effect of interaction of vapor molecules with individual DNA base molecules, given
TABLE I: Values for different model parameters used in the calculation of the current with $\gamma_0=3.3\text{eV}$ and $\varepsilon'_f=-0.7\text{ eV}$ for DMMP with DNA sequence 1.

| $\bar{t}(s)$ | $\bar{t}_1$ | $\bar{t}_2$ | $\bar{t}_3$ | $\bar{t}_4$ | $\bar{t}_5$ | $\bar{t}_6$ | $\bar{t}_7$ |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| $\Delta I(0)(\bar{t})/I_0$ | -0.3084 | -1.1369 | -1.5444 | -1.7050 | -1.9041 | -2.0848 | -2.3088 |
| $\varepsilon_f(\bar{t})(\text{eV})$ | 1.53 | 1.67 | 1.75 | 1.76 | 1.79 | 1.81 | 1.84 |
| $\Delta a_{A_1B_1}(\bar{t})(\text{Å})$ | -0.02 | -0.02 | -0.02 | -0.02 | -0.02 | -0.02 | -0.02 |
| $\Delta a_{B_1A_2}(\bar{t})(\text{Å})$ | -0.018 | -0.029 | -0.029 | -0.029 | -0.029 | -0.029 | -0.029 |
| $\Delta a_{A_2B_2}(\bar{t})(\text{Å})$ | -0.009 | -0.029 | -0.029 | -0.029 | -0.029 | -0.029 | -0.029 |
| $\Delta a_{B_2A_3}(\bar{t})(\text{Å})$ | — | — | -0.018 | -0.03 | -0.03 | -0.03 | -0.03 |
| $\Delta a_{A_3B_3}(\bar{t})(\text{Å})$ | — | — | — | -0.01 | -0.019 | -0.019 | -0.019 |
| $\Delta a_{B_3A_4}(\bar{t})(\text{Å})$ | — | — | — | — | -0.007 | -0.019 | -0.019 |
| $\Delta a_{A_4B_4}(\bar{t})(\text{Å})$ | — | — | — | — | — | -0.01 | -0.03 |
| $\Delta a_{B_4A_5}(\bar{t})(\text{Å})$ | — | — | — | — | — | — | -0.018 |

by changes in $a_{cc}$, on the electronic transport of graphene was studied quantitatively. For DMMP and N$_2$, values of $\Delta a_{cc}$ and $\varepsilon_f$ were found which were used to calculate the theoretical sensor response for two different DNA sequences and to compare with the experiment. The calculation suggests that for a particular target vapor, the same values of $\Delta a_{cc}$ due to the four DNA bases can predict the theoretical values of the current response for different DNA sequences. These calculations reproduced the experimental response and demonstrated a significant step towards an understanding of how the functionalization of graphene with DNA affects its electronic transport properties when used for detection of chemical vapors and hints on its use as a DNA analyser.

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FIG. 2: The sensor response $\Delta I(0)(\bar{t})/I_0$ versus exposure time $\bar{t}(s)$ for DMMP with DNA sequence 1. This plot shows agreement between the theory and experiment. Experimental data is used from Ref. [37].

FIG. 3: Schematic of the interaction of $N_2$ molecules with the ssDNA sequence 1 coated graphene.

Appendix A: Calculation of the sensor response

The sensor response of graphene coated with ssDNA sequence 1 when exposed to DMMP vapor is defined as

$$\Delta I^{(0)}(\bar{t})/I_0 = 1 - \frac{I^{(0)}(\bar{t})(vapor)}{I_0(\text{air})} = 1 - \frac{T(\varepsilon_f, \bar{t})}{T_0(\varepsilon_f', \bar{t}_{\text{max}})},$$  \hspace{1cm} (A1)
TABLE II: Values for different model parameters used in the calculation of the current with \( \gamma_0=3.3\text{eV} \) and \( \varepsilon_f'=-0.7\text{eV} \) for N\(_2\) with DNA sequence 1.

