SCREENING AND THE EFFECTIVE FINE STRUCTURE CONSTANT IN GRAPHENE

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DISSERTATION
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Abstract

This thesis discusses two main topics – the effective fine-structure constant of and dielectric screening in graphene, and a new coherent inelastic x-ray scattering technique for attosecond resolution imaging of excitations in crystalline materials. The strength of electron-electron interactions in graphene is expected to be large due to the unusual dispersion relation of graphene’s electrons and its two-dimensional nature, but evidence of strong-correlation effects and non-Fermi liquid behavior remains limited. We describe a method to probe the strength of these interactions, characterized by an effective fine-structure constant $\alpha^*(q, \omega)$, as measured with inelastic x-ray scattering (IXS) on graphite. We show how to convert our experimentally obtained spectra, which are proportional to the imaginary part of the response function of graphite, to the full response function of graphene. We compare these results to calculated response functions in the random phase approximation (RPA) with and without interlayer hopping terms, and determine that interlayer hopping alone cannot be responsible for the observed deviations away from the RPA, due to a combination of both electron-hole interactions (excitonic effects) and additional screening from the higher energy bands. Lastly, we describe the theoretical framework for coherent inelastic x-ray scattering, a method to measure the response function for inhomogeneous media, where the off-diagonal elements of the response function are non-trivial. We use a simple model to assess the experimental feasibility of our proposed method, and show that for a perfect crystal, a full three-dimensional experimental geometry is sufficient to recover the off-diagonal response of highly inhomogeneous materials.
To my family, new and old.
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Chapter 1

Introduction

Understanding interacting systems of many particles presents one of the most fundamental challenges in physics; indeed, the competition between the kinetic energy and the energy of interactions leads to a diverse set of problems ranging from quantum chromodynamics (QCD) to high-temperature superconductivity to nuclear physics. One of the greatest advances in resolving this problem, Landau’s Fermi liquid theory allows us to draw a one-to-one correspondence between a many-body system of strongly-interacting particles and a collection of weakly-interacting quasiparticles. Consider first the case of a weakly- or non-interacting Fermi gas in its ground state, where the fermions fill successively higher-energy states in accordance with the Pauli exclusion principle, up to a maximum wave vector, or Fermi momentum, $k_F$ related to the electron density $n$. Landau realized that for sufficiently slow “switching on” of an interaction, the low-energy excited states of the new interacting system carry the same quantum numbers of the original weakly-interacting system, and so can be similarly described by the addition (removal) of quasiparticles with momentum $k > |k_F|$ ($k < |k_F|$) from a filled Fermi sphere of radius $k_F$, where $k_F$ is the Fermi momentum of the non-interacting system with the same electron density $n$. These low-lying quasiparticles are long-lived due to “Pauli blocking,” as near the surface of the Fermi sphere, the number of available states for a quasiparticle to scatter into are restricted to a shell of thickness $|k - k_F|$ due to the Pauli exclusion principle and the filled Fermi sea. For two- and three-dimensional systems, the scattering rate of these quasiparticles goes as $|k - k_F|^2$, and thus vanishes as $k \rightarrow k_F$. Similar to the original particles in the non-interacting system, these quasiparticles are still fermions, and they carry an effective mass $m^*$ which describes their self-energy.

Landau originally used Fermi liquid theory to describe the excitation spectrum of $^3$He, but it has also been tremendously successful at describing the behavior of electrons in metals. Typical metals exhibit free electron behavior, even though the Coulomb interaction energy between the bare electrons is large; however, the material is dynamically polarizable, in that the electrons collectively screen the Coulomb interaction, weakening the repulsion and rendering it effectively short-ranged. Indeed, in metals, the relevant particle to consider is not the bare electron with its bare mass $m$, but the quasiparticle formed by the
electron and the cloud of positive charge (reduced electron density) that surrounds, or “dresses,” it. The original electron then has a renormalized effective mass \( m^* \) that describes this composite particle.

The Fermi liquid description is a powerful tool in the study of interacting systems, but it too has limitations. One-dimensional systems of interacting fermions do not support an adiabatic “turning on” of the interaction due to the degeneracy of the non-interacting states, and thus form a class of non-Fermi liquids called Luttinger liquids. Strong local interactions can also lead to metal-insulator transitions, as in the case of Mott insulators. And in materials with sufficiently low electron density, there are insufficient free electrons to screen the Coulomb interaction. This low density situation is of particular interest. Recall that the kinetic energy of a particle of mass \( m \) and momentum \( k \) is given by 

\[ E_K = \frac{\hbar^2 k^2}{2m} \]

For a \( d \)-dimensional system with electron density \( n_d \), the average distance between particles goes as \( n_d^{1/d} \), and thus 

\[ E_K \approx 2\hbar^2 \pi^2 n_d^{2/d}/m. \]

The Coulomb interaction is given by 

\[ V(r) = \frac{e^2}{\epsilon_0 r}, \]

where \( e \) is the electron charge and \( \epsilon_0 \) is the dielectric constant of the medium, so the interaction energy of the particle is 

\[ E_C \approx e^2 n_d^{1/d}/\epsilon_0. \]

Thus, the strength of interaction, \( r_s \), for a typical metal is given by[6]

\[ r_s = \frac{E_K}{E_C} \propto \left( \frac{n_0}{n_d} \right)^{1/d}, \tag{1.1} \]

where the quantity \( n_0 = (me^2/\hbar^2 \epsilon_0)^d \) depends only on material properties. Thus, we are in the Fermi liquid regime only at high electron densities, \( n_d \gg n_0 \), where the kinetic energy of the particle dominates, and a host of non-Fermi liquid behavior can be found in the low density regime, including Wigner crystallization.

We now finally come to graphene, a 2D sheet of carbon and the primary topic of this thesis, where the situation is even more drastic. As we will show in the next section and Appendix A, the electrons in graphene disperse linearly and their kinetic energy is given by 

\[ E_K = \pm \hbar v_F k, \]

where the \( \pm \) indicate the conduction and valence bands at the Dirac points. The average kinetic energy of the electrons is then given 

\[ E_K \approx \hbar v_F n^{1/2}, \]

and the bare interaction strength in graphene, \( \alpha_G \), is given by

\[ \alpha_G = \frac{E_K}{E_C} = \frac{e^2}{\epsilon_0 \hbar v_F}, \tag{1.2} \]

which is now \textit{independent} of the electron density \( n \). Here, \( \epsilon_0 \) is again the dielectric constant, and describes the dielectric constant of its environment. Substituting in for the Fermi velocity of graphene, \( v_F \approx 10^6 \) m/s (300 times smaller than speed of light \( c \)), we get \( \alpha_G \approx 2 \), which clearly does not satisfy the Fermi liquid condition – indeed, at first glance it appears that graphene is intrinsically strongly-correlated system, regardless of doping! Moreover, the density of
states $\rho(E)$ of graphene also vanishes at the Dirac points, so one might assume that for pristine, undoped graphene, the lack of free electrons leads to an unscreened, long-ranged Coulomb interaction between electrons. $\alpha_G$ (or simply $\alpha$) is typically called the fine-structure constant of graphene, in contrast to the fine-structure constant of quantum electrodynamics, $\alpha_{\text{QED}} = \frac{e^2}{\bar{h}c} \approx \frac{1}{137}$, which is the measure of the Coulomb interaction in the vacuum. $\alpha_G$, of course, represents only the bare, unscreened value of the interaction strength, and it remains an open question how to proceed theoretically from the simple non-interacting picture to one that includes higher-order interaction terms when a perturbative expansion is not in principle possible. Our goal in this thesis is to tackle this question from an experimental standpoint, to directly probe the value of the effective interaction strength and compare it to standard theoretical predictions for the true $\alpha^*$ in graphene.

This rest of this thesis is organized as follows: Chapter 2 outlines the band structure of graphene, and discusses the current understanding of interaction effects in graphene. In Chapter 3 we describe the inelastic x-ray scattering experimental setup used to measure the fine-structure constant of graphene, as well as the details of the Lindhard function calculation we perform to model the effects of interlayer hopping in graphite vis-à-vis graphene. In Chapter 4 we outline the data analysis needed to extract a fine-structure constant from the measured density-density response function. We show that interlayer hopping effects indeed have a negligible effect, and that the source of the increased screening is a combination of contributions from the $\sigma$-bands and excitonic effects. Chapter 5 is not directly related to graphene, but is concerned with a modification of the standard IXS experiment called coherent inelastic x-ray scattering, which is designed to further refine our knowledge of the fast dynamics of crystalline system. Lastly, Appendix A and Appendix B contain more detailed descriptions of the band-structure calculation of graphene and graphite, respectively.
Chapter 2

Graphene Basics

2.1 Atomic and Band Structure

Graphene was not successfully isolated until 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester[7]; since then, graphene has been the subject of intense experimental and theoretical research[1], and Geim and Novoselov subsequently won the Nobel Prize in Physics in 2010. The archetypal Dirac-like system, graphene is an allotrope of carbon, and consists of a two-dimensional sheet of carbon atoms arranged in a honeycomb lattice consisting of two interspersing symmetrically inequivalent triangular lattices (see Fig. 2.1). The reciprocal lattice is also triangular, with a hexagonal Brillouin zone (BZ), where the two symmetry inequivalent corners of the first BZ are typically labeled $K$ and $K'$. Graphene’s bonding structure consists of three $\sigma$-bonds between $sp^2$ electrons and one $\pi$-bond between the $p_z$ electrons. Nearest-neighbor tight-binding calculation using only the $p_z$ electrons are detailed in Appendix A, and produce the well known band-structure pictured in Fig. 2.4 with dispersion[8]

$$
\epsilon(k) = \pm \sqrt{3 + 2 \cos(\sqrt{3}k_ya) + 4 \cos\left(\frac{3k_xa}{2}\right) \cos\left(\frac{\sqrt{3}k_ya}{2}\right)}. \quad (2.1)
$$

The conduction and valence bands are cone-shaped due to their linear dispersions near the corners of the Brillouin zone (see Fig. 2.4), and indeed,

![Figure 2.1: Atomic structure of graphene (left) and reciprocal lattice of graphene (right)][1]. Graphene’s lattice consists of two symmetry inequivalent triangular lattices interlocking to form a honeycomb lattice, with $\mathbf{a}_1$ and $\mathbf{a}_2$ the Bravais lattice vectors and $\mathbf{d}_{1,2,3}$ the nearest-neighbor lattice vectors. The reciprocal lattice is also triangular, with lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$. The two symmetry inequivalent corners, $K$ and $K'$, are called the Dirac points.
The hopping parameter as \( v_F / \hbar = 11015106 \text{ ms}^{-1} \) and \( t / \hbar = 110153 \text{ eV} \), respectively. Experimental observation of the emergence of massless Dirac quasiparticles in graphene.

It is worth noting that the density of states for graphene is constant and independent of energy, which arises due to the quantization of the momentum in the direction perpendicular to the tube axis. This situation, which occurs due to the 1D nature of their electronic spectrum, implies a constant cyclotron mass.

