Dynamical Centrosymmetry Breaking in Graphene: A Novel Mechanism for Second Harmonic Generation

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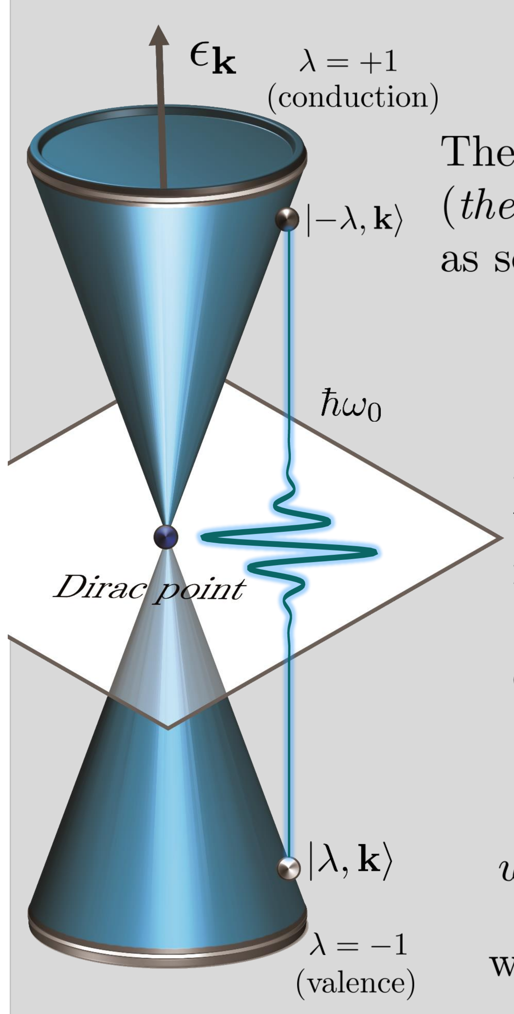
We discover an unusual phenomenon that occurs when a graphene monolayer is illuminated by a short and intense pulse at normal incidence. Due to pulse-induced oscillations of the Dirac cones, a dynamical breaking of the layer's centrosymmetry takes place, leading to the generation of second harmonic waves. We prove that this result can only be found by using the full Dirac equation and show that the widely used semiconductor Bloch equations fail to reproduce this and some other important physics of graphene. Our results open new windows in the understanding of nonlinear light-matter interactions in a wide variety of new 2D materials with a gapped or ungapped Dirac-like dispersion.

1 Theoretical Framework: Towards the *Dirac-Bloch Equations*

In the low-energy regime, electrons in graphene are described by massless relativistic fermions obeying the Dirac equation [3]. If one treats the optical field perturbatively and consequently applies the minimal substitution, the 2−spinor $|\psi_{\mathbf{k}}(t)\rangle$ representing a quasiparticle state of momentum $\mathbf{p} = \hbar\mathbf{k}$, Fermi velocity v_F and charge $-e$ satisfies the Dirac equation:



$$i\hbar\partial_t |\psi_{\mathbf{k}}(t)\rangle = v_F\, \boldsymbol{\sigma} \cdot \left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right) |\psi_{\mathbf{k}}(t)\rangle \quad (1)$$

The field-free energy dispersion is *linear* in momentum i.e. $\epsilon_{\mathbf{k}} = \lambda\hbar v_F |\mathbf{k}|$ (*the Dirac cones*) and admits electron ($\lambda = +1$) and hole ($\lambda = -1$) states as solutions [3]. In polar coordinates ($|\mathbf{k}|, \phi_{\mathbf{k}}$), they are:

$$|\lambda, \mathbf{k}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-\frac{i}{2}\phi_{\mathbf{k}}} \\ \lambda e^{\frac{i}{2}\phi_{\mathbf{k}}} \end{pmatrix} e^{-\frac{i}{\hbar}\epsilon_{\mathbf{k}} t} \quad (2)$$