| \( \bar{t}(s) \) | \( \bar{t}_1 \) | \( \bar{t}_2 \) | \( \bar{t}_3 \) | \( \bar{t}_4 \) | \( \bar{t}_5 \) | \( \bar{t}_6 \) | \( \bar{t}_7 \) |
|-----------------|----------|----------|----------|----------|----------|----------|----------|
| \( \Delta I^{(0)}(\bar{t})/I_0 \) | -2.5394  | -1.5962  | -1.2946  | -1.1855  | -0.9962  | -0.8542  | -0.5958  |
| \( \varepsilon_f(\bar{t})(\text{eV}) \) | 1.77     | 1.71     | 1.6      | 1.59     | 1.55     | 1.52     | 1.50     |
| \( \Delta a_{A_1B_1}(\bar{t})(\text{Å}) \) | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     |
| \( \Delta a_{B_1A_2}(\bar{t})(\text{Å}) \) | -0.009   | 0.004    | 0.004    | 0.004    | 0.004    | 0.004    | 0.004    |
| \( \Delta a_{A_2B_2}(\bar{t})(\text{Å}) \) | -0.029   | -0.018   | 0.022    | 0.022    | 0.022    | 0.022    | 0.022    |
| \( \Delta a_{B_2A_3}(\bar{t})(\text{Å}) \) | -0.03    | -0.03    | -0.01    | 0.004    | 0.004    | 0.004    | 0.004    |
| \( \Delta a_{A_3B_3}(\bar{t})(\text{Å}) \) | -0.019   | -0.019   | -0.019   | -0.007   | 0.004    | 0.004    | 0.004    |
| \( \Delta a_{B_3A_4}(\bar{t})(\text{Å}) \) | -0.019   | -0.019   | -0.019   | -0.019   | -0.01    | 0.004    | 0.004    |
| \( \Delta a_{A_4B_4}(\bar{t})(\text{Å}) \) | -0.03    | -0.03    | -0.03    | -0.03    | -0.03    | -0.018   | 0.022    |
| \( \Delta a_{B_4A_5}(\bar{t})(\text{Å}) \) | -0.018   | -0.018   | -0.018   | -0.018   | -0.018   | -0.018   | 0.002    |

FIG. 4: The sensor response \( \Delta I^{(0)}(\bar{t})/I_0 \) versus exposure time \( \bar{t}(s) \) for \( \text{N}_2 \) with ssDNA sequence 1. Experimental data is from Ref. [37]. Theoretical and experimental results are in agreement.

where \( T(\varepsilon_f, \bar{t}) \) and \( T_0(\varepsilon_f', \bar{t}_{\text{max}}) \) are transmission functions of the DNA coated graphene when exposed to gas and \( \text{N}_2 \), respectively.

To calculate the sensor response we consider a simple \( 9 \times 9 \) matrix.
### TABLE III: Values for different model parameters used in the calculation of the current with $\gamma_0=3.3\text{eV}$ and $\varepsilon_f'=-0.7\text{eV}$ for DMMP with DNA sequence 2.

| $\bar{t}(s)$ | $\bar{t}_1$ | $\bar{t}_2$ | $\bar{t}_3$ | $\bar{t}_4$ | $\bar{t}_5$ | $\bar{t}_6$ | $\bar{t}_7$ |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| $\Delta I^{(0)}(\bar{t})/I_0$ | -2.2054 | -3.3501 | -3.8368 | -4.2537 | -4.5883 | -4.8608 | -4.9574 |
| $\varepsilon_f(\bar{t})(\text{eV})$ | 1.74 | 1.79 | 1.83 | 1.84 | 1.87 | 1.89 | 1.9 |
| $\Delta a_{A_1B_1}(\bar{t})(\text{Å})$ | -0.009 | -0.009 | -0.009 | -0.009 | -0.009 | -0.009 | -0.009 |
| $\Delta a_{B_1A_2}(\bar{t})(\text{Å})$ | -0.007 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 |
| $\Delta a_{A_2B_2}(\bar{t})(\text{Å})$ | -0.01 | -0.022 | -0.022 | -0.022 | -0.022 | -0.022 | -0.022 |
| $\Delta a_{B_2A_3}(\bar{t})(\text{Å})$ | -0.01 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 |
| $\Delta a_{A_3B_3}(\bar{t})(\text{Å})$ | -0.007 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 |
| $\Delta a_{B_3A_4}(\bar{t})(\text{Å})$ | -0.01 | -0.03 | -0.03 | -0.03 | -0.03 | -0.03 | -0.03 |
| $\Delta a_{A_4B_4}(\bar{t})(\text{Å})$ | -0.018 | -0.03 | -0.03 | -0.03 | -0.03 | -0.03 | -0.03 |
| $\Delta a_{B_4A_5}(\bar{t})(\text{Å})$ | -0.01 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 | -0.019 |

**FIG. 5:** The sensor response $\Delta I^{(0)}(\bar{t})/I_0$ versus exposure time $\bar{t}(s)$ for DMMP with ssDNA sequence 2. Theoretical and experimental results are in agreement.