The density of states per unit cell, derived from Eq. (15) and the analytical expression for the density of states per unit area given by Eq. (20), is

\[
\rho(E) = \rho_0 \left( 1 - \frac{E}{E_0} \right)^{5/2}
\]

where

\[
E_0 = \frac{t}{2} E_{\hbar}\text{c}
\]

is the unit cell area given by

\[
A = \frac{4}{27} \pi \epsilon_0 \text{cm}^2
\]

and

\[
E_{\hbar}\text{c} = \frac{\hbar^2}{2m^*}
\]

is the energy at the Fermi level, \( \epsilon_0 \) is the energy gap, and \( m^* \) is the effective mass.

Due to this linear dispersion, the density of states for neutral graphene vanishes at the Dirac point (see Fig. 2.2), and so graphene is neither an insulator (it is gapless) nor is it a metal (it has no density of states at the Fermi energy); rather, it is a gapless semimetal. This peculiar situation suggests that interesting interaction effects may be in play—due to the lack of free electrons at neutral or light doping, graphene cannot in principle screen in the typical metallic way, and thus the electron-electron interaction can potentially lead to strong-correlation effects.

The situation in graphite is more complicated. The band structure of the \( p_z \) electrons in graphite was first calculated in 1947 by Wallace[8] using the...
in the usual case, first obtained by lattice. Left: energy spectrum around the Dirac point including substantially with energy. The expansion of the spectrum have Dirac points and where the plus sign applies to the upper broken and the $t_\perp$ = 0. For finite values of $t_\parallel/\hbar$, we show the full band structure of graphene with $k_\perp$ ± $\frac{q}{\sqrt{3}a}$, with a value close to the $F_0$ wall. Wallace, 1947

Figure 2.5: (a) (a-d) ARPES measurements of the electronic band structure for $k$ in the graphene plane as the number of graphene layers are increased from 1 to 4[11]. Images (e-h) show the same photoemission intensity as a function of $k_\perp$ and $k_\parallel$, and we see clearly that, as expected, for a single sheet of graphene (a), there is no dispersion in the direction perpendicular to the plane, but with additional layers the band quickly develops. (b) ARPES measurement of the band structure of graphite[10], where we see the parabolic dispersion (open circles) near the Fermi level and the formation of the pocket at the Fermi surface.

where $\gamma_1$ is the nearest-neighbor interlayer hopping potential (see App. B).

Instead of the bands meeting at a single point, an electron “pocket” forms at the Fermi surface as the low-energy quasiparticles change from massless Dirac fermions in graphene to massive quasiparticles in graphite with parabolic dispersion. This deformation can be observed in both few-layer graphene and graphite using ARPES[10, 11] (see Fig. 2.5).
2.2 Correlation Effects in Graphene

The presence of strong interactions in graphene has observable consequences. In the weak-coupling limit, electron-electron interactions are expected to produce a logarithmic renormalization of the Fermi velocity near the Dirac points[12–15].

If we take $\alpha_G$ and $v_F$ as the bare fine structure constant and the Fermi velocity, respectively, the renormalized values of $v_{FR}(q)$ and $\alpha_R(q)$ are given by[16, 17],

$$v_{FR}(q) = v_F \left[1 + \frac{\alpha}{4} \ln \left(\frac{\Lambda}{q}\right)\right], \quad (2.6)$$

$$\alpha_R(q) = \left(\frac{1}{\alpha} + \frac{1}{4} \ln \frac{\Lambda}{q}\right)^{-1}, \quad (2.7)$$

where $\Lambda$ is the high-momentum cutoff in the renormalization group approach. $\Lambda$ represents the length scale up to which the spectrum can be considered Dirac-like. Eq. 2.7 should produce logarithmically diverging bands near the Dirac points (see Fig. 2.7a), and as $v_F \to \infty$, $\alpha_R \to 0$, which suggests the weak-coupling approximation.

Though $\alpha_G \approx 2$ represents an intermediate-coupling scenario, there is extensive literature which treats the problem of interactions in the strong-coupling regime[18–34]. In particular, lattice Monte Carlo simulations have shown that in vacuum, at a critical value for the interaction strength of $\alpha_R = 1.11 \pm 0.06$, a gap spontaneously opens and graphene undergoes a semimetal-insulator transition[23]. These simulations used a linearized treatment of the Fermi velocity renormalization given by $v_{FR}/v_F = 1 + C\alpha_R$ (rather than a running logarithmic $v_{FR}$), which gives $V_{FR}/v_F \approx 3.3$ for the critical $\alpha_R = 1.11$.

As a 2D electronic system, graphene has also exhibited the integer quantum hall effect under a perpendicular magnetic field[35] at filling factors $\nu = \pm 2, \pm 6, \pm 10$, but at fields $B > 10$ T, fractional quantum hall states emerge at $\nu = 1/3$ and $2/3$[36]. The FQHE is a signature of electron-electron interactions emerging at sufficiently large $B$ such that the kinetic energy of the electrons is quenched. In the typical 2DEG case, the kinetic energy of the quasiparticles goes as $E_K \propto B$, whereas in the 2D Dirac system, $E_K \propto \sqrt{B}$[37]; the Coulomb energy, however, goes as $E_C \propto \sqrt{B}$ in both cases, so one expects the electron-electron interactions in graphene to be greatly enhanced at high fields. Indeed, experiments show that the FQHE persists in graphene at higher temperatures ($T > 10$ K) than in typical semiconductors, which suggests the presence of strong e-e interactions[36, 38–40].

2.3 Screening in Graphene

In real systems, particles interact not by the bare Coulomb interaction $U_0(q)$ but by an effective Coulomb interaction $U(q,\omega)$, with the dielectric function
\( \epsilon(q, \omega) \) relating the two\[6\],
\[
\epsilon(q, \omega) = \frac{U_0(q)}{U(q, \omega)}.
\] (2.8)

The interaction \( U(q, \omega) \) satisfies the Dyson equation
\[
U(q, \omega) = \frac{U_0(q)}{1 - \Pi(q, \omega)U_0(q)}
\] (2.9)

where \( \Pi(q, \omega) \) is the polarization of the medium (see App. B). Combining these two equations, we see that
\[
\epsilon(q, \omega) = 1 - U_0(q)\Pi(q, \omega).
\] (2.10)

In the random-phase approximation (RPA), we use the ring diagram approximation to \( \Pi(q, \omega) \) to compute the dielectric function. In the idealized, non-interacting case for Dirac fermions i.e. linearly dispersing bands that extend to infinity, the expression for the polarization of graphene is
\[
\Pi(q, \omega) = -\frac{q^2}{4\sqrt{(\hbar v_F q)^2 - \omega^2}}.
\] (2.11)

For \( q \to 0 \), Eq. 2.11 is a reasonable approximation, but in Sec. 3.8 we go beyond this approximation and compute \( \Pi(q, \omega) \) using the full \( \pi \)-band description that takes into account the crystal structure.

We can now write the screened \( \alpha(q, \omega) \) from Eq. 1.2 as an effective fine-structure constant \( \alpha^*(q, \omega) \) as
\[
\alpha^*(q, \omega) = \frac{\alpha(q, \omega)}{\epsilon(q, \omega)} = \frac{\epsilon^2}{\epsilon(q, \omega)\hbar v_F},
\] (2.12)

where the intrinsic polarizability of graphene acts as the dielectric function of its environment. Already, it is clear that this effective \( \alpha^* \) is not a universal measure of the strength of interactions in graphene, but rather in principle depends on momentum and energy. In particular, for transport measurements, it is the static, low-momentum value of \( \alpha^* \) that is important, so we should be interested in the asymptotic behavior of \( \alpha^* \) for \( q \to 0 \) and \( \omega \to 0 \).

The density-density response function \( \chi \) for a 2D medium is given by the Feynman integral
\[
\chi(x_1, x_2, t_1, t_2) = \Pi(x_1, x_2, t_1, t_2) + \int d^2x_3 d^2x_4 dt_3 dt_4 \Pi(x_1, x_3, t_1, t_3) V(x_3, x_4, t_3, t_4) \chi(x_4, x_2, t_4, t_2),
\] (2.13)
which, for a homogeneous medium, can be simplified significantly to

$$\chi(q, \omega) = \frac{\Pi(q, \omega)}{1 - U_0(q)\Pi(q, \omega)}. \quad (2.14)$$

From now on we will refer to the bare interaction $U_0(q)$ simply as $V(q)$. Combining this expression with our previous expression for the dielectric function, we can easily see that

$$\alpha^*(q, \omega) = \frac{\alpha}{\epsilon(q, \omega)} = \alpha [1 + V(q)\chi(q, \omega)]. \quad (2.15)$$

Eq. 2.15 is most useful since, as we will show in Sec. 3.1, the quantity $\chi(q, \omega)$ is directly measurable in a scattering experiment, whereas $\epsilon(q, \omega)$ is not.

Indeed, in an inelastic x-ray scattering experiment performed on graphite by Reed et al.[5], direct measurements of $\chi(q, \omega)$ of graphene in the momentum range $0.238 \text{Å}^{-1} < q < 7.88 \text{Å}^{-1}$ and energy range $-3 \text{eV} < \hbar\omega < 200 \text{eV}$ revealed that screening in graphene is not as small as previously predicted. A contour plot of the magnitude of $\alpha^*$ can be seen in Fig. 2.6a. [5] also found that their measured $\Pi(q) \propto q$ for $q \to 0$ as expected, and were able to extrapolate to find that $\lim_{q \to 0} \alpha^*(q, \omega) = 0.14 \pm 0.092 \approx 1/7$, which corresponds to a static dielectric constant of $\epsilon(0^+, 0) = 15.4^{+39.56}_{-6.45}$.

The observed screening is substantially larger than that of the bare $\alpha$, but what is the source of this enhanced screening? One possibility is the presence of the higher energy $\sigma$-bands, but the $\sigma$-bands are short-ranged, so their contribution to the screening should disappear asymptotically with $q \to 0$. Interestingly, though, [5] also observed a redshift in the spectral weight of both the $\chi$ and $\Pi$ functions of graphene with respect to the idealized Dirac fermion $\chi$ and $\Pi$ functions, as can be seen in Fig. 2.6b. Redshifts of spectral weight are typically associated with so-called “excitonic effects,” which we discuss in detail later in Sec. 3.9. Essentially, excitonic effects arise when electron-hole pairs spontaneously form from the filled Fermi sea, and their binding energy can renormalize the bands to lower energy. Although graphene does not form true bound electron-hole pairs (excitons), the attractive interaction between the electron and hole could be sufficient to account for the redshift in Fig. 2.6b. Unfortunately, the data in Fig. 2.6b leaves something to be desired – the energy resolution is 0.5 eV, and the observed shifts are $\approx 0.6 \text{eV}$, a similar redshift to the excitonic effects seen in calculated optical response function using the GW-Bethe Salpeter equation approach[41]. The experiment in [5] also had difficulty providing accurate measurements at low momentum values; indeed, the two momentum values in Fig. 2.6b are the two lowest measured, but the $q \to 0$ behavior of $\alpha^*$ and $\chi$ is the relevant quantity. Clearly, to truly understand the strength of interactions in graphene, we needed to develop a modified experimental setup optimized for low-momentum transfer signals.
Figure 2.6: (a): (A) Contour map of $|\alpha^*(q,\omega)|$ as a function of energy $E$ and momentum $q$. The white line indicates $E = \hbar q v_F$, the nominal dispersion for electrons in graphene; $\alpha^*$ is larger above the line than below. (B) The phase of $\alpha^*(veq,\omega)$ given in radians. (b): (A) Comparison of measured $\text{Im} \chi(q,\omega)$ to calculated values for infinitely linearly dispersing $\pi$ bands. (B) Comparison of measured $\text{Im} \Pi(q,\omega)$ to calculated values for infinitely linearly dispersing $\pi$ bands.
2.4 Recent Work

