Energy Anomaly and Polarizability of Carbon Nanotubes

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The energy of Fermi sea perturbed by an external potential is analyzed with the help of an energy anomaly. Using an example of massive Dirac fermions on a circle, we illustrate how the anomaly accounts for the contribution of the deep-lying states. The energy anomaly is a universal function of the applied field and is related to known field-theoretic anomalies. Applied to the transverse polarizability of carbon nanotubes, the anomaly reveals universality and scale invariance of the response dominated by π electrons. The electron band transformation in a strong field-effect regime is predicted.

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Fermion anomalies are universal contributions to the low-energy properties of field theory originating from the bottom of the filled Fermi-Dirac sea. The primary examples in high-energy physics are the spontaneously generated photon mass in $d = 1 + 1$ [1] and the Adler-Bell-Jackiw chiral anomaly [2] relating the decay of a pion into two photons to the number of quark colors [3]. Several instances of anomalies are known in solid state physics, with the chiral anomaly manifest in transport [4] and in fermion number fractionalization [5], and the parity anomaly in $d = 2 + 1$ linked to the quantum Hall effect [6].

Here we describe a new manifestation of fermion anomaly, appearing in the total energy of Fermi sea in the presence of an external field. While the net energy of Fermi-Dirac vacuum depends on ultraviolet cutoff, i.e., on the behavior at the bottom of the band, the external field-dependent part of the energy is cutoff insensitive. The latter energy is naturally divided into two parts, one given by a sum of the energy shifts of filled states near the Fermi level and another, equally important, representing the cumulative effect of the states deep below the Fermi level. The latter, anomalous part, traced to Schwinger anomaly [1], has a universal form and can be expressed through the properties near the Fermi level.

The Fermi sea energy field dependence is the physical quantity central for many physical properties of materials. As an application, below we consider the response of the carbon nanotube (NT) π electron band to perpendicular electric field. The aforementioned separation into the normal and anomalous parts enables one to handle energy in a fully general and, at the same time, case-specific way, taking full account of the level quantization, curved geometry, spatial inhomogeneity, etc. The NT π band is described by a tight-binding model on a honeycomb lattice [7]. Near the Fermi level, at the π band center, the NT electrons are described by $d = 2 + 1$ Dirac fermions moving on a cylindrical surface [8]. The Dirac model provides a simple analytic description of NT curvature and chirality [7,9], and of the effects of external fields [10] in both semiconducting and metallic NTs.

It might seem that understanding properties such as NT polarizability should require a detailed knowledge of the π electrons behavior on the lattice constant scale [11]. Here we find that, to the contrary, the energy can be accurately obtained from the Dirac model, provided the anomaly is taken into account. Our analysis provides new insight into NT properties: We identify the dominant role of π electrons response compared to that of other orbitals, and explain the origin of the scale invariant depolarization, independent of the NT diameter [11–13], qualitatively different from that of metallic and dielectric shells. Our approach, with electron interactions included in an RPA fashion [14], is not limited to linear response: we apply it to study NT electron band transformation in the field-effect regime.

The origin of the energy anomaly is exhibited most clearly by the example of chiral fermions on a circle $[0, 2\pi]$, described by the Hamiltonian $\mathcal{H} = -i\partial_{\theta} + U$, $U = 2a \cos\theta$. In the Fourier representation $|n\rangle = e^{in\theta}$, \mathcal{H} is given by an infinite three-diagonal matrix: $\mathcal{H}_{nn} = n$, $\mathcal{H}_{n n \pm 1} = a$. Eliminating the potential *U* by a gauge transformation $\psi(\theta) = e^{-2ia\sin\theta} \tilde{\psi}(\theta)$, $\tilde{\mathcal{H}} = -i\partial_{\theta}$, we see that the eigenvalues of H are integers independent of U .