At time $\bar{t}_1$: the DMMP molecule interacts with the guanine base attached to the carbon atom $B_1$ causing charge transfer to graphene which leads to changes $\Delta a_{A_1B_1}(\bar{t}_1)$ and $\Delta a_{B_1A_2}(\bar{t}_1)$ with the corresponding hopping integrals $\gamma_{11}(\bar{t}_1)$ and $\gamma_{12}(\bar{t}_1)$ while the other $a_{cc}$
TABLE IV: Values for different model parameters used in the calculation of the current with \( \gamma_0=3.3 \text{eV} \) and \( \epsilon_f'=-0.7 \text{eV} \) for N\textsubscript{2} with DNA sequence 2.

| \( \bar{t}(s) \) | \( \bar{t}_1 \) | \( \bar{t}_2 \) | \( \bar{t}_3 \) | \( \bar{t}_4 \) | \( \bar{t}_5 \) | \( \bar{t}_6 \) | \( \bar{t}_7 \) |
|-----------------|----------|----------|----------|----------|----------|----------|----------|
| \( \Delta I^{(0)}(\bar{t})/I_0 \) | -4.7486 | -4.4499 | -2.6233 | -2.3937 | -1.9362 | -1.5505 | -1.2979 |
| \( \epsilon_f(\bar{t})(eV) \) | 1.88     | 1.87     | 1.78     | 1.77     | 1.72     | 1.64     | 1.61     |
| \( \Delta a_{A_1B_1}(\bar{t})(\text{Å}) \) | 0.002    | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     |
| \( \Delta a_{B_1A_2}(\bar{t})(\text{Å}) \) | -0.01    | 0.004    | 0.004    | 0.004    | 0.004    | 0.004    | 0.004    |
| \( \Delta a_{A_2B_2}(\bar{t})(\text{Å}) \) | -0.022   | -0.01    | 0.004    | 0.004    | 0.004    | 0.004    | 0.004    |
| \( \Delta a_{B_2A_3}(\bar{t})(\text{Å}) \) | -0.019   | -0.019   | -0.007   | 0.004    | 0.004    | 0.004    | 0.004    |
| \( \Delta a_{A_3B_3}(\bar{t})(\text{Å}) \) | -0.019   | -0.019   | -0.019   | -0.01    | 0.004    | 0.004    | 0.004    |
| \( \Delta a_{B_3A_4}(\bar{t})(\text{Å}) \) | -0.03    | -0.03    | -0.03    | -0.03    | -0.03    | -0.03    | -0.01    |
| \( \Delta a_{A_4B_4}(\bar{t})(\text{Å}) \) | -0.03    | -0.03    | -0.03    | -0.03    | -0.03    | -0.03    | -0.01    |
| \( \Delta a_{B_4A_5}(\bar{t})(\text{Å}) \) | -0.01    | -0.01    | -0.01    | -0.01    | -0.01    | -0.01    | -0.01    |

FIG. 6: The sensor response \( \Delta I^{(0)}(\bar{t})/I_0 \) versus exposure time \( \bar{t}(s) \) for N\textsubscript{2} with ssDNA sequence 2. Theoretical and experimental results are in agreement.

remain unaffected with hopping integrals \( \gamma_0 \). The transmission
\[
\frac{T(\varepsilon_f, \bar{t}_1)}{T_0(\varepsilon'_f, \bar{t}_\text{max})} = \frac{4 \text{ Im}\Sigma_0^\infty \text{ Im}\Sigma_0^- \gamma_0^2(\varepsilon_f)\gamma_0^2(\varepsilon'_f)\gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2}{4 \text{ Im}\Sigma_0^\infty \text{ Im}\Sigma_0^- \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2}, \tag{A2}
\]