Since our original paper on the effective fine-structure constant of graphene, there has been substantial new theoretical and experimental work on the subject. In 2011, Yuan et al.[42] used the full π-band structure rather than just linearly dispersing bands extending to infinity, and performed RPA calculations with the π-bands to compute the polarization function of pure, single layer graphene. They performed this calculation in two ways, first with the Lindhard formula, and then with the use of the Kubo formula and a polynomial expansion of the time-evolution operator. Their results for graphene show good agreement between the $|\alpha^*(q,0)|$ using the full π-band RPA polarization function and the $|\alpha^*(q,0)|$ of the infinite linearly-dispersing band polarization function, with $|\alpha^*(q = 0.1,0)| \approx 0.63$ at the lowest momenta they computed. However, they also considered the case of graphite, and compute the RPA polarization function of graphite including the nearest neighbor interlayer hopping parameters $\gamma_1$ and $\gamma_3$ using the Kubo formula approach, and determined that $|\alpha^*| \approx 0.3$ after including those two hopping parameters and the screening effects of higher order bands using an effective background dielectric constant $\kappa(q)$. This led us to reconsider the role of interlayer hopping, which we had considered to be negligible compared to the effect of both the intralayer hopping parameter $t$ and the Coulomb interaction between layers. Could we simply be seeing a graphitic effect that would not be present in pure graphene?

There were, however, two problems apparent in [42]. First, the $|\alpha^*|$ reported for graphite in [42] is the screened fine-structure constant of the full three-dimensional graphite system, and not the fine-structure constant of a two-dimensional sheet of graphene embedded in a graphitic environment. Second, the expression used for the dielectric function of the system is not correct; in particular, Yuan et al. do not incorporate the screening contribution from the higher-order $\sigma$-bands in the appropriate way. These deficiencies in their calculation motivated us to perform our own RPA calculation. A more detailed discussion of [42] and our RPA calculation can be found in Sec. 3.8.

Experimental studies performed on graphene on various substrates reported values of the graphene fine structure constant of 0.9 and 0.61 for boron-nitride (BN) substrates[43, 44], 0.35 for a SiC(000-1) substrate[44], and 1.43 for a quartz substrate[44]. Clearly the dielectric environment of graphene plays an important role in its screening properties, and indeed, a beyond-RPA calculation of the $\alpha$ which included a first-order interaction correction to the polarization of order $O(\alpha)$ determined the static dielectric function of graphene to be of the form[17]

$$
\epsilon(q,0) = 1 + \frac{\pi}{2} \alpha_q + 0.778 \alpha_q^2, \quad \alpha_q \ll 1, \quad (2.16)
$$

where $\alpha_q$ is the renormalized value of $\alpha$, and is determined by the observable phase velocity of the quasiparticles, which of course includes details of the
background dielectric environment. In this framework, [17] well reproduces the experimental result in [43] when taking into account the BN substrate, but it also predicts a value of $\epsilon \approx 8.2$ for an unrenormalized value of $\alpha_q = 2.2$, which is trending towards our original result of $\epsilon = 15.4$ and suggests that we are indeed measuring an intrinsic value of graphene independent of its substrate (though Eq. 2.16 may break down for $\alpha_q$ so large). Eq. 2.16 implies that RPA may not be sufficient to capture the full screening interaction in graphene, and further motivated us to better understand its static, long-ranged dielectric function.

Measurements of the Fermi velocity through Shubnikov-de Haas oscillations (SdHO) seem to suggest a logarithmic renormalization of the Dirac bands, a hallmark of strong-correlation effects[45]. These experiments were performed on suspended graphene, and directly measured the cyclotron mass of the electrons $m_e$, which is related to the Fermi velocity by $v_F = \hbar (\pi n)^{\frac{1}{2}} / m_e$. As can be seen in Fig. 2.7b, there is a deviation away from the standard value of $v_F$, though possible linear fits are also presented. Indeed, the results in [45] are close to the value of linearized $v_{FR}/v_F \approx 3.3$ calculated in [23], which predicts gap generation. [45] shows that any gap must be $< 0.1$ meV, but does not preclude the existence of one. Zero-magnetic-field quantum capacitance measurements[46] and scanning tunneling spectroscopy[47] have produced similar evidence of logarithmically renormalized bands.

A detailed theoretical study of beyond-RPA effects in graphene[48] showed that for $\alpha < 0.78$, the weak-coupling approximation holds and the perturbative series is well-behaved up to two-loop corrections ($O(\alpha^2)$), with $O(\ln^2)$ terms emerging in the three-loop order in the undoped situation at the Dirac point. [48] notes that although there is good qualitative agreement between RPA in the
dynamically screened interaction and experiment, it is not clear why the RPA is justified given the unknown asymptotic convergence of the series. Additionally, real graphene samples are all doped, and even at low carrier density, disorder effects could be substantial.
Chapter 3

Experiment

3.1 IXS Measurement Theory

In order to measure the screening contribution to the fine-structure constant, we must first measure $\text{Im} \chi(q, \omega)$, the imaginary part of the density-density response function. Our experimental method to do so, inelastic x-ray scattering, involves a one photon in/one photon out scattering process. We can express the initial state of the composite photon-electron system then as $\vert i \rangle = a_{k_i \alpha i}^\dagger \vert m \rangle$ and the final state as $\vert f \rangle = a_{k_f \alpha f}^\dagger \vert n \rangle$, where the states $\vert m \rangle$ and $\vert n \rangle$ are the initial and final many-body electron states, respectively, and the operators $a_{k_i \alpha i}^\dagger$ and $a_{k_f \alpha f}^\dagger$ create the incoming and outgoing photon states, respectively, with momentum $k_i/f$ and polarization $\epsilon_{\alpha i}/\epsilon_{\alpha f}$. The doubly differential cross section associated with this process is

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{1}{\Phi} \frac{\partial^2 N}{\partial \Omega \partial E} = \left( \frac{e^2}{mc^2} \right)^2 \sum_{n,m} b_m \vert \langle n \vert \rho(q) \vert m \rangle \vert^2 \times \delta(E - E_n + E_m),$$

(3.1)

where $\partial^2 N/\partial \Omega \partial E$ is the density of final states and $\Phi$ is the incident flux. Here, $q = k_i - k_f$, the momentum transferred into the sample, and, similarly, $E = \hbar \omega = E_i - E_f$ is the energy transferred into the sample. The summation in Eq. 3.1 is called the dynamic structure factor,

$$S(q, \omega) = \sum_{n,m} b_m \vert \langle n \vert \rho(q) \vert m \rangle \vert^2 \times \delta(\hbar \omega - E_n + E_m),$$

(3.2)

where we sum over the final states and the initial states weighted by a thermal distribution factor,

$$b_m = e^{-\beta E_m} Z,$$

(3.3)

where $Z$ is the canonical partition function. The density operator $\rho(q)$ is given by the standard definition, $\rho(q) = \sum_i e^{-iq \cdot \mathbf{r}_i}$, with the sum over all lattice vectors. An IXS measurement produces spectra that are proportional to $S(q, \omega)$.

In particular, we are interested in the relation of $S(q, \omega)$ to the intrinsic charge response of the sample. The density-density response function captures
the charge response behavior to linear order,

$$\chi(x_1, x_2, t_1, t_2) = -\frac{i}{\hbar} \sum_m \langle m| [\rho(x_1, t_1), \rho(x_2, t_2)] |m\rangle \theta(t_1 - t_2). \quad (3.4)$$

Here, \(\theta(t)\) is the Heaviside step function. We assume translational invariance in time, taking \(\tau = t_1 - t_2\), and Fourier transform \(\chi\) into frequency space first

$$\chi(x_1, x_2, \omega) = -\frac{1}{2\pi\hbar} \int d\tau \int d\omega' \frac{e^{i(\omega+\omega')\tau}}{\omega' - i\eta} \left( \langle m| \rho(x_1, \tau) \rho(x_2, 0) |m\rangle - \langle g| \rho(x_2, 0) \rho(x_1, \tau) |g\rangle \right) \quad (3.5)$$

for positive infinitesimal \(\eta\), where we have used the identity

$$\theta(t) = \lim_{\eta \to 0^+} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega \frac{1}{\omega - i\eta} e^{i\omega t}. \quad (3.6)$$

Here \(\omega = \omega_1 - \omega_2\) and \(|g\rangle\) is the electron ground state. We insert a complete set of states into the dynamical structure factor term

$$\sum_n \langle m| \rho(x_1, \tau) |n\rangle \langle n| \rho(x_2, 0) |m\rangle. \quad (3.7)$$

So, we have

$$\chi(x_1, x_2, \omega)$$

$$= -\frac{1}{2\pi\hbar} \int d\tau \int d\omega' \frac{e^{i(\omega+\omega')\tau}}{\omega' - i\eta} \sum_k \left( \langle g| e^{i\frac{\omega_1}{\hbar}\tau} \rho(x_1) e^{-i\frac{\omega_2}{\hbar}\tau} |k\rangle \langle k| \rho(x_2) |g\rangle - \langle g| \rho(x_2) |k\rangle \langle k| \rho(x_1) |g\rangle \right)$$

$$= -\frac{1}{2\pi\hbar} \int d\tau \int d\omega' \frac{e^{i(\omega+\omega')\tau}}{\omega' - i\eta} \sum_k \left( e^{-i\omega_2\tau} \langle g| \rho(x_1) |k\rangle \langle k| \rho(x_2) |g\rangle - e^{i\omega_1\tau} \langle g| \rho(x_2) |k\rangle \langle k| \rho(x_1) |g\rangle \right)$$

$$= -\frac{1}{\hbar} \int d\omega' \frac{1}{\omega' - i\eta} \sum_k \left( \delta(\omega + \omega' - \omega_k) \langle g| \rho(x_1) |k\rangle \langle k| \rho(x_2) |g\rangle - \delta(\omega + \omega' + \omega_k) \langle g| \rho(x_2) |k\rangle \langle k| \rho(x_1) |g\rangle \right)$$

$$= -\frac{1}{\hbar} \left[ \sum_k \langle g| \rho(x_1) |k\rangle \langle k| \rho(x_2) |g\rangle \frac{1}{\omega - \omega_k - i\eta} - \sum_k \langle g| \rho(x_2) |k\rangle \langle k| \rho(x_1) |g\rangle \frac{1}{\omega + \omega_k - i\eta} \right] \quad (3.8)$$

If we assume a homogeneous medium i.e. translational invariance in position space, then the numerators in Eq. 3.8 reduce to \(\langle m| \rho(q) |n\rangle \langle n| \rho(-q) |m\rangle = |\langle m| \rho(q) |n\rangle|^2\). Using the identity

$$\lim_{\eta \to 0^+} \frac{1}{x \pm i\eta} = P \left( \frac{1}{x} \right) \mp i\pi\delta(x), \quad (3.9)$$

where \(P\) is the principal part integral, the imaginary part of Eq. 3.8 can be
simplified as

\[
\text{Im} \chi(x_1, x_2, \omega) = -\frac{\pi}{\hbar} \left[ \sum_k \langle g | \rho(x_1) | k \rangle \langle k | \rho(x_2) | g \rangle \delta(\omega - \omega_k) \\
- \sum_k \langle g | \rho(x_2) | k \rangle \langle k | \rho(x_1) | g \rangle \delta(\omega + \omega_k) \right].
\] (3.10)

This looks very similar to dynamic structure factor in Eq. 3.2. We need simply note from Eq. 3.2 that

\[
S(-q, \omega) = S(q, \omega) = e^{\beta \hbar \omega} S(q, -\omega),
\] (3.11)

which is an expression of the principle of detailed balance, and can substitute into Eq. 3.10 to recover the quantum mechanical version of the fluctuation dissipation theorem,

\[
S(q, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\beta \hbar \omega}} \text{Im} \chi(q, \omega).
\] (3.12)

Indeed, Eq. 3.12 allows us to relate our measured spectra to the density-density response of graphite. We describe the methods we use to normalize the data on an absolute scale, as well as how to convert our graphite spectra to graphene spectra, in more detail in Chapter 4.

