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Impurity resonances in carbon nanotubes

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Analytical expressions are derived for the self-energies of electrons in carbon nanotubes while interacting with impurity atoms. Results are reported for armchair and zigzag tubes. It is shown that the impurity causes a bound electron donor or acceptor state beneath every semiconductor band edge. If the tubes are metallic, these bound states become resonance states. The analytical formulas give resonance shapes in good agreement with former numerical calculations.

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I. INTRODUCTION

Several papers have been written on the effect of a nitrogen impurity on the density of states of a carbon nanotube.[1–5] Kostyrko *et al.*[2] showed that a nitrogen impurity gave a resonance in metallic tubes. This same resonance was later found by other workers.[3–5] The energy of the resonance is below any of the semiconductor bands, and not simply related to the energy levels of the nitrogen impurity. These calculations were all entirely numerical.

The same resonance is derived here by analytical arguments. The analytical derivation gives a simple interpretation to the origin of the resonance.

Our interest in these resonances comes from trying to understand the large Seebeck coefficient observed in multiwall nanotubes.[6–14] Since single wall tubes have electron-hole symmetry, the Seebeck coefficient should be zero. A large Seebeck can only be obtained by breaking electron-hole symmetry. Defect states do break symmetry, and offer a possible explanation for the large value of the Seebeck. In metallic tubes, the electrons are highly conducting. Are there resonances in these bands? Our analysis suggests that the resonances are primarily in the semiconducting bands. To a first approximation, a multiwall tube can be considered a system of parallel conductors: each tube is a separate line. The effective Seebeck coefficient of parallel conductors is

$$\langle S\rangle = \frac{\sum_j \sigma_j S_j}{\sum_j \sigma_j}, \tag{1}$$

where (σ_j, S_j) are the conductivity and Seebeck coefficient of each parallel tube. This classical formula suggests that the Seebeck coefficient in multiwall tubes is dominated by metallic tubes with a high conductivity. How do the resonances affect these results? This topic is taken up in Sec. V of the paper.

II. HAMILTONIAN

The word “graphene” denotes a single carbon layer with the graphite structure. A single wall carbon nanotube (SWCNT) could be constructed by cutting graphene into a strip, and then rolling the strip into a cylinder. Although nature does not prepare them that way, the idea of rolling up a strip is useful theoretically, since it provides a simple model for the electronic properties of the nanotubes.

A. Graphene

The energy bands of a pure SWCNT are easily derived from the tight-binding Hamiltonian for a sheet of graphene:[15–17]

$$H = H_0 + V, \tag{2}$$

$$H_0 = -J_0 \sum_{j,\delta,s} [C^{\dagger}_{Ajs} C_{B,j+\delta,s} + C^{\dagger}_{B,j+\delta,s} C_{Ajs}], \tag{3}$$

$$V = E_0 \sum_{\ell=1}^{N_i} C^{\dagger}_{Ajs} C_{Ajs}. \tag{4}$$

Graphene has two carbon atoms per unit cell, that are denoted A and B. Each atom has three neighbors, in the honeycomb lattice. The index j denotes a site $\mathbf{R}_j$ of the A sublattice, and $j+\delta$ are the B neighbors of A. The vector δ_i has three values. The index s denotes electron spin. It does not play a role in the analysis, so it is dropped from the notation. The coefficient $J_0 \sim 3.0$ eV is the transfer integral for a SWCNT. The perturbation V is from the N$_i$ nitrogen impurities on the lattice. We follow chemical convention, and include the impurity by giving it a different site energy E_0 than that of a carbon atom. The site energy for carbon is given as zero, and that defines the energy zero of the problem. We have also simplified the problem by having all of the nitrogen impurities on the A sublattice. It matters not which site is used for calculations of the T matrix for single site scattering. Details are given in the Appendix.

The sign of E_0 depends upon the impurity. For $E_0 < 0$ one gets donor resonances, while for $E_0 > 0$ one has acceptor resonances. Both situations are found in carbon nanotubes by introducing different gases into the sample chamber. Some gases cause a positive Seebeck coefficient while others cause a negative Seebeck coefficient. Presumedly the gases are adsorbed and cause scattering centers.