Applying techniques found in [2], we can show that a two-level system with a wavefunction *ansatz* $|\psi_{\mathbf{k}}\rangle = c_+ |+1, \mathbf{k}\rangle + c_- |-1, \mathbf{k}\rangle$ admits a time-dependent *polarisation* $q_{\mathbf{k}} \equiv c_+ c_-^* e^{-i(\Omega_{\mathbf{k}} - \omega_0 t)}$ and a *population inversion* $w_{\mathbf{k}} \equiv |c_+|^2 - |c_-|^2$ which are governed by dynamical equations we name the *Dirac-Bloch equations* (DBEs) [1]:

$$\dot{q}_{\mathbf{k}}(t) + i\left(2\dot{\Omega}_{\mathbf{k}}(t) - \omega_0 - i\gamma_2\right) q_{\mathbf{k}}(t) + \frac{i}{2} e^{i\omega_0 t}\dot{\theta}_{\mathbf{k}}(t) w_{\mathbf{k}}(t) = 0 \quad (3)$$

$$\dot{w}_{\mathbf{k}}(t) + \gamma_1 (w_{\mathbf{k}}(t) - w_{\mathbf{k}}^0) + i\dot{\theta}_{\mathbf{k}}(t)\left(q_{\mathbf{k}}(t) e^{-i\omega_0 t} - q_{\mathbf{k}}^*(t) e^{i\omega_0 t}\right) = 0 \quad (4)$$

where $\dot{\Omega}_{\mathbf{k}}(t) = (v_F/\hbar)[(p_x + (e/c)A(t))^2 + p_y^2]^{1/2}$ is the *dynamical phase* and $\dot{\theta}_{\mathbf{k}}(t) = e p_y E(t)/[(p_x + (e/c)A(t))^2 + p_y^2]$ the *dynamical angle*. $\gamma_{1,2}$ are dephasing coefficients and $w_{\mathbf{k}}^0$ is explained in Box 6.

Intraband and *interband* transitions contribute to the total integrated time-dependent current:

$$\mathbf{J}(t) = -\frac{e v_F g_s g_v}{4d\pi^2} \int \begin{pmatrix} \cos\theta_{\mathbf{k}} & \sin\theta_{\mathbf{k}} \\ \sin\theta_{\mathbf{k}} & -\cos\theta_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} w_{\mathbf{k}} - w_{\mathbf{k}}^0 \\ -2\mathrm{Im}(q_{\mathbf{k}} e^{-i\omega_0 t}) \end{pmatrix} d\mathbf{k} \quad (5)$$

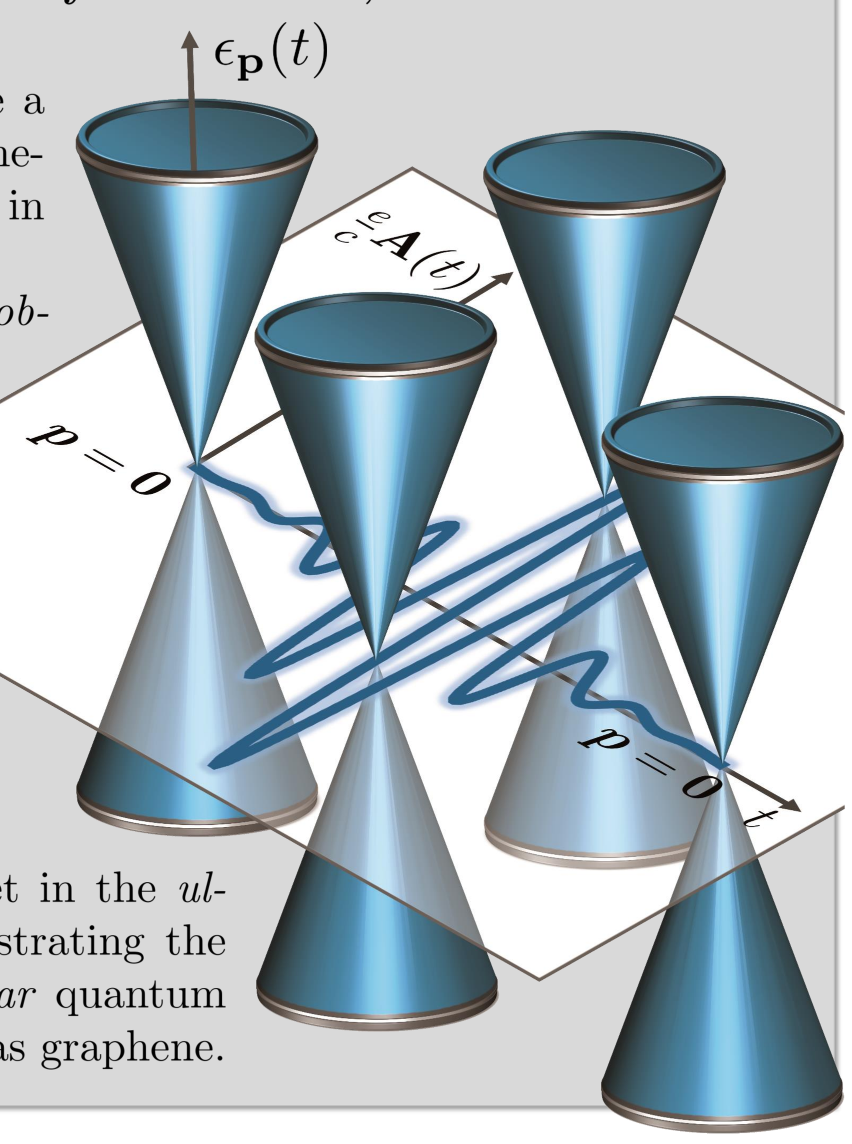
The *Semiconductor Bloch equations* (SBEs) are widely acknowledged as an excellent framework to study semiconductor optics [4,5] and have been extensively used to model light-matter interactions in graphene [6]. However, we theoretically demonstrate that the SBEs are an approximation of the DBEs and can be obtained once the dynamical role of the photon momentum is *neglected* [1].