### 3.2 From graphite to graphene

We perform our experiments on graphite, so it is necessary to convert our measured \( \chi_{3D}(q, \omega) \) to \( \chi_{2D}(q, \omega) \) for graphene. To do this, we start from three assumptions:

1. The graphene layers in graphite are infinitely thin, and we have infinitely many layers arranged periodically along the c-axis.
2. The electrons in the graphene layers are distributed homogeneously, thus rendering each layer identical.
3. The graphene layers in graphite interact only via the Coulomb interaction (there is no tight-binding hopping potential between them)

Assumptions 1 and 2 are clearly satisfied, as graphene is atomically thin, and we have already assumed a homogeneous medium in the fluctuation-dissipation theorem (Eq. 3.12). Assumption 3 essentially implies that the energy-scale of the interlayer hopping potential in graphite is significantly smaller than the energy scale of the Coulomb interaction between layers. We will see later that this is a reasonable approximation as well; for now, we shall proceed with the derivation to go from the 3D response of graphite to the 2D response of graphene.
Armed with these assumptions, we begin by expressing the response function of graphene in position space in terms of the polarization function. From Eq. 3.9, it is easy to see that in momentum space, we can write the following Dyson equation for the response:

\[
\chi_{2D}(q, \omega) = \frac{\Pi_{2D}(q, \omega)}{1 - V_{2D}(q)\Pi_{2D}(q, \omega)}.
\] (3.13)

Here, \(q\) refers to the momentum in the graphene planes. Note here that though this looks the RPA form of the \(\chi\)-function, we have not assumed that the \(\Pi\)-function here is the non-interacting one – indeed, the \(\Pi\)-function used here includes all possible polarization bubbles. The situation for graphite is more complicated. Because we do not have a homogeneous medium in the \(z\)-direction (along the \(c\)-axis), we start from the Feynman integral in position space:

\[
\chi(x_1, x_2, t_1, t_2) = \Pi(x_1, x_2, t_1, t_2) + \int d^3x_3 d^3x_4 dt_3 dt_4 \Pi(x_1, x_3, t_1, t_3) V(x_3, x_4, t_4) \chi(x_4, x_2, t_4, t_2).
\] (3.14)

Taking the second assumption of translational variance in the \(x-y\) plane, we can fourier transform \(x = x_1 - x_2\), and right the Coulomb interaction in a mixed representation as

\[
V(k, z_1, z_2) = \frac{2\pi e^2}{q^2} f(k, z_1, z_2),
\] (3.15)

\[
f(k, z_1, z_2) = e^{-k|z_1 - z_2|},
\] (3.16)

Taking the first assumption of \(\delta\)-localization of the electrons into the layers, the response function in momentum- and frequency-space must have the form

\[
\chi(k, z_1, z_2, \omega) = \sum_{l_1, l_2} \chi(k, l_1, l_2) \delta(z_1 - l_1d) \delta(z_2 - l_2d),
\] (3.17)

where the \(l_1, l_2\) indices run over the number of layers. The polarization function \(\Pi\) must then also have the same functional form:

\[
\Pi(k, z_1, z_2, \omega) = \sum_{l_1, l_2} \Pi(k, l_1, l_2) \delta(z_1 - l_1d) \delta(z_2 - l_2d).
\] (3.18)

We can use the form in Eq. 3.14 and write, suppressing the \(\omega\) dependence,

\[
\sum_{l_1, l_2} \delta(z_1 - l_1d) \delta(z_2 - l_2d) \chi(k, l_1, l_2) = \sum_{l_1, l_2} \delta(z_1 - l_1d) \delta(z_2 - l_2d) \left[ \Pi(k) \delta_{l_1, l_2} + \frac{2\pi e^2}{k} \Pi(k) \sum_{l_4} f(k, l_1d, l_4d) \chi(k, l_4, l_2) \right],
\] (3.19)
which simplifies to (suppressing the $k$’s and the $d$’s in the potential)

$$\chi(l_1, l_2) = \Pi \delta_{l_1, l_2} + \frac{2 \pi e^2}{k} \sum_{l'} f(l_1, l') \chi(l', l_2).$$

(3.20)

For a system with infinitely many layers, we can change variables to $\chi(l) = \chi(l_1 - l_2)$ and $\Pi(l) = \Pi(l_1 - l_2)$, and define the following transform

$$\chi(q_z) = \sum_l e^{i q_z l d} \chi(l), \quad \chi(l) = \frac{d}{2 \pi} \int_{-\pi/d}^{\pi/d} dq_z \chi(q_z) e^{-i q_z l d},$$

(3.21)

we can simplify Eq. 3.20 to a closed form, and replace the appropriate $k$’s and $\omega$’s:

$$\chi(q_z) = \Pi^0 + \Pi^0 \frac{2 \pi e^2}{k} \left[ e^{i q_z d - |l| k d} \right] \chi(q_z)
= \Pi^0 + \Pi^0 \frac{2 \pi e^2}{k} \chi(q_z) \frac{\sinh(kd)}{\cosh(kd) - \cos(q_z d)}
\Rightarrow \chi_{3D}(k, q_z) = \frac{\Pi_{3D}(k, q_z)}{1 - V_{2D}(k) F(k) \Pi_{3D}(k, q_z)},$$

(3.22)

where

$$F(k) = \frac{\sinh(kd)}{\cosh(kd) - \cos(q_z d)}$$

(3.23)

essentially describes how the 2D coulomb interaction can be generalized to a 3D interaction for a layered electron gas.

The last step is recognizing that Eq. 3.18 tells us how to relate $\Pi_{3D}(k, \omega)$ to $\Pi_{2D}(k, \omega)$. Indeed, changing variables to $l = l_1 - l_2$ is equivalent to integrating out one of the $\delta$-functions in Eq. 3.18, but we still have one more $\delta$-function. A straightforward simplification yields a simple relationship between the 3D and 2D polarization functions:

$$\Pi_{3D}(k, \omega) = \frac{\Pi_{2D}(k, \omega)}{d},$$

(3.24)

where, again, $k$ is the in-plane momenta. Eq. 3.24 follows directly from our three assumptions, and is thus technically true only in the limit that the layers are coupled only via the Coulomb interaction. We will in later sections refer to $\Pi_{2D}$ for a graphitic system including interlayer hopping terms and use Eq. 3.24 to approximate this quantity, but it should be understood that it is not entirely accurate.

Combining Eq. 3.24 and Eq. 3.22, we arrive at a conversion formula between our measured $\chi_{3D}(k, \omega)$ and the desired quantity, $\chi_{2D}(q, \omega)$ for graphene,

$$\chi_{2D}(q, \omega) = \frac{\chi_{3D}(q, \omega) d}{1 - V_{2D}(q) [1 - F(q, 0)] \chi_{3D}(q, \omega)}.$$

(3.25)
where $q_k$ is the momentum parallel to the Basal plane and $q_z$, the out-of-plane momentum, is set to zero.

We apply this formula using a scaling fit parameter, $\kappa$, to electron energy loss spectroscopy (EELS) data taken by Eberlein, et al. in 2008 [69] on graphite and a single layer of graphene. We applied our conversion formula on the unscaled graphite data and minimized with respect to the fit parameter, $\kappa$, to produce the 2D data shown in blue circles. The converted and measured data on graphene are very close to each other.

As a test, we apply this formula to data acquired from electron energy-loss spectroscopy (EELS) experiments on both graphite and freestanding graphene [3]. EELS measures the dielectric loss function of an electronic medium, which is equivalent to the density-density response function, so we are free to apply our conversion formula. Fig. 3.1 shows an EELS spectrum taken on graphite, which we then convert to the response of graphene using Eq. 3.25, and observe that the conversion reproduces the experimental 2D response at the same momentum transfer.

3.3 Sample Preparation

Experiments were performed on both 1-mm-thick high quality ZYA-grade highly-ordered pyrolytic graphite (HOPG) and “single-crystal” graphite. HOPG is not a true crystal – it is very well-ordered along the $c$-axis, perpendicular to the graphene planes, but the relative angular orientation between planes is not well specified. This, however, does not impact our results; indeed, within the approximation of homogeneously distributed electrons within the planes, the plane-to-plane angular orientation is unimportant. As a further test of this approximation, single-crystal natural graphite sample were obtained from John Jaczsyk’s group at Michigan Institute of Technology. Ultimately, the spectra taken from both the HOPG and single-crystal samples were not noticeably different.

Our HOPG samples are large enough to be mounted directly on metal posts using superglue, as shown in Fig. 3.2a. Because we perform our experiments with an incident photon energy of 7.81 keV, which corresponds to an attenuation length of $\approx 1$ mm in carbon, we first make sure our HOPG samples have the correct thickness within 10 $\mu$m, and use Scotch tape to mechanically exfoliate.
Figure 3.2: (a) HOPG sample (left) and LiF reference sample mounted in tantalum foil (right). (b) and (c), upstream and downstream views of the sample holder for the graphene flakes, respectively.

extra layers as needed. The single-crystal graphite flakes are too small (with diameters ranging from 3–5 mm) and too thin (≈ 60 mm) to be mounted directly onto posts, so we designed a brass mounting chamber which allows us to securely hold a ≈ 1 mm stack of these flakes. As can be seen in Figs. 3.2c and 3.2b, the graphite flakes are placed in the mounting well, followed by a small O-ring, followed by a top plate, the last of which is screwed down until it slightly compresses the O-ring, holding the flakes in place. The flakes are placed in random planar orientations in the mounting chamber, but as we will see in Sec. 3.2, the relative angular orientation of the flakes to each other is of no importance within the approximations used in the experiment. The mounting chamber has a 3 mm aperture to allow for x-ray transmission.

