

Supplementary information for: Resonant scattering by realistic impurities in graphene

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Here we give the details of the numerical approach of calculating the density of states and conductivity of graphene with realistic impurities. In our model, we use a full tight-binding Hamiltonian to calculate the density of states and conductivity by solving the time-dependent Schrödinger equation (TDSE) in real space. This differs from the numerical calculations of the conductivity of disordered two-dimensional massless Dirac fermions reported in Ref. [1, 2], where the single-valley Dirac Hamiltonian is used. A resulting advantage our method is that the energy range of the conductivity can cover all the spectrum, not only around the Dirac point. Moreover, we do not need to diagonalize the whole Hamiltonian to obtain the energy eigenstates which allows us to carry out calculations of relatively large samples, e.g., containing up to $N = 8192 \times 8192$ carbon atoms. The memory and CPU time in our algorithm is *linearly* dependent on the size of the sample. In the following we first explain how we obtain the density of states and afterwards how the conductivity is calculated using a Kubo formula.

DENSITY OF STATES

The tight-binding Hamiltonian of the graphene with resonant impurities can be represented as

$$H = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j + \varepsilon_d \sum_k d_k^\dagger d_k + V \sum_k (d_k^\dagger c_k + H.c.), \quad (1)$$

where t is the nearest-neighbor hopping between the carbon atoms, V is the hopping between the carbon atoms and resonant impurities, and ε_d is the on-site energy of impurities.

The density of states (DOS) describes the number of states at each energy that are available to be occupied. An algorithm based on the evolution of TDSE to find the eigenvalue distribution of very large matrices is described in Ref [3]. The main idea is using a random superposition of all basis states as an initial state $|\varphi\rangle$:

$$|\varphi\rangle = \sum_i a_i |i\rangle, \quad (2)$$

where $\{|i\rangle\}$ are the basis states and $\{a_i\}$ are random complex numbers. After performing the time evolution to get the wave function at equal time intervals by solving the TDSE and calculating the correlation function on each time step,

$$\langle \varphi | e^{-iHt} | \varphi \rangle, \quad (3)$$

the Fourier transform on these correlation functions yields the spectral function of the initial state as

$$d(\varepsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\varepsilon t} \langle \varphi | e^{-iHt} | \varphi \rangle dt. \quad (4)$$

Averaging over many different samples (initial states) leads to the density of states as

$$\rho(\varepsilon) = \lim_{S \rightarrow \infty} \frac{1}{S} \sum_{P=1}^S d_P(\varepsilon). \quad (5)$$

For a large enough system, e.g., a graphene sample consisting of $4096 \times 4096 \approx 1.6 \times 10^7$ atoms, one initial random superposition state (RSS) contains already contributions from sufficiently many eigenstates that its spectral function is approximately equal to the DOS of an infinite system, i.e.,

$$\rho(\varepsilon) \approx d(\varepsilon). \quad (6)$$

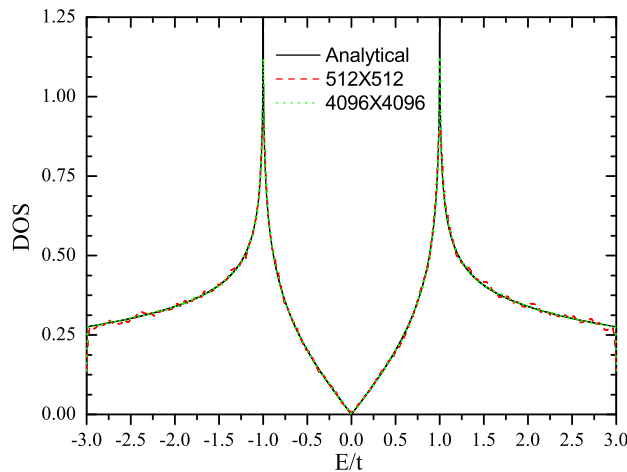


Figure 1: (Color online) Comparison of the analytical DOS (black solid) with the numerical results of a sample contains 512×512 (red dash) or 4096×4096 (green dot) carbon atoms.

We would like to emphasize that any orthogonal and complete basis can be used to represent $|\varphi\rangle$. In the tight-binding model of graphene, it is convenient to use the real space basis. A detailed analysis of this method is given in Ref. [3].