where

\[
|G^{(0)r}_{\text{grp}}(\varepsilon_f, \bar{t}_1)| = \left|\varepsilon_f^6(\bar{t}_1) - \varepsilon_f^7(\bar{t}_1)\gamma_{11}(\bar{t}_1) - \varepsilon_f^7(\bar{t}_1)\gamma_{12}(\bar{t}_1) - \varepsilon_f^7(\bar{t}_1)\gamma_{10}^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 \right.
- \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \left.ight.
+ \varepsilon_f^3(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \left.ight.
- \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \left.ight.
- \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \left.ight.
+ \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \left.ight.
+ \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \left.ight.
+ \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \left.ight.
+ \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 - \varepsilon_f^7(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{11}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{12}(\bar{t}_1)\gamma_0^2 + \varepsilon_f^5(\bar{t}_1)\gamma_{10}^2 \right)
\tag{A3}
\]

and

\[
|G^{(0)r}_{\text{grp}}(\varepsilon'_f, \bar{t}_\text{max})| = \varepsilon'_f^6 - 8\varepsilon'_f^7 \gamma_0^2 + 21\varepsilon'_f^8 \gamma_0^4 - 20\varepsilon'_f^9 \gamma_0^6 + 5\varepsilon'_f^{10} \gamma_0^8. \tag{A4}
\]

Here we have neglected the contribution from the on-site energy as we are interested in the transport properties (hopping), and the energy independent self-energy terms are also ignored for simplification of the calculation.
Using the form for the hopping integral \( \gamma_{ij}(\Delta a_{cc}(\bar{t})) = \gamma_0 \exp(-\Delta a_{cc}(\bar{t})/a_0) \) the transmission function ratio becomes

\[
\frac{T(\varepsilon_f, \bar{t}_1)}{T_0(\varepsilon'_f, \bar{t}_{\text{max}})} = \frac{4 \text{ Im}\Sigma_S \text{ Im}\Sigma_D \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2 \gamma_0^2}{|G_{GP}^{(0)}(\varepsilon_f, \bar{t}_1)|_{3\times 9}^2 |G_{GP}^{(0)}(\varepsilon'_f, \bar{t}_{\text{max}})|_{9\times 9}^2}.
\]

(Eq. A5)

Equations (A3) and (A5) give two model parameters \( \Delta a_{cc}(\bar{t}) \) and \( \varepsilon_f(\bar{t}) \). To calculate the current we find the values of these two parameters.

The following steps are used to calculate the sensor response:

- The constants \( \gamma_0, \varepsilon'_f(\bar{t}_{\text{max}}) \) and \( a_0 \) are set as 3.3 eV, -0.7 eV, and 0.33 Å, respectively, which give the best matching between the theoretical and experimental results.
- A range of the values of the Fermi level \( \varepsilon_f(\bar{t}) \) is set from 0.01 to 4 with an interval of 0.01.
- At time \( \bar{t}_1 \): the gas molecule interacts with the guanine base causing changes \( \Delta a_{A_1B_1}(\bar{t}_1) \) and \( \Delta a_{B_1A_2}(\bar{t}_1) \). The best fitted values of \( \Delta a_{A_1B_1}(\bar{t}_1) \) and \( \Delta a_{B_1A_2}(\bar{t}_1) \) due to guanine base are

\[
\Delta a_{A_1B_1}(\bar{t}_1) = -0.02
\]

\[
\Delta a_{B_1A_2}(\bar{t}_1) = -0.018
\]
- Substituting these values in the transmission function ratio, Eq. (A5), and using Eq. (A1) the sensor response is calculated.
- To read the values of the current with corresponding values of \( \varepsilon_f(\bar{t}_1) \) explicitly, a Matrix is defined as

\[
A = \{\varepsilon_f(\bar{t}_1), \Delta I^{(0)}(\bar{t}_1)/I_0\}.
\]
To read the elements of the matrix A the following code is typed

\[
A[\{1, 2, 3, 4, 5, 6, 7, 8, 9, 10\}] // MatrixForm
\]

where the upper row shows the values of \(\varepsilon_f(\bar{t}_1)\) and the lower row shows the corresponding values of the sensor response.

Similarly other matrix elements are read as

\[
A[\{91, 92, 93, 94, 95, 96, 97, 98, 99, 00\}] // MatrixForm
\]

where the sensor response \(\Delta I^{(0)}(\bar{t}_1)/I_0=0.0176127\) at \(\varepsilon_f(\bar{t}_1)=0.88\) highlighted with a circle is the theoretical sensor response which matches with the experimental result very well.