3.4 Experimental setup

Our experiments were carried out at Sector 9 of the Advanced Photon Source at Argonne National Laboratory. A simple schematic of the beamline from x-ray production to detector is shown in Fig. 3.3. X-rays are produced when 7.9 GeV electrons are steered from the storage ring into the alternating magnetic field field of two sequentially arranged undulators, which are tuned to maximize x-ray production at our specific energy of 7.81 keV. Nevertheless, the energy profile of these initial x-ray photons, called the “white beam,” is too broad for inelastic x-ray scattering operation, and are passed through a primary monochromator, which consists of a two-bounce Si(111) crystal assembly mounted on a Kohzu rotation stage. The primary monochromator is kept under UHV, and cooled continuously by an Oxford cryopump. Because we used two undulators, essentially doubling the power deposited on the primary monochromator, additional care needed to be taken to ensure the system was thermally stable throughout the course of a beamrun.

To further monochromatize the beam, the x-rays are passed through a sec-
ondary monochromator, which is a Si(444) channel cut crystal mounted on a stepper motor stage. The beam is then passed through a set of focussing mirrors (one horizontal and one vertical) which reduce the angular divergence. Next, the beam passes through a pair of ion chambers which measure the beam position,
Figure 3.3: (a) Schematic of x-ray beamline. (b) Diagram of 2m arm[49]. (c) A typical Ge(733) diced and bent analyzer (actual analyzer used was Si(444)).

which is fed back to the piezoelectric motor on the primary monochromator to maintain a consistent beam position.

Once inside the experimental hutch, the beam enters another pair of ion chambers, which record the beam position right before it enters the last vacuum beam pipe and into the sample chamber. The sample chamber is a sealed, cylindrical container with an entrance for the incident x-rays and a Kapton window for scattered photons. The chamber is mounted around the sample such that the scattering point is near the axis of symmetry of the chamber, and a motorized arm with a beamstop attachment can be rotated about this same axis. The beamstop is a stainless steel blade with lead tape (see Fig. 3.6), and is used to absorb the transmitted direct beam before it can scatter downstream of the sample. The full assembly is secured to the diffractometer using standard optical post assemblies.

Once the x-rays scatter off the sample, they exit the sample chamber and enter a helium-filled flight path attached to the 2θ arm of the diffractometer. The scattered photons then reflect off of the Si(444) analyzer at the end of the helium flight path, and backscatter into the Mythen strip detector below the sample chamber. Almost the entire assembly is under rough or ultra high vacuum, reducing the amount of scattering both upstream and downstream of the sample, which is essential to limiting the extent of the quasielastic peak’s tails.
3.5 Optics Selection and Resolution

Before we proceed, it is important to explain why we have chosen this specific combination of incident energy, secondary monochromator, and analyzer. As discussed earlier in Sec. 2.3, the region of interest is the low-momentum, low-energy region, and thus we must be able to subtract the quasielastic background as confidently as possible in the few eV region, which involves both reducing the intensity of the quasielastic background relative to the sample signal and also controlling its lineshape. We can deal with the former by improving the FWHM of the incident beam, which will reduce the intensity of the tails; however, the IXS scattering cross-section is very small compared to the elastic cross section, so there is also a great need to increase the total number of incoming photons. As mentioned in Sec. 3.4, we use two undulators to effectively double our incident counts, but the cooling power of the primary monochromator’s cryopump is such that we must operate above ≈ 7 keV to maintain thermal stability. We must also make sure that the energy resolution of our setup is sufficient to distinguish the features we want to see, and the energy resolution is essentially given by the intrinsic energy resolution of the analyzer. Ideally, this energy resolution is well-matched to the FWHM of the incoming beam, so that we are not “throwing away” counts outside the analyzer’s resolution. How then, to decide the correct combination of optics to optimize both the incident beam profile and the analyzer?

Thankfully, we can turn to dynamical diffraction theory to predict the intrinsic widths of both the incident optics and the analyzer. Dynamical diffraction theory describes the waves in a lattice, and differs from traditional geometric diffraction theory – which gives rise to the classic Bragg’s law – in that it is a complete solution of Maxwell’s equations in a lattice, and as such takes into account various additional effects such as refraction, absorption, interference, finite thickness crystals, and primary extinction[50, 51]. A complete accounting of dynamical diffraction theory is beyond the scope of this thesis, but the primary result of interest is the derivation of the amplitude of the reflectivity \( r \) of an absorbing, perfect crystal for a given Bragg reflection \( G \), given by[52]

\[
r(\text{Re} x_c) = \begin{cases} 
\frac{1}{x_c + \sqrt{x^2_c - 1}} = x_c - \frac{x^2_c - 1}{2}, & \text{Re } x_c \geq 1 \\
\frac{1}{x_c i\sqrt{1-x^2_c}} = x_c - i \frac{\sqrt{1-x^2_c}}{2}, & \text{Re } x_c \leq 1 \\
x_c - \frac{x^2_c - 1}{2} = x_c + \frac{x^2_c - 1}{2}, & \text{Re } x_c \leq -1 
\end{cases}
\]  

(3.26)

\[
x_c = m \pi \frac{\zeta}{g} - \frac{g_0}{g},
\]  

(3.27)

\[
g_0 = \left( \frac{2d^2 r_0}{mv_c} \right) F_0, \quad g = \left( \frac{2d^2 r_0}{mv_c} \right) F,
\]  

(3.28)

\[
\zeta = \frac{G}{G} = \frac{\Delta E}{E} = \frac{\Delta k}{k},
\]  

(3.29)
Figure 3.4: (a) Reflectivity curve for Si(444) at an incident energy of 7.9 keV, presented as a function of the angular deviation away from the nominal Bragg angle. The curve is off-center due to refraction effects, and shows the typical asymmetry due to higher absorption at higher angles. (b) Dumond diagram for a Si(111) two-bounce primary monochromator and Si(444) two-bounce secondary “channel cut” monochromator, as a function of angular deviations away from the nominal Bragg condition, and deviations in energy (in meV) away from 7.9 keV.

where $m$ is the reflection order, $r_0 = 2.82 \times 10^{-5}$ Å is the Thompson scattering amplitude, $v_c$ is the volume of the unit cell, $d$ is the spacing between reflecting layers ($G = 2\pi/d$), $F$ and $F_0$ describe the absorption factors (standard values are tabulated in Henke tables[53]), and $\zeta$ is a relative deviation factor away from the nominal reciprocal lattice vector $G$. The absolute square of Eq. 3.26 is the intensity reflectivity near a Bragg reflection, and we can use this to produce Darwin-Prins, or just “Darwin,” curves similar to the one in Fig. 3.4a. It is straightforward to consider the geometry of the primary and secondary monochromator to calculate a joint intensity reflectivity plot that represents the final reflectivity after the four reflections shown in Fig. 3.3. Fig. 3.4b shows this joint reflectivity map, typically called a Dumond diagram.

To find the optimal incident energy and optics combination, we simply considered the options available at Sector 9 and computed the FWHM in energy of the incident beam, the intensity per meV of the incident beam, and the energy resolutions of various analyzers given those incident energies. Incident energies for calculation are typically selected near atomic absorption edges for accurate energy calibration. Table 3.1 summarizes our dynamical diffraction theory calculations.

Because we are interested in $\alpha(q, \omega)$ for $q \to 0$ and $\omega \to 0$, we ideally want low incident energy to facilitate small momentum transfer measurements, high energy resolution, high intensity per meV, and a well-matched analyzer-to-secondary-monochromator bandpass. From Table 3.1, it is clear that our optimal choice considering these four requirements is a Si(444) secondary monochromator and a Si(444) analyzer. These are idealized calculations, and our final
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<th>Analyzer</th>
<th>Sec. Mono. Bandpass (meV)</th>
<th>Ana. Bandpass (meV)</th>
<th>Intensity/meV (arb. units)</th>
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Table 3.1: Table of calculated values for a Si(111) primary monochromator and selected secondary monochromators and analyzers.

Experimentally observed resolutions for energy and momentum (measured as the FWHM of the elastic scattering signal from two layers of Scotch tape) were $\Delta E \approx 0.18$ eV and $\Delta q \approx 0.2$ $\text{Å}^{-1}$.

### 3.6 Alignment

The first step in any beamline experiment is diffractometer alignment. As can be seen in Fig. 3.3b, we use a six-circle Huber diffractometer. We are interested only in momentum transfers in the graphene layers, so we need accurate control of only the $\phi$ (which determines the angle of incidence on the sample) and $2\theta$ (which determines the magnitude of the momentum transferred into the sample) rotations to probe the relevant regions of momentum space. Experimentally, this amounts to first placing the center of rotation of the diffractometer in the beam path, and ensuring that the scattering plane formed by the $2\theta$ and $\phi$ rotation axes corresponds to the correct momentum transfers into the sample. Locating the center of rotation of the diffractometer involves mounting a goniometer on the $\phi$-stage and placing a pin head in the goniometer to act as the presumptive center of rotation. We use a telescope to watch the motion of the pin head as we rotate the $\phi$-stage, adjusting the position of the pin head using the manual goniometer $x$ – $y$ translation stages until the tip of the pin does not move as
we rotate in $\phi$. This tells us rotation axis of the $\phi$-stage. We then use the large $\chi$-ring of the diffractometer and adjust the position of the $\phi$-stage along its $z$-axis until the pin head is centered on both the $\chi$ and $\phi$ rotation axes. This procedure determines the diffractometer’s center of rotation for our purposes.

Once we have the center of rotation, we attach burn paper to the pin head to identify where the beam is relative to the diffractometer, and move the diffractometer table in its $x-y$ plane to until the pin head intersects the burn spot. Now the beam is passing through the diffractometer’s center of rotation. The final step in alignment is to align the scattering plane of the diffractometer to the incident beam direction, so we place a fluorescence screen on the analyzer with markings that indicate the center of the analyzer crystal, and move the $2\theta$ arm in both the $\alpha$ and $2\theta$ directions until the direct incident beam hits the marked center of the fluorescence screen. This ensures that the incident beam path is in the $2\theta-\phi$ scattering plane, and we are finished aligning the diffractometer.

We mount the sample on the $\phi$-stage and align the graphene planes perpendicular to the stage by eye. To ensure that we know the orientation of the sample relative to the diffractometer, we find the (002) reflection on a fluorescence screen and note its location on a video monitor. Then, we rotate $\phi$ by $180^\circ$, and if graphene layers are perpendicular to the $\phi$ stage, we should see the (002) reflection fall on the same location on the video monitor as the (002). If the offset is large, we can adjust the sample mount itself to account for this discrepancy. Typically, though, we are offset by $<1$ cm at the 1 m distance of the analyzer, which corresponds to a deviation of $\approx 0.6^\circ$. Due to the form of the 3d-2d conversion, Eq. 3.22, and specifically the form of Eq. 3.23, this is well within the sensitivity of the experiment, and we ignore these small deviations. Eq. 3.22 also assumes that we have a homogeneous medium in the graphene planes, so we need only ensure that the c-axis is in the scattering plane and can safely ignore the orientation within the planes.