2 Centrosymmetry Breaking Mechanism

Due to the centrosymmetry of graphenes honeycomb lattice, even-harmonic generation is expected to be absent [3].

However, unlike the SBEs, the DBEs encapsulate a symmetry breaking mechanism — the centrosymmetry $\mathbf{k} \to -\mathbf{k}$ and hence also $\mathbf{r} \to -\mathbf{r}$, respectively in momentum and direct space.

Graphically, the Dirac cones are *dynamically* and *globally* shaken by the time-dependent pulse momentum $(e/c)\mathbf{A}(t)$.

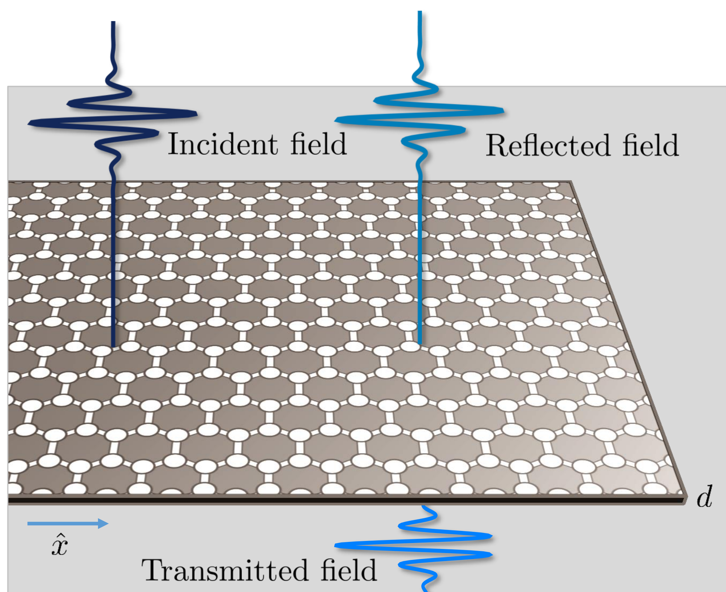


We prove this mechanism produces SHG waves that do not average out to zero after integration over the momenta.

With a Dirac-like spectum of energy gap E_g, we estimate the SBEs can be used for pulse intensities $I \ll I_{\mathrm{crit}} = \frac{1}{8}c\varepsilon_0 \left(E_g\omega_0/(ev_F)\right)^2$ and for pulse frequencies satisfying $\omega_0 t_0 < E_g/(4\hbar\omega_0)$.

These conditions can never be simultaneously met in the *ultrashort* and *intense* optical regime [1] — demonstrating the inadequacy of the SBEs in dealing with *nonlinear* quantum light-matter processes in ungapped systems, such as graphene.