The energy anomaly arises when the interaction *U* is *truncated* at a certain energy scale. To that end, let us consider a more general three-diagonal matrix

$$
\mathcal{H}_{nn} = n, \qquad \mathcal{H}_{n\,n+1} = \mathcal{H}_{n+1\,n} = a_n \qquad (1)
$$

 $(n \in \mathbb{Z})$, with the sequence a_n having different limits at $n \rightarrow \pm \infty$: $a_{n \rightarrow -\infty} = 0$, $a_{n \rightarrow +\infty} = a$. Although now the energy levels depend on a_n , the above argument for spectrum robustness at constant a_n indicates that this dependence is exponentially small at large $|n|$. The level shifts are significant for only a relatively small cluster of levels around $n \approx n_*$ where the switching of a_n from 0 to *a* occurs.

Notably, the sum of all level shifts, $\delta \text{ tr} \mathcal{H} = \sum_{n} \delta \epsilon_n$, depends only on the asymptotic values $a_{n \to \pm \infty}$, while other details of the sequence a_n do not matter. To see this, we truncate the matrix H at some large positive and negative

 $n = \pm N$, in which case the trace of this $(2N + 1) \times (2N + 1)$ 1) matrix is finite and explicitly a independent. Since at $N \gg n_*$, the mutual influence of the levels at $n \simeq n_*$ and $n \approx N$ is exponentially small, the effect on trH due to truncating at $n \approx N$ is negative of that due to a_n switching at $n \approx n_*$, both being universal. [The levels at $n \approx -N$ are unaffected by the truncation since $a_{n\to -\infty} = 0$ and H is diagonal.] Thus the sum of the level shifts at $n \approx n_*$ depends only on $a_{n=+\infty} = a$, giving a cutoff-independent contribution to $\delta \text{tr} \mathcal{H}$.

The universal value $E_{\text{anom}} = \delta \text{ tr } \mathcal{H}$ can be evaluated using slowly varying a_n , $|da_n/dn| \ll |a_n|$. In this case, since the levels are unperturbed by constant a_n , the level shifts will be small, which warrants using perturbation theory. Gradient expansion $a_{n+\Delta n} = \bar{a} + b\Delta n$, $b =$ da_n/dn , yields

$$
\mathcal{H} = -i\partial_{\theta} + 2\bar{a}\cos\theta + b\{e^{i\theta}(-i\partial_{\theta}) + \text{H.c.}\}.
$$

The gauge transformation $\psi(\theta) = e^{-2i\bar{\alpha}\sin\theta} \tilde{\psi}(\theta)$ transforms H into

$$
\tilde{\mathcal{H}} = -i\partial_{\theta} + b\{e^{i\theta}(-i\partial_{\theta} - 2\bar{a}\cos\theta) + \text{H.c.}\}.
$$
 (2)

The energies ϵ_n obtained in the lowest order of perturbation theory are $\epsilon_n = \langle n | \tilde{H} | n \rangle = n - 2b\bar{a}$. The sum of these level shifts, given by a full derivative, depends only on the asymptotic of *an*:

$$
E_{\text{anom}} = -\sum_{n} 2b\bar{a} \simeq -\int_{-\infty}^{\infty} dn \, 2a_n \frac{da_n}{dn} = -a^2. \tag{3}
$$

For a complex sequence a_n , Eq. (3) is generalized to $E_{\text{anom}} = -|a|^2$. The relation of this result with fermionic energy emerges when one considers the quenching of the external field $a_n = a$ coupling to the states at the Fermi sea bottom, modeled by $a_{n \le n_*} = 0$. We find that the anomalous contribution E_{anom} is universal; i.e., it depends only on the properties near the Fermi level [15]. The anomaly contributes additively to the energy along with the contributions due to fermion mass and confinement (see below).