### 3.7 Sample Chamber

The most important motivating factor for redesigning our sample chamber was the need to reduce upstream scattering from the incident Kapton windows. In the original iteration of the graphite IXS experiment, incident x-rays passed through an upstream beam pipe, then through the Kapton exit window of the beam pipe, and finally through the Kapton entrance window of the sample chamber. This produced elastic scattering which then had to be blocked with the tantalum mounting foil, but of course not all of this background signal could be removed and it contributed to the resulting signal. Moreover, elastic scattering from upstream windows specifically result in increased background signal on the energy-loss side of the quasielastic peak, which can be seen in the scattering geometry shown in Fig. 3.5.

As can be seen, an elastic signal before the beam hits the sample will reflect
Figure 3.5: Elastic scattering from different source points. Notice that upstream scattering appears as energy-loss signal after it Bragg reflects off of the analyzer because the perceived $2\theta$ off the analyzer is larger, which the software interprets as lower outgoing energy.

Figure 3.6: Sample chamber schematic

off the analyzer and into the detector at a higher $2\theta$ angle than an elastic signal originating at the sample. Larger $2\theta$ angles imply lower energy due to Bragg’s law, and so any upstream sources of elastic background will contribute solely to the energy-loss signal. Downstream scattering off of the sample chamber’s exit window can be mitigated by the beamstop, and any additional leakage downstream enters only on the energy-gain side. So indeed, it is clear that controlling upstream scattering is paramount to producing a good signal-to-noise ratio in the low-energy energy-loss region, the principal region of interest. Downstream scattering scattering enters as a shoulder on the energy-gain side of the spectrum, and is thus significantly less important in the data analysis.

The new sample chamber is thus designed to connect directly to the incident beam pipe. A schematic of the sample chamber is shown in Fig. 3.6. The chamber is cut from PVC pipe, with a 90° window cut parallel to the base. The incident side of the chamber has a Kwik-Fit (KF) flange for attaching directly to the incident beam pipe via standard KF locking clamps and O-rings. In order to allow for the sample to rotate around the $\phi$-axis, the sample mounting post
is separate from the plates, with a double O-ring seal allowing for a \( \phi \)-rotation that is decoupled from the cylindrical body. To keep the cylinder stable and level while the sample rotates freely, standard optical posts to screw into the two end plates, and a combination of these optical posts attach directly to the \( \chi \)-ring of the Huber diffractometer as an additional support structure. Because we need only rough vacuum, the assembly is sufficient to maintain a seal.

Alignment of the full sample chamber and optical post assembly can be broken into the following steps:

1. Mount the sample post on the \( \phi \)-stage of the diffractometer.

2. Adjust the diffractometer table position until the beam hits the sample.

3. Replace the windowed beam pipe with our unwindowed beam pipe, and maintain the correct height of the beam pipe using the support structure in Fig. 3.7. This support structure is especially useful when switching from tape to graphite, as it maintains the position of the beam pipe while disassembling and reassembling the chamber.

4. Mount the cylindrical body on the sample post.

5. Connect the KF flange of the cylindrical body to the beam pipe with a small bellows.

6. Secure the cylinder with optical posts.

Subsequent to this procedure, we also check the position of the beamstop, which we do by placing the detector in the \( 2\theta = 0 \) position, and rotate the beamstop through the transmitted beam. This produces scans like the one in Fig. 3.8, which we use to identify the center of the beam profile in terms of the beamstop’s angular position, and then move the beamstop to the smallest angle possible that still blocks the entire transmitted beam. Our new sample chamber uses a motorized beamstop with an encoder, allowing us to reproducibly determine the angular position of the beamstop, which then sets the lowest \( 2\theta \) attainable without the beamstop casting a shadow on the analyzer. Typical lowest angular positions are \( \approx 1.5^\circ \), depending on the beam profile of a specific experimental run.

### 3.8 Random Phase Approximation

To compare our measured spectra with theory, we model the density-density response function of graphene directly. Consider first the density-density correlation function from Eq. 3.4. This correlation function can be described diagrammatically as the following Dyson series where the so-called polarization bubble in the diagram describes all scattering processes that are connected only by one Coulomb line. In the random phase approximation, we approximate the
(a) Interior of sample chamber. Note the beamstop mounted on a rotation stage.

(b) Incident beampipe that attaches directly to the sample chamber. Note the optical stand on the left that acts as an additional support for the beampipe.

(c) Downstream view of the sample chamber. Note the optical posts that act as additional supports to maintain the chamber position, as well as the stepper motor on the left side that drives the beamstop. Note also the exit window covered in Kapton, and the helium flight path in the lower-left corner.

(d) Sample mounting plate. Note the O-ring seal, and the small goniometer stage on which the sample is mounted.

(e) Fully assembled sample chamber.

(f) Full assembled sample chamber. Note the KF flange that attaches to the incident beampipe via a short bellows.

Figure 3.7: Various pictures of the final experimental setup.
Figure 3.8: Scan of beamstop position. The beamstop position is indicated by an arbitrary angle $\theta$, and the center is determined by inspection of the plot, and angular position is typically set $\approx 1.5^\circ$ away from the center.

\[ \begin{array}{c}
\sim \sim \sim = \sim \sim + \sim \sim \sim
\end{array} \]

Figure 3.9: Diagrammatic form of the screened interaction.

polarization function, or $\Pi(q, \omega)$ function, in the non-interacting limit, where the diagrammatic expansion becomes Fig. 3.10 and the $\Pi(q, \omega)$ function is evaluated using the ground state electron wavefunctions. This is also sometimes referred to as the Lindhard approximation, where one assumes the polarization function is that of a homogeneous electron gas. In this non-interacting limit for the polarization, we may write the polarizability as

\[ \Pi^0(q, \omega) = -\frac{g_s}{(2\pi)^2} \lim_{\eta \to +0} \int_{BZ} dk d k' \sum_{s, s'} \bigg| \langle \psi_s(k) | \rho(q) | \psi_{s'}(k') \rangle \bigg|^2 \]

\[ \times \frac{n_F[E_s(k)] - n_F[E_{s'}(k')]}{E_s(k) - E_{s'}(k')} + \omega + i\eta \]

\[ = -\frac{g_s}{(2\pi)^2} \lim_{\eta \to +0} \int_{BZ} dk d k' \sum_{s, s'} \bigg| \frac{\phi_I(k)^* \phi_I(k')}{|\phi_I(k)|} \bigg|^2 \bigg| \delta(k' - (k + q)) \frac{n_F[E_s(k)] - n_F[E_{s'}(k')]}{E_s(k) - E_{s'}(k') + \omega + i\eta} \bigg|^2 \]

\[ \times \frac{n_F[E_s(k)] - n_F[E_{s'}(k + q)]}{E_s(k) - E_{s'}(k + q) + \omega + i\eta} \]

\[ = -\frac{g_s}{4(2\pi)^2} \lim_{\eta \to +0} \int_{BZ} dk \sum_{s, s'} \bigg| \frac{\phi_I(k)^* \phi_I(k + q)}{|\phi_I(k + q)|} \bigg|^2 \bigg| \frac{n_F[E_s(k)] - n_F[E_{s'}(k + q)]}{E_s(k) - E_{s'}(k + q) + \omega + i\eta} \bigg|^2 \]

\[ \times \frac{n_F[E_s(k)] - n_F[E_{s'}(k + q)]}{E_s(k) - E_{s'}(k + q) + \omega + i\eta} \] (3.30)
where $n_F(E) = 1/(e^{(E-\mu)/kT} + 1)$ is the Fermi distribution for chemical potential $\mu$, $\eta$ is a convergence factor, $s,s'$ are the band indices for the conduction and valence bands ($\pm 1$), and $\phi_I(k)$ is essentially a matrix element of the form $\langle \psi | H | \psi' \rangle$ computed in Basis 1 (see App. A for a detailed discussion). Eq. 3.30 can be easily computed for arbitrary momentum $q$ and energy $\omega$ using numerical integration over the Brillouin zone (BZ). We perform this integration in MatLAB, using a Monte Carlo numerical integration method for computational speed, where we sum a random sampling of the integrand in the Brillouin zone. The number of sample points needed for the integral to converge is determined by the value of $\eta$ – for an $\eta$ of 0.001, 1000000 points in $k$-space were used for good convergence. Our RPA calculations assume an infinite layer of graphene, and agree well with similar RPA calculations of the $\pi$-function from [42].

Figure 3.11: Crystal structure of ABA stacked graphite.

In order to include interlayer hopping effects, we consider a periodic layered system of graphene with infinitely many layers. There are two possible stackings for graphene, ABA and ABC, which differ only in the relative angular orientation of next-nearest layers, as shown in Fig. 3.11. For this thesis, we present calculations performed with ABA-stacking only, as differences in the computed polarization functions between the two stackings are negligible, and ABA is the more common stacking found in nature. We use the most-commonly used values for the hopping parameters $t = 3$ eV, $\gamma_1 = 0.4$ eV, and $\gamma_3 = 0.3$ eV[1].

The extension of our Lindhard equation, Eq. 3.30, to the 3-dimensional ABA-stacked graphite case is then trivial, as we can simply compute the new eigenfunctions of the graphite Hamiltonian, recompute the relevant matrix elements, and do the numerical integration over the new 3-dimensional Brillouin zone rather than the 2-dimensional BZ for graphene. The integrand for this numerical integration is too lengthy to present here, but can be found in its entirety in Appendix B. The key difference in the computation of the 3-dimensional po-
larization is the lack of a simple closed form solution for the eigenfunctions of the Hamiltonian, so we use the linear algebra package in MatLAB to numerically calculate the eigenfunctions of the Hamiltonian at each sampled point in \( k \)-space. It is then straightforward to numerically integrate the Lindhard integrand over the BZ to get \( \Pi_{3D} \) directly (though we still keep the momentum transfer in the graphene planes with \( q_z = 0 \)).