To illustrate the convergence properties, here, we compare the analytical and numerical results of the density of states for a clean graphene in Fig. 1. The analytical results as obtained in Ref. [4] are

$$\rho(E) = \begin{cases} \frac{2E}{t^2\pi^2} \frac{1}{\sqrt{F(E/t)}} \mathbf{K}\left(\frac{4E/t}{F(E/t)}\right), & 0 < E < t, \\ \frac{2E}{t^2\pi^2} \frac{1}{\sqrt{4E/t}} \mathbf{K}\left(\frac{F(E/t)}{4E/t}\right), & t < E < 3t, \end{cases} \quad (7)$$

where $F(x)$ is given by

$$F(x) = (1+x)^2 - \frac{(x^2-1)^2}{4}, \quad (8)$$

and $\mathbf{K}(m)$ is the elliptic integrals of first kind:

$$\mathbf{K}(m) = \int_0^1 dx [(1-x^2)(1-mx^2)]^{-1/2}. \quad (9)$$

It becomes clear that our numerical results fit very well the analytical expression, and that the difference between the numerical and analytical results becomes smaller when using larger sample size (see the difference of a sample with 512×512 or 4096×4096 in Fig. 1). In fact, the LDOS of a sample containing 4096×4096 is approximately the same as DOS of a pure graphene, which indicates the high precision of the algorithm.

From the numerical calculations of DOS we find that a RSS $|\varphi\rangle$ typically contains all the eigenstates with approximately equal probabilities. Therefore, we can also use $|\varphi\rangle$ as a starting state to calculate the DC conductivity by using the Kubo formula, as we will show in the next section.

KUBO FORMULA

The Kubo formula of non-interacting electrons can be expressed as [5, 6]

$$\sigma = -\frac{1}{V} \text{Tr} \left\{ \frac{\partial f}{\partial H} \int_0^\infty dt \frac{1}{2} [JJ(t) + J(t)J] \right\}. \quad (10)$$

where f is the Fermi-Dirac distribution, and $J(t)$ is Heisenberg representation of the current operator J . At zero temperature, $\frac{\partial f}{\partial H}$ can be simplified as

$$-\frac{\partial f}{\partial H} = \delta(E_F - H), \quad (11)$$

where E_F is the Fermi energy. Now Eq. (10) becomes

$$\sigma_{T=0} = \frac{\pi}{NV} \text{Re} \sum_{m,n=1}^N \langle n|J|m\rangle \langle m|J|n\rangle \delta(E_F - E_m) \delta(E_F - E_n), \quad (12)$$

where E_n is the energy of the eigenstate $|n\rangle$.

An approximation of eigenstates $|n\rangle$, or a random superposition of degenerate eigenstates can be obtained by using the spectrum method [7]. Suppose a random superposition state $|\varphi\rangle$ is the initial state of the system. As proved during the calculation of its spectral function, it contains all the eigenstates and we can, therefore, represent it as $|\varphi\rangle = \sum_n A_n |n\rangle$. The state at time t is

$$|\varphi(t)\rangle = e^{-iHt} |\varphi\rangle. \quad (13)$$

By performing the Fourier transform directly on $|\varphi(t)\rangle$ we get

$$\begin{aligned} |\tilde{\Psi}(\varepsilon)\rangle &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\varepsilon t} \cdot |\varphi(t)\rangle \\ &= \frac{1}{2\pi} \sum_n A_n \int_{-\infty}^{\infty} e^{-i(\varepsilon - E_n)t} |n\rangle \\ &= \sum_n A_n \delta(\varepsilon - E_n) |n\rangle, \end{aligned} \quad (14)$$

which can be normalized as

$$|\Psi(\varepsilon)\rangle = \frac{1}{\sqrt{\sum_n |A_n|^2 \delta(\varepsilon - E_n)}} \sum_n A_n \delta(\varepsilon - E_n) |n\rangle. \quad (15)$$

It is clear that $|\Psi(\varepsilon)\rangle$ is an eigenstate if it is a singlet state or a random phase superposition of all the degenerate eigenstates with energy ε . Although $|\Psi(\varepsilon)\rangle$ is written in the energy basis, the actual basis used to represent the state $|\varphi(t)\rangle$ can be any orthogonal and complete basis, such as the real space used in the tight-binding model of graphene.