Electrons in a nanotube, a cylinder of radius *R*, are described by $d = 2 + 1$ massless Dirac model [8]. The states in a transverse field, labeled by momentum *k* along the tube, can be viewed as massive $d = 1 + 1$ Dirac fermions on the NT circumference, the circle $0 < y < 2\pi R$:

$$
\mathcal{H}_D = -i\hbar v \hat{\alpha} \partial_y + \hbar v k \hat{\beta} + U(y), \tag{4}
$$

with $U(y)$ the transverse field potential and $h\nu k$ the Dirac "mass." (Here $\hat{\alpha} = -\sigma_x$ and $\hat{\beta} = \sigma_y$ [7].) We assume generic quasiperiodic boundary conditions $\psi(y + 2\pi R) =$ $e^{2\pi i \delta} \psi(y)$. At $U = 0$, the energy levels

$$
\epsilon_n^{\pm} = \pm \sqrt{\Delta_R^2(n+\delta)^2 + (\hbar v k)^2}, \qquad \Delta_R \equiv \hbar v / R,
$$

describe NT subbands. The phase δ determines NT properties: $\delta = \pm \frac{1}{3}$ for semiconducting NT, $\delta = 0$ for metallic

NT, and $|\delta| \ll 1$ for the tubes with a small gap induced by curvature [9] or by parallel magnetic field [10].

For the Fermi sea energy change at finite *U*, the naive answer would be the sum over occupied states $W = \sum \delta \epsilon_n$, $\delta \epsilon_n \equiv \epsilon_n |_{U} - \epsilon_n|_{U=0}$. The level shifts $\delta \epsilon_n$ become very small away from the band center, so that the sum giving *W* converges at $|n| \gg kR$: In this limit, with the contribution of finite mass being negligible, the Dirac problem (4) decouples into *two* chiral fermion modes, each having *U*-independent spectrum. However, despite the absence of level shifts, the states with large $|n|$ contribute to the *U*-dependent energy via anomaly due to the bandwidth cutoff, $(\hbar v/R)n_* \sim -10$ eV for carbon. As described above, the anomaly depends only on the properties near the band center:

$$
E_{\text{anom}} = -\frac{N_f}{2\pi\hbar v} \int_0^{2\pi R} U^2(y) dy,\tag{5}
$$

where $N_f = 4$ is the number of electron flavors associated with spin and the Dirac points K , K^{\prime} [7]. Note that the energy (5) is *additive* for multiple fermion flavors, contrary to fermion-doubling cancellation typical of the chiral anomaly effects [16].

One can interpret Eq. (5), somewhat loosely, as a counterterm that eliminates the nonphysical contribution of infinite Fermi sea in the model (4), i.e., the states outside the carbon band. A photon mass $m_{\gamma}^2 = e^2/\pi$ appears in $d = 1 + 1$ QED [1] after integration over massless fermions. Equation (5) exhibits a similar effect in the Dirac system in an external electromagnetic field eA_u = *U*(*y*), 0), with the mass term $\int d^2x \frac{1}{2} m^2 x \frac{d^2y}{dx^2} = -\int E_{\text{anom}} dt$ in the action. (We point out a distinction of our approach and Coleman's analysis [17] of the massive Schwinger model in external field, which yields an effective action containing the field intensity rather than potential.)

The energy anomaly is related to the chiral anomaly in $d = 1 + 1$, since in this case the chirality $\gamma^5 = \hat{\alpha}$ enters the Hamiltonian (4). Such a relation can be established via the change in the functional measure [18]. We note that a chiral gauge transformation $(h = v = 1)$

$$
\psi(y) = e^{-i\gamma^5 \phi(y)} \tilde{\psi}(y), \qquad \phi = \int^y dy' U(y'), \quad (6)
$$

preserves the boundary conditions on ψ , turning (4) into

$$
\tilde{\mathcal{H}}_D = -i\hat{\alpha}\partial_y + ke^{2i\hat{\alpha}\phi(y)}\hat{\beta}.\tag{7}
$$