Eq. 3.30, however, only includes the \( \pi \)-bands, and there are of course additional screening contributions from the \( \sigma \)-bands. If we assume that the \( \sigma \)-bands are distinct from the \( \pi \)-bands, we can treat the screening from higher-energy bands in the same way as \[42\], as a background dielectric constant in the following form\[54\]:

\[
\kappa(q) = \frac{\kappa_1 + 1 - (\kappa_1 - 1)e^{-qL}}{\kappa_1 + 1 + (\kappa_1 - 1)e^{-qL}},
\]

(3.31)

where \( \kappa_1 \approx 2.4 \) is the dielectric constant of graphite, \( L = d_m + (N_{layer} - 1)d \) is the total height of the graphitic system in terms of the number of layers \( N_{layer} \) and the height of a graphene layer \( d_m \approx 2.8\AA \). As expected \( \kappa = 1 \) for graphene as \( q \to 0 \) since the \( \sigma \)-bonds are short-range, and \( \kappa = \kappa_1 \) for graphite as \( q \to 0 \). To incorporate this contribution into the overall screening in graphene or graphite, we need to consider how to compute the dielectric function of a system where we treat the electrons from the \( \pi \)-bands and \( \sigma \)-bands as two separate fermionic species. In general, we can write the Hamiltonian for such a system as

\[
H = H_0 + H_I + H_U,
\]

(3.32)

where

\[
H_0 = \sum_{k\sigma} E_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k\sigma} E_k g_{k\sigma}^\dagger g_{k\sigma},
\]

(3.33)

describes the non-interacting Hamiltonian for the fermionic operators of the \( \pi \)- and \( \sigma \)-electrons, \( g(g^\dagger) \) and \( c(c^\dagger) \), respectively.

\[
H_I = \sum_q V(q)\hat{\rho}_\pi(-q)\hat{\rho}_\pi(q) + 2 \sum_q V(q)\hat{\rho}_\pi(-q)\hat{\rho}_\sigma(q) + \sum_q V(q)\hat{\rho}_\sigma(-q)\hat{\rho}_\sigma(q),
\]

(3.34)

is the Coulomb interaction energy, with

\[
\hat{\rho}_\pi(q) = \sum_{k\sigma} c_{k+q,\sigma}^\dagger c_{k\sigma} , \quad \hat{\rho}_\sigma(q) = \sum_{k\sigma} g_{k+q,\sigma}^\dagger g_{k\sigma}
\]

(3.35)

the particle densities and \( V(q) = 2\pi e^2/q \), and

\[
H_U = \sum_q [U_\sigma(q)\hat{\rho}_\sigma(q) + U_\pi(q)\hat{\rho}_\pi(q)]
\]

(3.36)

is an external potential with couples to the density. A standard calculation\[55\]
lets us write the equations of motion for this system in matrix form as
\[
\begin{pmatrix}
\langle \hat{\rho}_s(q, i\omega) \rangle \\
\langle \hat{\rho}_\pi(q, i\omega) \rangle 
\end{pmatrix}
= \frac{1}{\epsilon(q, i\omega)} \mathbf{M}
\begin{pmatrix}
U_s(q) \Pi_s(q, i\omega) \\
U_\pi(q) \Pi_\pi(q, i\omega)
\end{pmatrix}
\]
(3.37)
where
\[
\mathbf{M} = \begin{pmatrix}
1 - V(q)\Pi_\pi(q, i\omega) & V(q)\Pi_s(q, i\omega) \\
V(q)\Pi_\pi(q, i\omega) & 1 - V(q)\Pi_s(q, i\omega)
\end{pmatrix}
\]
(3.38)
and
\[
\epsilon(q, i\omega) = \det \mathbf{M} = 1 - V(q)\Pi_\pi(q, i\omega) - V(q)\Pi_s(q, i\omega)
- [V^2(q) - V(q)V(q)]\Pi_\pi(q, i\omega)\Pi_s(q, i\omega)
\]
(3.39)
is the dielectric function of the system, where \(\Pi_\pi\) and \(\Pi_s\) are the polarization functions of the \(\pi\)- and \(\sigma\)-electrons, respectively. Simplifying, we have
\[
\epsilon(q, i\omega) = 1 - V(q)\Pi_\pi(q, i\omega) - V(q)\Pi_s(q, i\omega)
- \kappa_s(q) - V(q)\Pi_\pi(q, i\omega),
\]
(3.40)
where we have defined
\[
\kappa_s(q) = 1 - V(q)\Pi_s(q, i\omega)
\]
(3.41)
as the background dielectric constant due to the \(\sigma\)-electrons. It is clear then that our expression for the dielectric function of our graphitic system should be
\[
\epsilon(q, \omega) = \kappa(q) - V(q)\Pi(q, \omega),
\]
(3.42)
where \(\kappa(q)\) is from Eq. 3.31 and \(\Pi(q, \omega)\) is from Eq. 3.30. This is in contrast to the expression in [42], where they use the expression \(\epsilon(q, \omega) = 1 - V(q)\Pi(q, \omega)/\kappa(q)\).

Clearly, we can write the response function \(\chi\) for 2D graphene by simply using our calculated polarizability for the \(\pi\)-bands from Eq. 3.30 and using Eq. 3.13, except with the background dielectric screening from the \(\sigma\)-bands included properly,
\[
\chi_{2D-\text{RPA}}(q, \omega) = \frac{\Pi_{2D-\text{RPA}}}{\kappa(q) - V(q)\Pi_{2D-\text{RPA}}(q, \omega)},
\]
(3.43)
where \(\kappa\) is that of SLG, and similarly for the 3D response,
\[
\chi_{3D-\text{RPA}}(q, \omega) = \frac{\Pi_{3D-\text{RPA}}}{\kappa(q) - F(k)V(q)\Pi_{3D-\text{RPA}}(q, \omega)},
\]
(3.44)
where \(\kappa\) is that of MLG. The associated 2D response of graphene as measured in graphite would correspond to applying the conversion formula from Eq. 3.25 to
3.9 **Excitonic Effects**

The original experiment proposed excitonic effects as the source of the enhanced screening seen in the measured spectra. Here, we give a brief overview of the theory behind excitonic shifts. Consider first a filled Fermi sea, as shown in Fig. 3.12. We can transfer momentum $q$ and energy $\hbar v_F q$ to a particle from the valence band to the conduction band, and such excitations form a continuum of possible excitations for $\omega(q) > v_F q$. In the RPA, the electron and hole do not interact, but in principle, the particle and the hole it left behind are attracted to each other and can sometimes form a bound state, called an exciton. This attractive interaction reduces the energy of the bands by the binding energy. Excitonic effects can be seen in the optical ($q = 0$) response of semiconductors[56], and are not typically observed in metals, where screening is strong, though they have been observed in lower-dimensional metallic and semimetallic materials such as carbon nanotubes[57].

Theoretically, the presence of bound states can be captured by a two-particle correlation function, the Bethe-Salpeter equation[58, 59]. The Feynman diagram for the electron-hole bound pair is often approximated by the so-called “ladder” diagram, as shown in Fig. 3.13.
Figure 3.13: “Ladder” diagram approximation for the Bethe-Salpeter equation.
Chapter 4

Analysis and Results

4.1 Background Subtraction

All our measured energy loss spectra contain a peak lineshape that is a quasielastic background, which must be subtracted from the data to recover $\chi(q, \omega)$. Several lineshapes can be used to model the quasielastic peak, but we consider two function, a voigt function

$$V(x; A, w_G, w_L, x_0, B) = B + A \frac{2 \ln 2}{\pi^{3/2} w_G^2} \int_{-\infty}^{\infty} \frac{dx'}{2} e^{-x'^2} \left( \sqrt{\frac{\ln 2}{w_G^2}} + \sqrt{\frac{4 \ln 2 (x-x_0)}{w_G^2}} - x' \right)$$

which is a Lorentzian profile convolved with a Gaussian profile, and a pseudovoigt function,

$$V_p(x; A, S, w_G, w_L, x_0, B) = A \left[ \eta \frac{w_L}{\pi ((x-x_0)^2 + \eta^2)} + (1 - \eta) \frac{1}{w_G \sqrt{2\pi}} e^{-\frac{(x-x_0)^2}{2w_G^2}} \right] + B$$

which is an approximation of a voigt function, and is simply a linear combination of a lorentzian and a gaussian. In both cases $A$ is the amplitude, $B$ is a constant background offset, $w_G$ is the Gaussian width, $w_L$ is the Lorentzian width, and $x_0$ is the center of the profile. For the pseudovoigt function, the parameter $\eta$ simply sets the weight of the Gaussian and Lore and $S$ is a parameter that allows for asymmetry between the left- and right-hand sides of the profile, which is required due to the differences between upstream and downstream scattering outlined in Sec. 3.7. In practice, the pseudovoigt fit the peaks better than the corresponding voigt functions, so we ultimately used only pseudovoigt functions to fit the quasielastic peak. We also experimentally found $B = 0$ by moving the system out of alignment and measuring the “dark” counts. Peak fitting is performed with MatLAB’s lsqcurvefit method, which uses a trust-region-reflective algorithm to adjust the fitting parameters. Fitting voigt and pseudovoigt functions is a nonlinear regression problem, and thus we try to avoid local minima in the fitting algorithm by using random initial parameters and performing many
Figure 4.1: (a) and (c), energy-loss spectra for $q = 0.212$ Å$^{-1}$ and $q = 0.282$ Å$^{-1}$, respectively, with elastic line fit and subtraction, along with corresponding sum-rule normalizations in (b) and (d), respectively.

Figure 4.1 shows typical background subtractions for two different momentum values. As can be seen, the pseudovoigt function very nicely fits the shape of the quasielastic line. However, because the tails of the quasielastic background extend into the region of interest, there is some uncertainty in the subtraction itself. We model this uncertainty by fitting the quasielastic line using different initial parameters, as well as fitting the peak using different ranges of energy, the latter of which can be thought of as a form of jackknife resampling since adjusting the range of $\omega$ over which we fit the quasielastic peak simply adds or removes points in a deterministic way.

### 4.2 Normalization and Kramers-Kronig Transform

We need $\chi$ in absolute units to determine a value for $|\alpha^*|$. This, then presents a two-fold problem: 1) how do we determine the normalization for our data and 2) since we only measure $\text{Im } \chi$, how do we recover $\text{Re } \chi$? We normalize our data to linear interpolated data spectra from the previous experiment in [5], so we will describe both how the original normalization was done and our procedure to patch our new spectra to the old. In the original experiment, the normalization was obtained first by accounting for the sample’s self-absorption (see Fig. 4.2 and [4]) and incident angle, which reduces the scattered intensity in the following way: Next, we find the best fit of the data to the Thomas-Reiche-Kuhn $f$-sum.
rule, which states that
\[ \int_0^\infty d\omega \Im \chi(q, \omega) = \frac{\hbar q^2}{2m} = \Im \chi(q), \] (4.3)
where \( n \) is the electron density, we use 4 electrons in the unit cell to account for the \( \pi \)- and \( \sigma \)-electrons, and \( m \) is the bare electron mass. This, of course, requires us to define \( \Im \chi(q, \omega) \) for arbitrarily high \( \omega \) in order to capture the full range of excitations, so we extrapolate our data using a Gaussian tail that is fit to the measured tail. Performing the integral in Eq. 4.3 and then fitting \( \Im \chi(q) \) to a quadratic using a global multiplicative factor for all \( q \)'s, we recover the fitted \( \Im \chi(q) \) in Fig. 4.5. Note that we only fit to a quadratic up to 5 Å\(^{-1}\) due to the onset of the Compton profile, which begins to include scattering from the deeper 1s core electrons, thus conflicting with our use of only 4 electrons in the unit cell.