The hopping Hamiltonian H_0 is easily diagonalized by going to wave vector coordinates

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$$C_{A,j}=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_j}C_{A\mathbf{k}}, \tag{5}$$

$$C_{B,j+\delta}=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_j+\delta)}C_{B\mathbf{k}}, \tag{6}$$

$$H_0=-J_0\sum_{\mathbf{k}}[C_{A\mathbf{k}}^{\dagger}C_{B\mathbf{k}}\gamma(k)+C_{B\mathbf{k}}^{\dagger}C_{A\mathbf{k}}\gamma^{*}(\mathbf{k})], \tag{7}$$

$$\gamma(k)=\sum_{\delta} e^{i\mathbf{k}\cdot\delta}, \tag{8}$$

and N is the number of A atoms in the tube. In graphene, the three neighbors of A are given in terms of the nearest neighbor distance a:

$$\delta_1=a(1,0),\quad \delta_2=\frac{a}{2}(-1,\sqrt{3}),\quad \delta_3=\frac{a}{2}(-1,-\sqrt{3}), \tag{9}$$

$$\gamma(\mathbf{k})=e^{i\theta_x}+2\cos(\theta_y)e^{-i\theta_x/2}, \tag{10}$$

$$\theta_x=k_xa,\quad \theta_y=\frac{\sqrt{3}}{2}k_ya. \tag{11}$$

The Hamiltonian (7) can be diagonalized by writing $\gamma(k)=|\gamma(k)|e^{i\xi(k)}$ and absorbing the phase $\xi(k)$ into the operator C_{Bk}:

$$\tilde{C}_{B\mathbf{k}}=C_{B\mathbf{k}}e^{i\xi(k)}, \tag{12}$$

$$H_0=-J_0\sum_{\mathbf{k}}|\gamma(\mathbf{k})|[C_{A\mathbf{k}}^{\dagger}\tilde{C}_{B\mathbf{k}}+\tilde{C}_{B\mathbf{k}}^{\dagger}C_{A\mathbf{k}}], \tag{13}$$

$$|\gamma(\mathbf{k})|=[1+4\cos(3\theta_x/2)\cos(\theta_y)+4\cos^2(\theta_y)]^{1/2}. \tag{14}$$

Define a set of new operators

$$\alpha_{\mathbf{k}}=\frac{1}{\sqrt{2}}(C_{A\mathbf{k}}+\tilde{C}_{B\mathbf{k}}), \tag{15}$$

$$\beta_{\mathbf{k}}=\frac{1}{\sqrt{2}}(C_{A\mathbf{k}}-\tilde{C}_{B\mathbf{k}}), \tag{16}$$

$$H_0=\sum_{\mathbf{k}}[E_{\alpha}(\mathbf{k})\alpha_{\mathbf{k}}^{\dagger}\alpha_{\mathbf{k}}+E_{\beta}(\mathbf{k})\beta_{\mathbf{k}}^{\dagger}\beta_{\mathbf{k}}], \tag{17}$$

$$E_{\alpha}(\mathbf{k})=-J_0|\gamma(\mathbf{k})|,\quad E_{\beta}=J_0|\gamma(\mathbf{k})|. \tag{18}$$

In terms of these states, the interaction with nitrogen is

$$V=\frac{E_0}{2N}\sum_{i=1}^{N_i}\sum_{\mathbf{k},\mathbf{k}'}[\alpha_{\mathbf{k}}^{\dagger}+\beta_{\mathbf{k}}^{\dagger}][\alpha_{\mathbf{k}'}+\beta_{\mathbf{k}'}]\exp[i\mathbf{R}_i\cdot(\mathbf{k}'-\mathbf{k})]. \tag{19}$$

The form of this interaction changes in the nanotube.

B. SWCNT

Repeat the above analysis for a SWCNT. Rolling up the graphene sheet to make a cylinder, and a nanotube, makes the system periodic in one direction. In the case of an armchair (n,n) tube, the system is periodic in the x-direction. For n equivalent A sites around the circumference, which are $3a$ apart, then $3an=2\pi R$, where R is the radius of the tube. The quantization gives $2\pi Rk_x=2\pi p$, where p is an integer. These relations mean that

$$\frac{3}{2}\theta_x=\frac{3}{2}k_xa=\frac{\pi p}{n}\equiv\phi_p. \tag{20}$$

The y axis is along the length of the nanotube. Call this direction z, $k_y=k_z$. Since the unit cell length along the tube is $c=\sqrt{3}a/2$, then $\theta_y\equiv\theta=k_zc$. The quantum numbers of electron states in the armchair tube are (k_z,p), where $-\pi/c<k_z<\pi/c, p=0,1,2,...,n-1$. The total number of A atoms in the tube is $N=nN_z$, where N_z is the number of unit cells along the axis of the tube. For an armchair tube, the Hamiltonian is

$$H_0=\sum_{k_z,p}[E_{\alpha}(k_z,p)\alpha_{k_z,p}^{\dagger}\alpha_{k_z,p}+E_{\beta}(k_z,p)\beta_{k_z,p}^{\dagger}\beta_{k_z,p}], \tag{21}$$

$$E_{\alpha,\beta}(k_z,p)=\mp J_0[1+4\cos(\theta)\cos(\phi_p)+4\cos^2(\theta)]^{1/2}, \tag{22}$$

$$V=\frac{E_0}{2nN_z}\sum_{i=1}^{N_i}\sum_{k_z,k_z',p,p'}[\alpha_{k_z,p}^{\dagger}+\beta_{k_z,p}^{\dagger}][\alpha_{k_z',p'}+\beta_{k_z',p'}]\times\exp[i\ell_i(k_z'-k_z)c+i2\pi(p-p')m_i/n], \tag{23}$$

where ℓ is the unit cell along the tube, and m is the position of the A atom around the tube. These two indices denote the position of the A-atom in the tube. Interaction (23) forms the basis for the calculation of the resonance state.