The anomaly (5) arises from the Jacobian of the transformation (6). Consider infinitesimal change of the background field $U(y)$ by $\delta U(y)$, which yields $\psi' = e^{i\gamma^5 \lambda(y)} \psi$, $\lambda(y) \equiv \int^y dy' \delta U(y')$. The corresponding Jacobian $J =$ $\exp\{2i \int dt dy \mathcal{A}\lambda(y)\}$ [19] changes the action by $-i \ln J =$ $-\delta E_{\text{anom}}t$, yielding $\delta E_{\text{anom}} = \frac{1}{\pi} \int dy \lambda \partial_y U$, with $\mathcal{A} =$ anom tr $\gamma^5 = \frac{1}{2\pi} \epsilon^{\mu\nu} F_{\mu\nu} = -\partial_y U(y)/2\pi$ the chiral anomaly [3]. Integration by parts gives the variation $\delta E_{\text{anom}} = -\frac{1}{\pi} \int dy U \delta U$, from which the result (5) follows. This approach can be extended to include electron interactions.

Turning to the NT response to transverse electric field,

$$
U(y) = -e\mathcal{E}R\cos(y/R),\tag{8}
$$

we relate polarizability to the sum of Stark shifts

$$
E_0(k) = \sum_n \delta \epsilon_n(k), \tag{9}
$$

 $\delta \epsilon_n(k) = \epsilon_n(k)|_{\mathcal{E}} - \epsilon_n(k)|_{\mathcal{E}=0}$, taken over all occupied states, with *k* the electron momentum along the tube. We obtain the shifts $\delta \epsilon_n(k)$ from the Hamiltonian (4). In this calculation, the anomaly (5) must be added to account for the finite band cutoff, formally absent in (4).

The main effect of electron interaction is depolarization, i.e., screening of the field inside NT. To obtain the RPA screening function [11,14] of the NT cylinder, we first show how the problem is reduced to the calculation of electron energy in the presence of an external field. The Gauss's law relates the fields inside and outside the tube with the induced surface charge density σ ,

$$
\mathcal{E}_{\text{ext}} = \mathcal{E} + \frac{1}{2} 4\pi N_f \sigma, \qquad \sigma = \mathcal{P}/(\pi R^2), \qquad (10)
$$

where P is the dipole moment per flavor and per unit NT length, and the factor $1/2$ accounts for depolarization in cylindrical geometry. In Eq. (10) we projected the actual charge density on the $\cos\varphi$ harmonic, $\varphi \equiv y/R$, as $\sigma(\varphi) \rightarrow N_f \sigma \cos \varphi$, ignoring higher order harmonics. The problem is then reduced to evaluating the dipole moment, given by $P = -dW(E)/dE$, where $W(E)$ is one fermion flavor energy as a function of the inner field,

$$
W = N_f^{-1} \int_{-\infty}^{\infty} \{ E_0(k) + E_{\text{anom}} \} \frac{dk}{2\pi}.
$$
 (11)

Combining this with Eq. (10), and using dimensionless $u = e\mathcal{E}R/\Delta_R$, we obtain $u_{ext} = u + 2N_f \frac{e^2}{\hbar v} \mathcal{P}(u)$. Once the dipole moment $P(u)$ is known, this relation determines the inner field u in terms of the outer field u_{ext} .

Taking the Stark shifts $\delta \epsilon_n(k)$ to the lowest order in $\mathcal E$ and evaluating the integral over k (see Fig. 1), we obtain

$$
W = -\frac{\alpha}{2}u^2, \qquad \alpha = \begin{cases} 0.196\dots & \text{for } \delta = 1/3, \\ 0.179\dots & \text{for } \delta = 0. \end{cases}
$$
 (12)

Notably, the linear relation $P = \alpha u$ holds up to very large fields $u \sim 1$ (Fig. 1, inset), giving the depolarization

$$
\mathcal{E}_{\text{ext}} = \left(1 + 2N_f \alpha \frac{e^2}{\hbar v}\right) \mathcal{E}.\tag{13}
$$

With $e^2/\hbar v = 2.7$ this gives $\mathcal{E}_{ext}/\mathcal{E} = 5.24$ for $\delta = 1/3$, and $\mathcal{E}_{ext}/\mathcal{E}=4.87$ for $\delta=0$, in excellent agreement with the full tight-binding calculations [11].