At time \(\bar{t}_2\): the DMMP molecule interacts with the adenine base attached to the carbon atom \(A_2\) leading to changes \(\Delta a_{B_1A_2}(\bar{t}_2)\) and \(\Delta a_{A_2B_2}(\bar{t}_2)\) with corresponding hopping integrals \(\gamma_{12}(\bar{t}_2)\) and \(\gamma_{22}(\bar{t}_2)\), whereas \(\Delta a_{A_1B_1}(\bar{t}_2)\) remains unaffected. The best fitted values of \(\Delta a_{B_1A_2}(\bar{t}_2)\) and \(\Delta a_{A_2B_2}(\bar{t}_2)\) due to adenine base are
\[ \Delta a_{A_1B_1}(\bar{t}_2) = -0.02 \]
\[ \Delta a_{B_1A_2}(\bar{t}_2) = -0.018 - 0.011 = -0.029 \]
\[ \Delta a_{B_1A_3}(\bar{t}_2) = -0.009 \]

Similarly, the sensor response is calculated at next instants of time.

- **At \( \bar{t}_3 \):** the changes in \( \Delta a_{cc} \) due to guanine base are
  \[ \Delta a_{A1B1}(\bar{t}_3) = -0.02 \]
  \[ \Delta a_{B1A2}(\bar{t}_3) = -0.029 \]
  \[ \Delta a_{A2B2}(\bar{t}_3) = -0.009 - 0.02 = -0.029 \]
  \[ \Delta a_{B2A3}(\bar{t}_3) = -0.018 \]

- **At \( \bar{t}_4 \):** the changes in \( \Delta a_{cc} \) due to thymine base are
  \[ \Delta a_{A1B1}(\bar{t}_4) = -0.02 \]
  \[ \Delta a_{B1A2}(\bar{t}_4) = -0.029 \]
  \[ \Delta a_{A2B2}(\bar{t}_4) = -0.029 \]
  \[ \Delta a_{B2A3}(\bar{t}_4) = -0.018 - 0.012 = -0.03 \]
  \[ \Delta a_{A3B3}(\bar{t}_4) = -0.01 \]

- **At \( \bar{t}_5 \):** the changes in \( \Delta a_{cc} \) due to cytosine base are
  \[ \Delta a_{A1B1}(\bar{t}_5) = -0.02 \]
  \[ \Delta a_{B1A2}(\bar{t}_5) = -0.029 \]
  \[ \Delta a_{A2B2}(\bar{t}_5) = -0.029 \]
  \[ \Delta a_{B2A3}(\bar{t}_5) = -0.03 \]
  \[ \Delta a_{A3B3}(\bar{t}_5) = -0.01 - 0.009 = -0.019 \]
  \[ \Delta a_{B3A4}(\bar{t}_5) = -0.007 \]

- **At \( \bar{t}_6 \):** the changes in \( \Delta a_{cc} \) due to thymine base are
  \[ \Delta a_{A1B1}(\bar{t}_6) = -0.02 \]
  \[ \Delta a_{B1A2}(\bar{t}_6) = -0.029 \]
\[ \Delta a_{A_2B_2}(\bar{t}_6) = -0.029 \]
\[ \Delta a_{B_2A_3}(\bar{t}_6) = -0.03 \]
\[ \Delta a_{A_3B_3}(\bar{t}_6) = -0.019 \]
\[ \Delta a_{B_3A_4}(\bar{t}_6) = -0.007 - 0.012 = -0.019 \]
\[ \Delta a_{A_4B_4}(\bar{t}_6) = -0.01 \]

- **At \( \bar{t}_7 \):** the changes in \( \Delta a_{cc} \) due to guanine base are

\[ \Delta a_{A_1B_1}(\bar{t}_7) = -0.02 \]
\[ \Delta a_{B_1A_2}(\bar{t}_7) = -0.029 \]
\[ \Delta a_{A_2B_2}(\bar{t}_7) = -0.029 \]
\[ \Delta a_{B_2A_3}(\bar{t}_7) = -0.03 \]
\[ \Delta a_{A_3B_3}(\bar{t}_7) = -0.019 \]
\[ \Delta a_{B_3A_4}(\bar{t}_7) = -0.019 \]
\[ \Delta a_{A_4B_4}(\bar{t}_7) = -0.01 - 0.02 = -0.03 \]
\[ \Delta a_{B_4A_5}(\bar{t}_7) = -0.018 \]

Similar steps are followed for the calculation of the sensor response when graphene coated with ssDNA sequence 2 is exposed to DMMP and \( \text{N}_2 \).

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