If $p=0$, $\cos(\phi_p)=1$, the armchair tube has a dispersion of

$$E_{\alpha,\beta}(k_z,0)=\mp J_0[1+2\cos(\theta)]. \tag{24}$$

The energies vanish at $\theta=2\pi/3,\cos(\theta)=-1/2$. These bands are called "metallic bands" since they have no energy gap. The other armchair bands are called semiconductor bands since they have a gap. Write the dispersion as

$$E_{\alpha,\beta}(k_z,p)=\mp J_0\{[\cos(\phi_p)+2\cos(\theta)]^2+\sin^2(\phi_p)\}^{1/2}. \tag{25}$$

The minimum value of the square root occurs when $2\cos(\theta)=-\cos(\phi_p)$. The semiconductor energy gap is $E_g(p)=2J_0\sin(\phi_p)$.

A similar analysis can be done for zigzag $(0,n)$ tubes. In this case, the strip is cut so that x axis is along the axis of the tube, and becomes the new z direction. The y axis is around the tube, and $\theta_y=\phi_p$ and $\theta_x=k_zc=\theta$. The interaction also has the form of Eq. (23), except now the electron eigenvalues are

$$E_{\alpha,\beta}(k_z,p)=\mp J_0[1+4\cos(\theta)\cos(\phi_p)+4\cos^2(\phi_p)]^{1/2} \tag{26}$$

For zigzag tubes the minimum band energy is at two locations: (i) $\theta=k_z c=0$,

$$E_{\alpha,\beta}(0,p)=\mp J_0|1+2\cos(\phi_p)|. \tag{27}$$

This dispersion is zero only if $\phi_p=\pi p/n=2\pi/3$, which requires that n be divisible by three. (ii) The second minimum is at $\theta=\pi$

$$E_{\alpha,\beta}(\pi,p)=\mp J_0|1-2\cos(\phi_p)|, \tag{28}$$

which vanishes if $\phi_p=\pi/3$.

III. SINGLE SITE SCATTERING THEORY

The scattering potential (23) is the basis for the scattering between the band electrons and the nitrogen defect. The first step is to derive the single site T matrix for scattering of an electron from one impurity.[18] Using standard Green's function methods,[18] gives a self-energy

$$\Sigma_0(i\omega_m)=\frac{cE_0}{2-E_0\sigma(i\omega_m)}, \tag{29}$$

$$\sigma(i\omega_m)=\frac{1}{nN_z}\sum_{k_z p}\left[\frac{1}{i\omega_m-E_\alpha(k_z,p)}+\frac{1}{i\omega_m-E_\beta(k_z,p)}\right], \tag{30}$$

where $i\omega_m$ is the Matsubara discrete frequency,[18] and $c=N_i/N$ is the concentration of defects. The summation over $p=0,1,\ldots,n-1$. This expression is derived in the Appendix.

The retarded function is found from the analytical continuation $i\omega_m\rightarrow E+i\eta$, where η is infinitesimal. The retarded $\sigma(E+i\eta)=\sigma_r(E)-i\sigma_i(E)$ has real and imaginary parts. Since $E_\beta=-E_\alpha$, then

$$\sigma_r(E)=\frac{2E}{n}\sum_p\int_{-\pi}^{\pi}\frac{d\theta}{2\pi}\frac{1}{E^2-E_\alpha(\theta,p)^2}, \tag{31}$$

$$\sigma_i(E)=\frac{\pi}{n}\sum_p\int_{-\pi}^{\pi}\frac{d\theta}{2\pi}\{\delta[E-E_\alpha(\theta,p)]+\delta[E+E_\alpha(\theta,p)]\}. \tag{32}$$