The screening (13) is radius independent and is nearly the same in the metallic and semiconducting NTs. The latter is not surprising: screening is absent in a single 1*d* mode approximation, since polarizability is related to dipolar transitions between *different* subbands. The scale

FIG. 1 (color online). Partial dipole moment $P(k) =$ $-d(E_0(k) + E_{\text{anom}})/du$ as a function of *k*, obtained from (11) for semiconducting NT, where $u = e\mathcal{E}R^2/\hbar v$ is dimensionless field. Note the cancellation between $E_0(k)$ and the anomaly (5) at $kR \gg 1$, enforcing convergence of $P = \int P(k)dk/2\pi$. Note also that $P(k \rightarrow 0)$ is dominated by the anomaly, since $E_0 = 0$ at $k =$ 0 due to the chiral gauge invariance (6). Inset: Dipole moment P per one fermion flavor versus *u* for metallic and semiconducting NT. Straight lines represent weak field linearization (12). Arrow marks the field $u \approx 1.2$ for which velocity changes sign in metallic NT (see text and Fig. 2).

invariance of (13) obtained for a hollow NT cylinder resembles depolarization in a massive dielectric cylinder [20–22]. The dipole moment of π electrons, found to scale with R^2 , should be contrasted to $P \propto R$ for a hollow dielectric shell. The universal scale invariant result (13) reflects the dominant role of π electrons in transverse response as compared to other carbon orbitals.

To emphasize the role of anomaly in this calculation, we note that omitting this contribution would have led to a wrong sign of the response and also to a divergence. Indeed, because of an upward shift of the filled levels ϵ_n^- (Fig. 2), we have $P_0 = dE_0/du > 0$, corresponding to an unphysical ''diamagnetic'' polarization sign. Also, the *k* dependence $E_0(k)$ causes an ultraviolet divergence in the integral $P = \int P(k)dk/2\pi$, since $E_0(k)$ increases with $|k|$, saturating at $\vert k \vert R \gg 1$ at an asymptotic value $\frac{1}{2}u^2$. Both difficulties are resolved by taking into account the negative $E_{\text{anom}} = -\frac{1}{2}u^2$. The resulting integral (11) converges after $E_0(k)$ is offset by E_{anom} (Fig. 1).

To illustrate the effect of the transverse field, here we examine the NT electron spectrum. The changes are most dramatic in a strong field [12], which mixes different NT subbands, $u \approx 1$, or $e\mathcal{E}R \approx \Delta_R$, $\mathcal{E}[MV/cm] \approx$ 5.26/ R^2 [nm²]. In metallic NTs the electron velocity $v =$ $d\epsilon/dp$ decreases and can even reverse sign, causing Fermi surface breakup. This could lead to interesting many-body effects such as the Luttinger correlations increase due to enhanced $e^2/\hbar v$, or instability with respect to exciton formation for the negative- v states. Semiconducting NTs exhibit the effective mass sign change, accompanied by

FIG. 2 (color online). Electron bands transformation in the strong field-effect regime, $u = e\mathcal{E}R/\Delta_R \sim 1$. Top: Velocity reversal in metallic NT occurs at $u > u_c \approx 1.2$. Bottom: Effective mass sign change in semiconducting NT at $u > u_c \approx 0.62$. The bands are shown for *u* below and above the critical value. Inset: Energy gap suppression in a semiconducting NT.

field-induced suppression of the excitation gap (Fig. 2) that could be manifest in activated transport. The above screening calculation provides an estimate for the fields necessary to observe these effects. The relatively small outer-toinner field ratio \simeq 5, as well as availability of NTs of a few nm radius, puts the required voltage across the tube in a feasible range of a few volts.

In summary, we considered the energy of the Fermi sea for Dirac fermions in an external field, expressed via energy anomaly through low-energy properties. The energy anomaly, applied to the polarizability of nanotubes, provides insight in their response properties, notably the scale invariance of depolarization, the difference of screening in semiconducting and metallic NT, and the relative importance of the π band compared to other carbon bands. Electron bands exhibit a dramatic change in the strong field-effect regime.

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