By using the quasieigenstates $|\Psi(\varepsilon)\rangle$ obtained from the spectrum method in Eq. (14), we will prove below that

$$\sigma = \frac{\rho(\varepsilon)}{V} \int_0^{\infty} dt \text{Re} [e^{-i\varepsilon t} \langle \varphi | J e^{iHt} J | \varepsilon \rangle] \quad (16)$$

is approximately equal to $\sigma_{T=0}$ in the Kubo formula (10), where $|\varphi\rangle$ is the same initial random superposition state in Eq. (13), and

$$|\varepsilon\rangle = \frac{1}{|\langle \varphi | \Psi(\varepsilon) \rangle|} |\Psi(\varepsilon)\rangle. \quad (17)$$

Eq. (16) is finally used in the numerical calculation. The proof of Eq. (16) reads as follows: First by using the expression of $|\Psi(\varepsilon)\rangle$ in Eq. (15) we get

$$|\langle \varphi | \Psi(\varepsilon) \rangle| = \sqrt{\sum_n |A_n|^2 \delta(\varepsilon - E_n)}, \quad (18)$$

and

$$|\varepsilon\rangle = \frac{1}{\sum_n |A_n|^2 \delta(\varepsilon - E_n)} \sum_n A_n \delta(\varepsilon - E_n) |n\rangle. \quad (19)$$

Now, the conductivity in Eq. (16) becomes

$$\begin{aligned} \sigma &= \frac{1}{V} \frac{\rho(\varepsilon)}{\sum_n |A_n|^2 \delta(\varepsilon - E_n)} \int_0^{\infty} dt \text{Re} [e^{-i(\varepsilon - E_m)t} \sum_{m,k} A_k^* \langle k | J | m \rangle \langle m | J \sum_n A_n \delta(\varepsilon - E_n) | n \rangle] \\ &= \frac{\pi}{V} \frac{\rho(\varepsilon)}{\sum_n |A_n|^2 \delta(\varepsilon - E_n)} \text{Re} \sum_{m,k,n} A_n A_k^* \langle k | J | m \rangle \langle m | J | n \rangle \delta(\varepsilon - E_m) \delta(\varepsilon - E_n). \end{aligned} \quad (20)$$

Separating the sum in $\sum_{m,k,n}$ into two parts with $k = n$ and $k \neq n$, respectively, we get the conductivity as

$$\begin{aligned} \sigma = & \frac{\pi}{V} \frac{\rho(\varepsilon)}{\sum_n |A_n|^2 \delta(\varepsilon - E_n)} \text{Re} \sum_{m,n} |A_n|^2 \langle n | J | m \rangle \langle m | J | n \rangle \delta(\varepsilon - E_m) \delta(\varepsilon - E_n) \\ & + \frac{\pi}{V} \frac{\rho(\varepsilon)}{\sum_n |A_n|^2 \delta(\varepsilon - E_n)} \text{Re} \sum_{m,k \neq n} A_n A_k^* \langle k | J | m \rangle \langle m | J | n \rangle \delta(\varepsilon - E_m) \delta(\varepsilon - E_n). \end{aligned} \quad (21)$$

When the sample size $N \rightarrow \infty$, as proved in the numerical calculation of the DOS, a RRS $|\varphi\rangle$ in the real space contains all the energy eigenstates with approximately equal probability. Therefore, we have $|A_n|^2 \approx 1/N$, $\rho(\varepsilon) \approx \sum_n |A_n|^2 \delta(\varepsilon - E_n)$, and the second term in above expression is close to zero because of the cancellation of random complex coefficients $A_n A_k^*$. This finally proves that

$$\begin{aligned} \sigma = & \frac{\rho(\varepsilon)}{V} \int_0^\infty dt \text{Re} [e^{-i\varepsilon t} \langle \varphi | J e^{iHt} J | \varepsilon \rangle] \\ \approx & \frac{\pi}{NV} \text{Re} \sum_{m,n} \langle n | J | m \rangle \langle m | J | n \rangle \delta(\varepsilon - E_m) \delta(\varepsilon - E_n). \end{aligned} \quad (22)$$

The accuracy of our numerical algorithm to calculate the DC conductivity is mainly determined by the size of the sample, the time interval and total number of time steps used in the Fourier transform of Eq. (14) and in the integral in Eq. (16). The main computational limiting factor for the numerical evaluation of Eq. (16) is the amount of the physical memory available to store $|\varepsilon\rangle$.

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- [1] K. Nomura and A. H. MacDonald, Phys. Rev. Lett. **98**, 076602 (2007).
 - [2] J. H. Bardarson, J. Tworzydło, P.W. Brouwer and C.W. J. Beenakker, Phys. Rev. Lett. **99**, 106801 (2007).
 - [3] A. Hams and H. De Raedt, Phys. Rev. E **62**, 4365 (2000).
 - [4] J. P. Hobson and W. A. Nierenberg, Phys. Rev. **89**, 662 (1953).
 - [5] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
 - [6] A. Ishihara, Statistical Physics (Academic Press, New York, 1971).
 - [7] D. Kosloff and R. Kosloff, J. Comput. Phys. **52**, 35-53 (1983)