The integrals are easy to do for a zigzag tube

$$\varepsilon=\frac{E}{J_0},\quad \varepsilon_0=\frac{E_0}{J_0},\quad c_p\equiv\cos(\phi_p),\quad s_p=\sin(\phi_p), \tag{33}$$

$$E_0\sigma_r(E)=\frac{2\varepsilon\varepsilon_0}{n}\times\sum_p\frac{\mathrm{sgn}(\varepsilon^2-1-4c_p^2)}{\{[\varepsilon^2-(1+2c_p)^2][\varepsilon^2-(1-2c_p)^2]\}^{1/2}}, \tag{34}$$

$$E_0\sigma_i(E)=\frac{2|\varepsilon|\varepsilon_0}{n}\times\sum_p\frac{1}{\{[(1+2c_p)^2-\varepsilon^2][\varepsilon^2-(1-2c_p)^2]\}^{1/2}}. \tag{35}$$

In both terms the expression is zero if the argument of the square root is negative. A special case is metallic zigzag tubes where $\cos(\phi_p)=c_p=\pm1/2$. The real part has a root $\sqrt{\varepsilon^2(\varepsilon^2-4)}$ and is only nonzero if $|\varepsilon|>2$. The imaginary term has a root $\sqrt{\varepsilon^2(4-\varepsilon^2)}$ and is only nonzero if $2>|\varepsilon|$. At $E=0$ this term is $E_0\sigma_i(0)=\varepsilon_0/n$. The imaginary term is proportional to the density of states of the tube without impurities.

Similar expressions for the armchair tubes are more complicated. The metallic tubes $(p=0,c_p=1)$ have

$$E_0\sigma_r(E,p=0)=\frac{\varepsilon_0}{n}\left[\frac{\mathrm{sgn}(\varepsilon-1)}{\sqrt{(\varepsilon-3)(\varepsilon+1)}}+\frac{\mathrm{sgn}(\varepsilon+1)}{\sqrt{(\varepsilon+3)(\varepsilon-1)}}\right], \tag{36}$$

$$E_0\sigma_i(E,p=0)=\frac{\varepsilon_0}{n}\left[\frac{1}{\sqrt{(3-\varepsilon)(\varepsilon+1)}}+\frac{1}{\sqrt{(\varepsilon+3)(1-\varepsilon)}}\right]. \tag{37}$$

Again the terms are nonzero only if the argument of the square root is positive. The real part is zero for $1>\varepsilon>-1$. The imaginary term is nonzero for $3>\varepsilon>-3$ but both terms contribute only for $1>\varepsilon>-1$. The terms in Eqs. (31) and (32) with $p\neq0$ have an imaginary part

$$E_0\sigma_i(E)=\frac{\varepsilon_0|\varepsilon|}{n}\sum_p\frac{1}{\Omega_p}\left[\frac{1}{\sqrt{4-(c_p+\Omega_p)^2}}+\frac{1}{\sqrt{4-(c_p-\Omega_p)^2}}\right], \tag{38}$$

$$\Omega_p=\sqrt{\varepsilon^2-s_p^2}. \tag{39}$$

Each term in the series over p is zero unless $\varepsilon^2>s_p^2$. The integral for the real part has two expressions depending upon the sign of $\varepsilon^2-s_p^2$:

If $\varepsilon^2>s_p^2$ then

$$E_0\sigma_r(E)=\frac{\varepsilon_0\varepsilon}{n}\sum_p\frac{1}{\Omega_p}\left[\frac{1}{\sqrt{(c_p+\Omega_p)^2-4}}+\frac{1}{\sqrt{(c_p-\Omega_p)^2-4}}\right]. \tag{40}$$

If $\varepsilon^2<s_p^2$ then

$$E_0\sigma_r(E)=-\frac{\varepsilon\varepsilon_0}{n\sqrt{2}}\sum_p\frac{\sqrt{\Delta_p+4+\Xi_p^2-c_p^2}}{\Xi_p\Delta_p}, \tag{41}$$

$$\Xi_p^2=s_p^2-\varepsilon^2,\quad \Delta_p^2=(\varepsilon^2+3)^2+16\Xi_p^2. \tag{42}$$

A dimensionless self-energy for the electron is defined from Eq. (29) as

$$\Sigma_0(i\omega_n)=cJ_0\tilde{\Sigma}(i\omega_n), \tag{43}$$

$$\tilde{\Sigma}(i\omega_n)=\frac{\varepsilon_0}{2-E_0\sigma(i\omega_m)}. \tag{44}$$

The retarded function is obtained by the analytical continuation[18] $i\omega_n=E+i\eta$, and the real and imaginary parts are

$$S(E)=\mathrm{Re}\{\tilde{\Sigma}(E+i\eta)\} \tag{45}$$

$$\Gamma(E)=-\mathrm{Im}\{\tilde{\Sigma}(E+i\eta)\}. \tag{46}$$

This function is useful to calculate since it is independent of concentration.