3 Configuration Studied

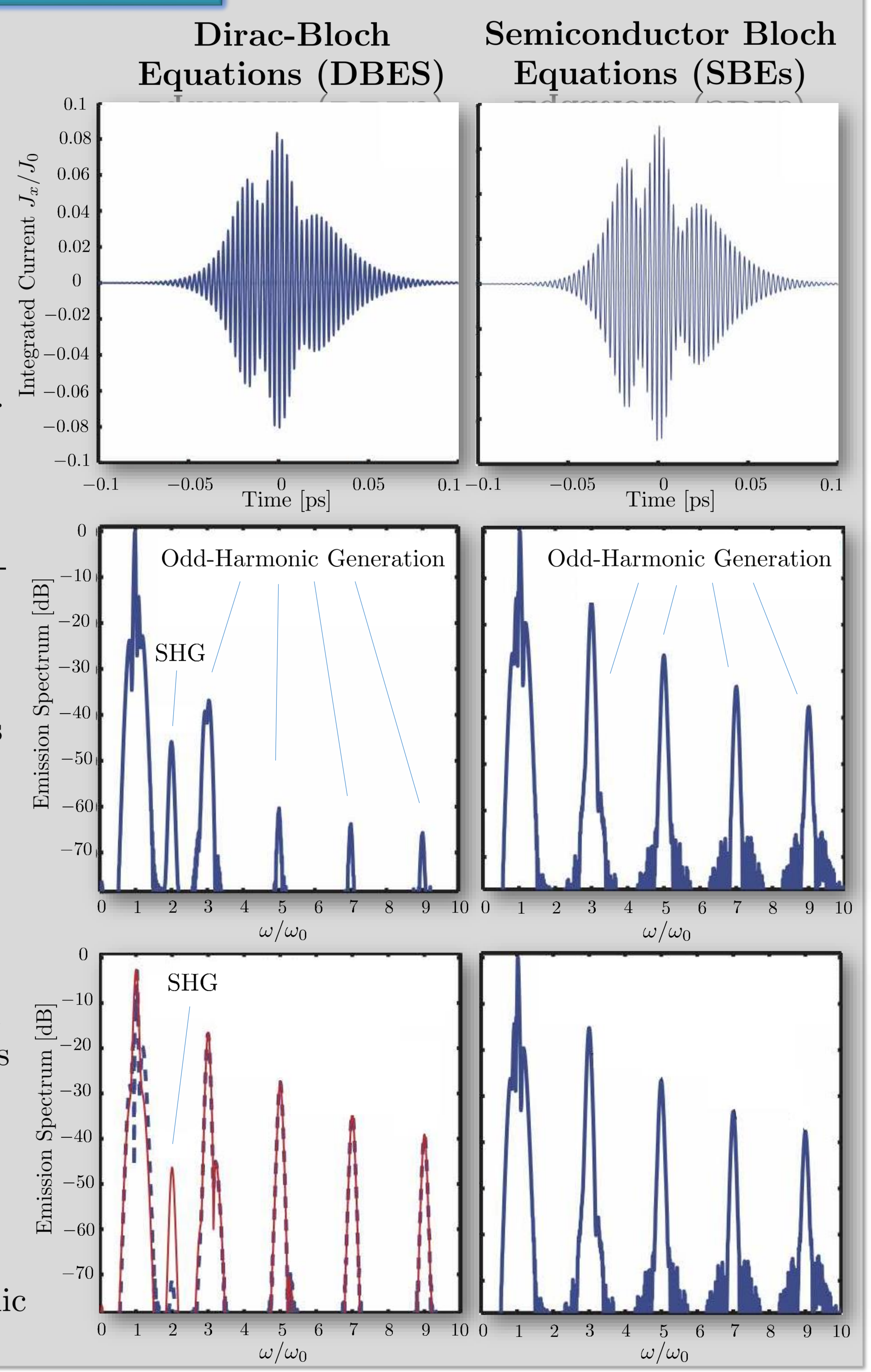


We consider a perfect, defect-free suspended layer of graphene when illuminated perpendicularly by a space-independent, temporally localised pulse with electromagnetic vector potential $\mathbf{A}(t)$ and electric field $\mathbf{E}(t) = -(1/c)\partial_t\mathbf{A}$, of central frequency $\omega_0 = 7.85$ MHz, wavelength $\lambda = 800$ nm, intensity $I = 114$ GW/cm^2 and duration $t_0 = 110$ fsec. The pulse is linearly polarised along an arbitrary direction $\hat{x}$ on the plane.