Figure 1 shows a graph of $\Gamma(E)$ for armchair (6,6) and zigzag (0,6) tubes. The horizontal axis is $\varepsilon=E/J_0$ over a limit scale. For these figures we have selected $\varepsilon_0=E_0/J_0=-2.0$, which are typical numbers for nitrogen impurities. Several peaks are shown. Each peak is associated with a semiconductor band edge. Part (a) shows an armchair tube. For $n=6$ there are semiconductor band edges at $\varepsilon=0.50$, 0.866, and 1.00. Each resonance is caused by the factor of $(1-E_0\sigma_r)$ going to zero as σ_r diverges at the van Hove singularity. Since the tubes are metallic, the imaginary part of the self-energy is nonzero, so the result is a Fano shaped resonance. Precisely this behavior is found in all of the numerical calculations. Similar results are shown in part (b) for zigzag tubes. For a (0,6) tube, semiconductor band edges are found at $\varepsilon=0.732$ and 1.00. This case has only two peaks. For $p=3$ the band has no dispersion $(\varepsilon=1)$ and the imaginary part diverges.

The general behavior puts a resonance peak at energies below each semiconductor band edge. If the tubes were not metallic, the first resonance would be sharp in energy—it would be a true bound state. For higher band edges, the imaginary part is nonzero and the resonance has a nonzero width.

IV. DENSITY OF STATES

The various resonance states found numerically were usually part of the density of states. The above expressions for the self-energy are used to derive an analytical expression for the density of states. The starting point is Eq. (A16) from the Appendix:

$$\tilde{\sigma}(ip)=\frac{1}{N}\sum_{\mathbf{k}}\frac{2(ip-\Sigma_0)}{(ip-\Sigma_0)^2-E_\alpha(\mathbf{k})^2}. \tag{47}$$

The density of states is the imaginary part of the retarded form of this expression:

$$N(E)=-\mathrm{Im}\left\{\sum_p\int_{-\pi}^{\pi}\frac{d\theta}{2\pi}\frac{2[E-\Sigma_0(E)]}{[E-\Sigma_0(E)]^2-E_\alpha(\theta,p)^2}\right\}. \tag{48}$$

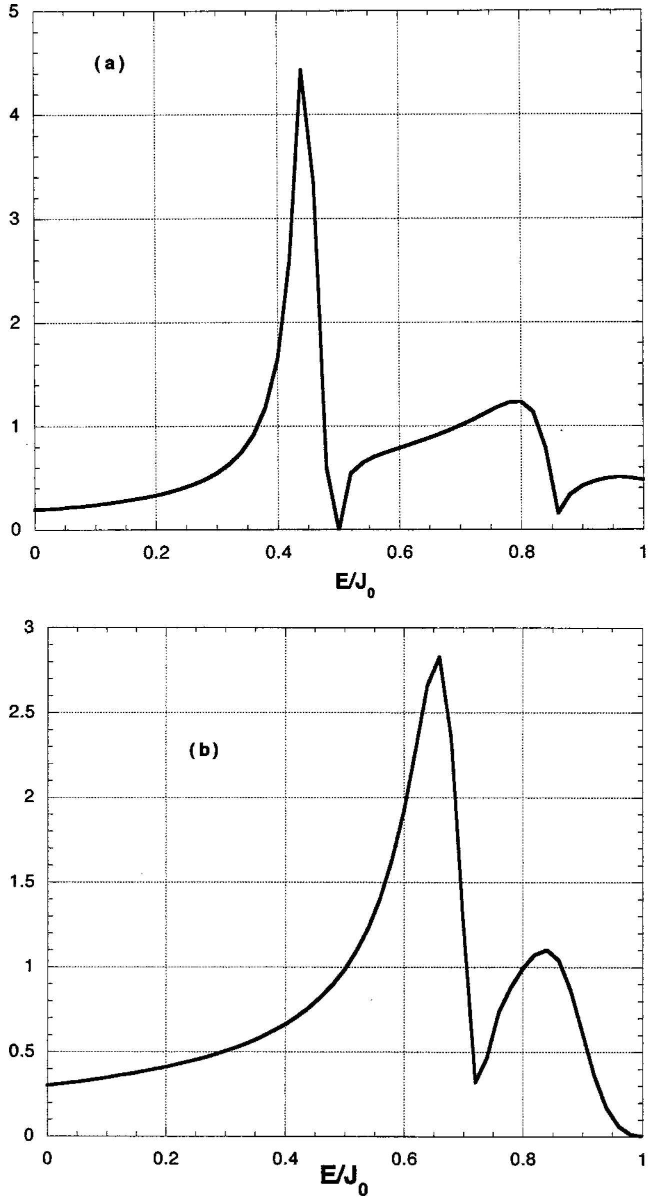

FIG. 1. $\Gamma(E)$ from Eq. (46). (a) For an armchair tube with $n=6$. Resonances occur at the three semiconductor band edges at $\varepsilon=E/J_0=0.50$, 0.886, and 1.00. (b) For a zigzag tube with $n=6$. Resonances occur at semiconductor band edges when $\varepsilon=0.732$ and 1.00.

This integral is similar to Eq. (31), with E replaced by $[E-\Sigma_0(E)]$. Keep in mind that $\Sigma_0(E)$ is a complex function with real and imaginary parts.

As an example, we evaluate the density of states for zigzag tubes. Start from Eq. (34), and replace $\varepsilon\rightarrow\varepsilon-c(S-i\Gamma)$. The imaginary part is

$$N(\varepsilon)=\frac{2\varepsilon\varepsilon_0}{n}\sum_p\frac{\sin(U_p)}{V_p}, \tag{49}$$

$$U_p=\frac{1}{2}\sum_{j=1}^{4}\alpha_j,\quad \tan(\alpha_j)=\frac{c\Gamma}{\varepsilon-cS-\varepsilon_j}, \tag{50}$$

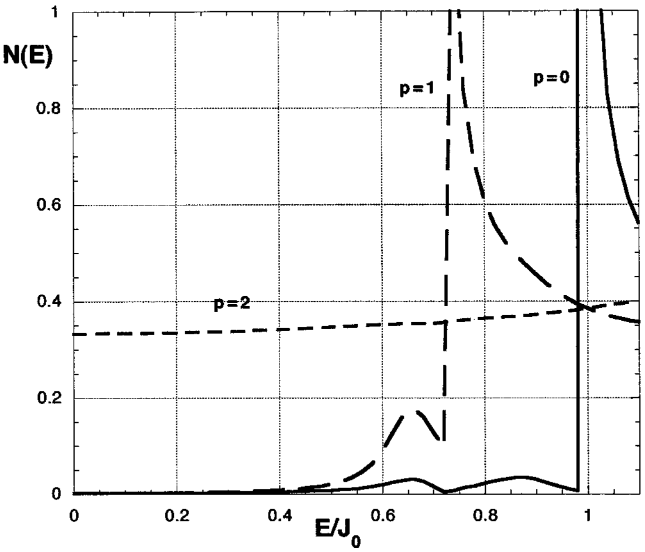

FIG. 2. Density of states $N(E)$ from Eq. (49) for a zigzag tube with $n=6$ and $c=0.02$. Results are plotted for three bands: $p=0$, 1, 2. $p=2$ is the metallic band.

$$V_p=\prod_{j=1}^{4}[(\varepsilon-cS-\varepsilon_j)^2+c^2\Gamma^2]^{1/4}, \quad \varepsilon_j=\pm(1\pm 2c_p). \tag{51}$$

This expression is graphed in Fig. 2 for $c=0.02, \varepsilon_0=-2.0$, and several values of p for a (0,6) zigzag tube. The bands for $p=0$ and 1 are semiconductor bands. The impurity state makes a resonance in the density of states of these two bands. The resonance is located beneath the energy band minimum of the impurityless crystal. The band with $p=2$ is the metallic conduction band when $n=6$. In this case the impurity state makes no discernable resonance in the density of states. The metallic band is carrying most of the electrical current, and this band does not have a density of state resonance from the nitrogen defect. Any contribution to the Seebeck coefficient, from this defect, must occur by one of two mechanisms: (i) The electron lifetime $\hbar/\tau(E)=c\Gamma(E)$ does have a resonance, and this enters the calculation of the Seebeck coefficient. (ii) An electron in a metallic band could scatter to a semiconductor band by either phonon or impurity scattering. This scattering could be virtual, but the electron could have a resonance behavior. This latter process is probably weak. Our conclusion is that the defect levels mainly affect the Seebeck coefficient, of electrons in metallic bands, through the contribution to the quasiparticle lifetime. There is a negligible contribution to the density of states.

V. DISCUSSION

We have derived analytical expressions for the self-energy of electrons in armchair and zigzag nanotubes when scattering from point impurities. The impurity is modeled as a lattice site with a different site energy E_0 than carbon sites. This model is used by chemists in doing tight-binding models for molecules.

Our present model assumed the impurity could be modeled by a site energy. If we change the sign of the site energy (E_0), the resonance moves to negative energies. For a donor or acceptor impurity, where the interaction with the electron is Coulomb's law, the calculation will be somewhat different. Recently we solved[19] the problem of an electron bound to a donor on a nanotube using $V=-e^2/r$. In this case there are also bound states below every semiconductor band edge. This case give similar resonances below every band edge. Using a Coulomb potential, rather than a site energy, does not change the basic phenomena. Both cases yield resonances.