4 Numerical Implementation

The DBEs and SBEs for a specific momentum state were solved with an explicit, highly accurate, adaptive sixth-order Runge-Kutta algorithm, written in JULIA. In the coherent regime ($\gamma_1 = \gamma_2 = 0$), we use the probability conservation $|w_{\mathbf{k}}|^2 + 4|q_{\mathbf{k}}|^2 = |w_{\mathbf{k}}^0|^2$ to set a tolerance control. A total of 2000×300 momentum states were numerically integrated.

5 High Harmonic Generation



Total Integrated Current in time domain $\mathbf{J}(t)$

The study of the integrated current spectrum allows us to investigate nonlinear optical processes by analysing High Harmonic Generation. The current obtained by either the DBEs or the SBEs does not show substantial differences in time domain. However...

Total Integrated Current Spectrum $|\omega\tilde{\mathbf{J}}(\omega)|$

Once the total integrated current spectrum is obtained, it shows SHG only when obtained by using the DBEs. Furthermore, the SBEs overestimate higher odd-harmonic generation. This shortcoming of the SBEs makes them inadequate for probing nonlinear phenomena.

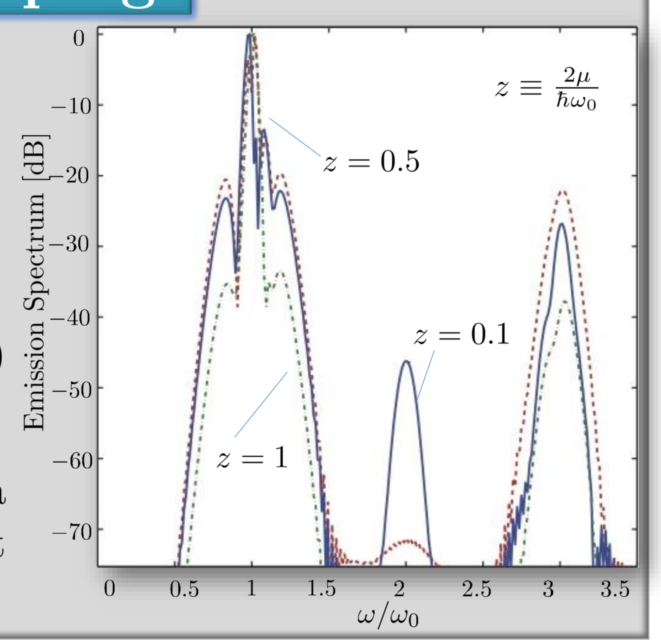
Intraband vs Interband Currents

By separating the intraband (red) and interband (blue, dashed) contributions to the integrated current obtained using the DBEs, one can verify that the SHG is a pulse-driven process, predominantly observed through the *intraband* current. Both currents seem to contribute equally for Odd-Harmonic Generation.

6 The Effect of Temperature and Doping

When undoped and at $T = 0$, the starting population is $w_{\mathbf{k}}^0 = -1$. For a general temperature T and Fermi level μ, the Fermi-Dirac distribution of holes and electrons allows the initial population inversion for a momentum state to be given by:

$$w_{\mathbf{k}}^0 = -\frac{\sinh\left(\frac{\hbar v_F |\mathbf{k}|}{k_B T}\right)}{\cosh\left(\frac{\hbar v_F |\mathbf{k}|}{k_B T}\right) + \cosh\left(\frac{\mu}{k_B T}\right)} \quad (6)$$



The total current spectrum obtained using the DBEs shows a *drastic* SHG supression for larger doping levels for a sample at room temperature ($T = 300$ °K).

7 Conclusions & Future Work

- Optical properties of condensed-matter systems described by relativistic quasiparticles cannot be investigated using the Semiconductor Bloch Equations when probed with intense and ultrashort pulses (in the nonlinear regime), ultimately failing to predict SHG.
- This SHG mechanism should *not* be confused with the Galvanic or Dynamical Photon Drag Effect [7].
- The same formalism will be applied to two-dimensional massive Dirac fermions; compounds such as transition-metal dichalcogenides (e.g. WSe_2, MoS_2) and phosphorene are reported to be well-represented by such a quasiparticle picture [8]

8 References

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