The Seebeck coefficient has been measured for several nanotubes systems: mats of tubes, multiwall tubes, and ropes of tubes. In most cases the Seebeck is a relatively large number at room temperature, such as 60–80 μV/K. Such a large number is unexpected for an energy band system with electron-hole symmetry. The Seebeck coefficient must be related to extrinsic processes, such as defects. This viewpoint is reinforced by the experimental observation that the sign of the Seebeck can be changed by exposure to external gases.[20–23] Presumedly the gas molecules attach themselves to the tubes, and create a local electronic perturbation. The sign of the Seebeck coefficient depends upon whether the electronic perturbation acts as an acceptor or as a donor.

There has been several suggestions that the Seebeck coefficient is due to phonon drag.[12,14,24,25] We have an unpublished proof that the phonon-drag gives a negligible Seebeck in a system with electron-hole symmetry. If there is phonon drag, it must exist because of its coupling to the defect states. The so-called "phonon-drag peak" also changes sign with exposure to different gases. In one dimension, unlike two or three dimensions, the electronic coupling to defects and phonons cannot be treated separately. Issues such as localization require they be treated together. Our own guess, at this point, is that the phonons do play a role in conjunction with the defect states. The first step in such a theory would be an understanding of the defect states, which is the topic of the present paper.

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APPENDIX: MULTISITE SCATTERING

The scattering of an electron from a single defect is given by Eq. (29), which is the T matrix for the scattering. A complete theory also has contributions from scattering by more than one defect at a time. Here we derive a formula for this contribution. The potential energy, such as Eq. (19), has a phase factor. In each order of perturbation theory, we must find all terms that make this phase factor vanish. It is just a counting problem, and it is easier to use the notation of Eq. (19) then the similar expression (23) for a SWCNT. Define the operator $A_k=\alpha_k+\beta_k$ and the Green's function[18]

$$\mathcal{G}^{(0)}(ip,\mathbf{k}) = -\int_0^\beta d\tau e^{ip\tau}\langle T_\tau A_k(\tau)A_k^\dagger(0)\rangle \tag{A1}$$

$$\begin{aligned} &= \frac{1}{ip-E_\alpha(k)} + \frac{1}{ip-E_\beta(k)} \\ &= \frac{2ip}{(ip)^2-E_\alpha^2}. \end{aligned} \tag{A2}$$

(1) In first order perturbation theory, one has $\mathbf{k}'=\mathbf{k}$ and the phase factor vanishes. The self-energy is $\Sigma^{(1)}=cE_0/2$.

(2) In second-order perturbation theory, the self-energy has the form

$$\Sigma^{(2)}(ip) = \frac{E_0^2}{(2N)^2}\sum_{\mathbf{p},j,\ell}\mathcal{G}^{(0)}(ip,\mathbf{p})\exp[i(\mathbf{p}-\mathbf{k})\cdot(\mathbf{R}_j-\mathbf{R}_\ell)].$$

The phase factor can be zero two ways: (i) $\mathbf{p}=\mathbf{k}$ which gives $\Sigma^{(1)2}\mathcal{G}^{(0)}(ip,\mathbf{k})$, or else (ii) $\mathbf{R}_j=\mathbf{R}_\ell$, which gives that $c(E_0/2)^2\sigma(ip)$:

$$\Sigma^{(2)}(ip) = c(E_0/2)^2[\sigma(ip)+c\mathcal{G}^{(0)}]. \tag{A3}$$

The second term in brackets is a correction of $O(c^2)$.

(3) In third-order perturbation theory, we have many terms:

$$\begin{aligned} \Sigma^{(3)} = \frac{E_0^3}{(2N)^3}&\sum_{\mathbf{p}_1,\mathbf{p}_2,j,\ell,m}\mathcal{G}^{(0)}(ip,\mathbf{p}_1)\mathcal{G}^{(0)}(ip,\mathbf{p}_2) \\ &\times\exp[i\mathbf{p}_1\cdot(\mathbf{R}_\ell-\mathbf{R}_j)+i\mathbf{p}_2\cdot(\mathbf{R}_j-\mathbf{R}_m) \\ &+i\mathbf{k}\cdot(\mathbf{R}_m-\mathbf{R}_\ell)]. \end{aligned} \tag{A4}$$

There are many ways to make the phase factor vanish. Each term is multiplied by $(E_0/2)^3$:

$$\mathbf{k}=\mathbf{p}_1=\mathbf{p}_2 \quad \text{gives} \quad c^3\mathcal{G}^{(0)}(ip,\mathbf{k})^2,$$

$$\mathbf{R}_j=\mathbf{R}_\ell=\mathbf{R}_m \quad \text{gives} \quad c\sigma(ip)^2,$$

$$\mathbf{k}=\mathbf{p}_1\neq\mathbf{p}_2, \quad \mathbf{R}_m=\mathbf{R}_\ell \quad \text{gives} \quad c^2\sigma(ip)\mathcal{G}^{(0)}(ip,\mathbf{k}),$$

$$\mathbf{k}=\mathbf{p}_2\neq\mathbf{p}_1, \quad \mathbf{R}_\ell=\mathbf{R}_j \quad \text{gives the same as above},$$

$$\mathbf{p}_1=\mathbf{p}_2\neq\mathbf{k}, \quad \mathbf{R}_j=\mathbf{R}_m \quad \text{gives} \quad c^2\sigma^{(2)}(ip), \quad \text{where}$$

$$\sigma^{(2)}(ip) = \frac{1}{N}\sum_{\mathbf{p}}\mathcal{G}^{(0)}(ip,\mathbf{p})^2. \tag{A5}$$

The total of all of these terms is

$$\Sigma^{(3)} = c(E_0/2)^3[(\sigma+c\mathcal{G}^{(0)})^2+c\sigma^{(2)}]. \tag{A6}$$

All of these self-energy terms multiply $\mathcal{G}^{(0)2}$. Dyson's equation for a single site is generated by the expansion

$$\begin{aligned} \mathcal{G} = \mathcal{G}^{(0)}\{1&+\mathcal{G}^{(0)}(cE_0/2)[1+(E_0/2)(\sigma+c\mathcal{G}^{(0)}) \\ &+(E_0/2)(\sigma+c\mathcal{G}^{(0)})^2+\cdots]\} \end{aligned} \tag{A7}$$

$$= \mathcal{G}^{(0)}\left[1+\frac{c(E_0/2)\mathcal{G}^{(0)}}{1-(E_0/2)(\sigma+c\mathcal{G}^{(0)})}\right] \tag{A8}$$

$$= \mathcal{G}^{(0)}\left[1+\frac{\Sigma_0\mathcal{G}^{(0)}}{1-\Sigma_0\mathcal{G}^{(0)}}\right] = \frac{\mathcal{G}^{(0)}}{1-\Sigma_0\mathcal{G}^{(0)}} \tag{A9}$$

where Σ_0 is defined in Eq. (29). This derivation gives the single site T matrix. However, it does not account for the third-order term with $\sigma^{(2)}$. This latter contribution comes from using interacting Green's function in σ:

$$\tilde{\sigma}(ip) = \frac{1}{N}\sum_{\mathbf{p}}\mathcal{G}(ip,\mathbf{p}). \tag{A10}$$

Using the expansion for $\mathcal{G}$ in Eq. (A7) gives the series

$$\tilde{\sigma}(ip) = \sigma + c(E_0/2)\sigma^{(2)} + \cdots. \tag{A11}$$

We have checked in higher orders of perturbation series, and found this interpretation is correct, in that all terms in the above series are generated. It does not account for all higher-order terms.

A better derivation includes the possibility that the impurity atom is equally likely to be on the A or B site. The number on A is N_{Ai}, and that on B is N_{Bi}:

$$c = \frac{N_{Ai}+N_{Bi}}{N}, \quad \delta = \frac{N_{Ai}-N_{Bi}}{N}. \tag{A12}$$

If we assume the impurity locations are random, the statistics of large numbers gives that $\langle\delta\rangle=0$, and $\langle\delta^2\rangle=c^2/N_i$. We can set $N_{Ai}=N_{Bi}=N_i/2$ and neglect the fluctuations around this mean configuration.

We repeat the above derivation. In summing over sites, the A sites cannot equal to the B sites. The same self-energy (29) is obtained but now it is the self-energy of $\mathcal{G}_\alpha$ and $\mathcal{G}_\beta$:

$$\mathcal{G}_0(ip,\mathbf{k}) = \frac{1}{ip-E_\alpha(\mathbf{k})-\Sigma_0(ip)}, \tag{A13}$$

$$\mathcal{G}_\beta(ip,\mathbf{k}) = \frac{1}{ip-E_\beta(\mathbf{k})-\Sigma_0(ip)}, \tag{A14}$$

$$\tilde{\sigma}(ip) = \frac{1}{N}\sum_{\mathbf{k}}[\mathcal{G}_\alpha(ip,\mathbf{k})+\mathcal{G}_\beta(ip,\mathbf{k})], \tag{A15}$$

$$\tilde{\sigma}(ip) = \frac{1}{N}\sum_{\mathbf{k}}\frac{2(ip-\Sigma_0)}{(ip-\Sigma_0)^2-E_\alpha(\mathbf{k})^2}. \tag{A16}$$

The latter expression is the starting point for the calculation of the density of states.

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