Once we have \( \Im \chi \) in absolute units from the \( f \)-sum rule, we still need \( \Re \chi \) in order to extract a fine-structure constant from our spectra. Unfortunately, we do not directly measure \( \Re \chi \) in the experiment. This is in essence a variant of the phase problem of traditional x-ray diffraction, where the measured intensities relate only to the magnitude and not the phase of the static structure factor \( S(q) \). Recall, however, the explicit form of the \( \chi \)-function itself from Eq. 3.4:
\[ \chi(x_1, x_2, t_1, t_2) = -\frac{i}{\hbar} \sum \langle m | [\rho(x_1, t_1), \rho(x_2, t_2)] | m \rangle \theta(t_1 - t_2). \]
The Heaviside step function \( \theta(t_1 - t_2) \) implies that \( \chi(x_1, x_2, t_1, t_2) \) is a \textit{causal} function – indeed, we have been careful to use the retarded form of the density-density response function. The imaginary and real parts of \( \chi(q, \omega) \) are related...
by the well-known Kramers-Kronig relation:

$$\text{Re} \chi(q, -q, \omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty d\omega' \frac{\omega' \text{Im} \chi(q, -q, \omega')}{(\omega')^2 - \omega^2}, \quad (4.4)$$

where we have used the causality property of $\chi(x_1, x_2, t_1, t_2)$ to simplify the standard Kramers-Kronig integral to an integral over only positive $\omega$, which is especially useful since our experiment only measures energy-loss. In fact, the Eq. 4.4 presents two difficulties: 1) the upper bound corresponds to infinite energy loss, which we cannot measure, and 2) the integral requires a continuous integrand to ensure causality, and we measure can only measure $\chi(q, \omega)$ and discrete energy points $\omega$. We have already dealt with the former by appending a Gaussian tail to $\text{Im} \chi$. The solution to the latter is simply linear interpolation between the points. We choose linear interpolation to give the most honest interpretation of the data, as higher-order splines can add new extrema. It is then straightforward to compute the principal part integral in Eq. 4.4. We use a convergence factor of 0.001 eV for the principal part integral. A typical calculation of $\text{Re} \chi$ is shown in Fig. 4.4, compared to a density functional theory calculation at a similar momentum value from [60].

4.3 Results and Discussion

Armed with our conversion formula from Eq. 3.25, we are finally able to plot the $\chi$- and $\pi$-functions of our graphite samples. Fig. 4.5 shows both $\chi_{3D}$ and $\chi_{2D}$ for our graphite samples, along with RPA calculations with and without interlayer hopping. The first thing to note is that RPA with $\pi$-bands does a poor job of predicting the energy of the $\pi$-plasmon at $\approx 8$ eV. We attempted to improve the
Figure 4.4: Comparison of real part. More detail goes here.

Figure 4.5: (a) Measured and theoretical $\chi_{3D}(q, \omega)$. Both calculated spectra are for infinite multi-layer graphene both with and without interlayer hopping ($\gamma_{1,3} \neq 0$ and $\gamma_{1,3} = 0$, respectively). (a) Measured and theoretical $\chi_{2D}(q, \omega)$. Red and green spectra are $\chi_{2D}$ that use $\kappa = 2.4$, whereas the orange spectrum uses $\kappa(q)$ for graphene. In both (a) and (a), the vertical line denotes $\hbar \nu_f q$ for the given $q$, and the calculated spectra have been multiplied by an arbitrary constant to facilitate visual comparisons of plasmon dispersion.
agreement by adjusting the parameters $t$, $\gamma_{1,3}$, and $\kappa_1$, but any parameters that produced the correct plasmon dispersion were dramatically different from the commonly accepted values\cite{1, 61} of $t = 3$ eV, $\gamma_1 = 0.4$ eV, $\gamma_3 = 0.3$ eV, and $\kappa_1 = 2.4$. Changes to these parameters also dramatically changed the overall shape of the spectrum in $\chi$. We thus show only the spectra calculated using the commonly accepted values for the hopping parameters and $\kappa_1$. Second, we note that there is significant discrepancy between the absolute intensities of the experimental and calculated $\chi$-functions; the calculated spectra in Fig. 4.5 have been multiplied by arbitrary constants between 0.15 and 1 in order to make their absolute intensities comparable to the measured data, and this is done only to make comparisons between theory and experiment easier to see by eye. This discrepancy in overall intensity is likely due to the presence of the $\sigma$-bands, and strongly manifests itself in the $\text{Im}\, \chi$-function because $\chi$ depends not just on the low-energy excitation spectrum but also the excitation spectrum of the higher-energy bands, which we only model here with Eq. 3.31. This is a known feature of the $\chi$-function\cite{60, 61}. We do see that as $q \to 0$, the multiplicative factor tends to 1, which implies that the influence of the $\sigma$-bands decreases with decreasing momentum, as is expected. This discrepancy in intensity disappears in $\text{Im}\, \Pi(q, \omega)$, where the low-energy spectrum does not depend on the details of the higher-energy bands – this can be seen in Fig. 4.6, where the $\Pi$-functions are plotted without additional multiplicative factors.

We are now finally ready to consider the source of the increased screening we observe in both the original experiment and our new experiment. In particular, we want to know if this screening is due to the graphitic dielectric environment of the HOPG i.e. the interlayer hopping parameters $\gamma_1$ and $\gamma_3$, the $\sigma$-bands, or excitonic effects. In our original experiment, we proposed excitonic effects as a possible explanation for the enhanced screening evident in our reduced $\alpha^*$. The hallmark of excitonic effects is the shift of spectral weight to lower-energy in the polarization function, which is typically due to the formation of bound excitons, but may also be due to dynamical particle-hole excitations that renormalize the bands to lower energy. As can be seen in the data in Fig. 4.6, we do see excitonic-like shifts of approximately 1 eV for the largest momenta, and as $q \to 0$, the shifts appear to be less pronounced, essentially disappearing for the lowest measured momentum transfer at $q = 0.212$ Å$^{-1}$. We do, however, see in Fig. 4.5b that the spectral weight discrepancy in $\chi(q, \omega)$ persists at all our measured momenta, which suggests that the $\sigma$-bands play a role in screening even at momenta as low as $q = 0.212$ Å$^{-1}$, or equivalently, a distance of approximately 20 lattice parameters.

What is most relevant is the static value of $\alpha^*$ as $q \to 0$, which determines the strength of the Coulomb interaction in low-energy experiments such as transport. Figs. 4.7a and 4.7b show our results for experimental and calculated values of $\chi(q, 0)$ and $\alpha^*(q, 0)$, respectively. We perform RPA calculations in three different regimes: (1) single-layer graphene (SLG), (2) infinite multi-
Figure 4.6: \( \text{Im} \Pi(q, \omega) \) from experiment and calculation. Note that the intensity discrepancy seen in \( \chi \) is no longer seen here.
layer graphene (MLG) without interlayer hopping, and (3) infinite MLG with interlayer hopping (graphite). MLG without interlayer hopping still includes the background dielectric constant \( \kappa \), so results for MLG without interlayer hopping can be interpreted as those of a single graphene sheet embedded in graphite which couples to the graphite through only the Coulomb interaction and higher-order bands. As can be seen from both plots, SLG deviates from multi-layer graphene for \( q < \sim 1.5 \ \text{\AA}^{-1} \) due to the presence of the background dielectric constant \( \kappa(q) \), which is 1 for SLG as \( q \rightarrow 0 \) but 2.4 for MLG with and without interlayer hopping. Differences in MLG due to interlayer hopping do not enter substantially into the RPA result until \( q < \sim 0.3 \ \text{\AA}^{-1} \). In this way, we can be confident in our assumption that the layers are coupled primarily by Coulomb interaction.

We look next at the asymptotic behavior of \( \chi_{2D} \) and \( \chi_{3D} \). Because \( \Pi_{2D} \propto q \) for \( q \rightarrow 0 \), we expect \( \chi_{3D}/q \propto q \) and \( \chi_{2D}/qd \rightarrow \) a constant in this regime, and we can clearly see that our measured \( \chi_{3D} \) goes to zero linearly as \( q \rightarrow 0 \). \( \chi_{2D}/qd \) also clearly asymptotes to a non-zero value, and we can estimate \(-\chi_{2D}/qd \approx 0.003 \) for \( q \rightarrow 0 \), which gives \( \alpha^* \approx 0.20^1 \). In particular, the fact that Eq. 3.25 recovers the correct asymptotic behavior for \( \chi_{3D} \) and \( \chi_{2D} \) implies that we are correctly measuring the \( \chi \)-function of graphene. Our estimate for \( \chi_{2D} \) is larger than the previous experiment’s, but still smaller than the RPA value.

Similarly, Fig. 4.7b compares the static \( \alpha^*(q, 0) \) from our original experiment to our current data and RPA calculations. Our new data suggests that \( \alpha^* \) is larger than the one previously measured, but is within the error bars of the

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1 In particular, the value of \( \alpha^* \approx 0.3 \) in Ref. [42] is not directly comparable with this value, as in that paper \( \alpha^* = \alpha/\epsilon_{3D} \), where \( \epsilon_{3D} \) as 1 - \( 1/2(q^2)F(q)\Pi_{3D}(q, \omega)d \), which differs from our definition from Eq. 3.42. Since we are interested in the 2D response derived from graphite, Eq. 3.42 is the more relevant quantity.
original experiment’s. Due to the definition of $\alpha^*$, our estimated error of 5% in 
$\text{Im} \chi_{3D}$ produces very large error bars in $\alpha^*$, so it is more instructive to look at 
the asymptotic behavior of $\chi_{2D}$ itself to obtain the asymptotic behavior of $\alpha^*$.

We clearly see that aside from the lowest momentum value at $q = 0.212$ 
Å$^{-1}$, the experimental values of $\alpha^*$ are all lower than the RPA value even with 
non-zero interlayer hopping parameters $\gamma_1$ and $\gamma_3$ and background screening 
from $\kappa$, suggesting that either we are underestimating the contribution of the 
$\sigma$-bands with $\kappa$ or we are indeed seeing excitonic effects. Though we cannot 
distinguish between excitonic effects and $\sigma$-band screening, it is clear that both 
are contributing for $q > 0.212$ Å$^{-1}$, and their combined observed screening 
correction is substantially larger than that of our RPA calculation, with or 
without interlayer hopping.
Chapter 5

Coherent Inelastic X-ray Imaging

Electron dynamics underlie all fundamental phenomena in chemistry, biology and materials physics. Recent advances in attosecond laser sources have created widespread interest in studying such electronic processes in real time, particularly in cases where spatial information, e.g., about the detailed configuration of electron wave packets, can be inferred.[63–65]

We recently proposed a different approach to attosecond imaging based on inelastic x-ray scattering (IXS).[66] Unlike more common, time-domain approaches that exploit state-of-the-art laser technology, in the IXS approach one achieves high spatial and temporal resolution by performing measurements in momentum and frequency space, and solving the inverse scattering problem to reconstruct events in real space and time.[66] This approach, which we will refer to here as “IXS imaging” has been used to study collective electron dynamics in liquid water,[67] excitons in large-gap insulators,[68] and to measure the effective fine structure constant of graphene.[5]

There is a limitation on the imaging aspect of this approach. IXS imaging reveals, in principle, the charge response function, \( \chi(x_1, x_2, t) \), which describes the amplitude that a point disturbance in the density at location \( x_1 \) will propagate to \( x_2 \) after elapsed time \( t \).

\[ \chi(q_1, q_2, \omega) \]

In reciprocal space this quantity is a function of two momenta, \( \chi(q_1, q_2, \omega) \), but conventional IXS probes only its diagonal components, \( \chi(q, -q, \omega) \), resulting in a real-space response function, \( \chi(x, t) \), that depends on only one spatial variable. The temporal properties of \( \chi(x, t) \) are causal and quantitatively accurate, but the spatial part corresponds to an average over all source locations in the system.[69] If the system of interest is homogeneous, for example a free electron metal such as aluminium, this spatial averaging results in no loss of information. In an inhomogeneous system, however, important, local features may be averaged out.

To overcome this limitation one must measure the off-diagonal momentum components of \( \chi(q_1, q_2, \omega) \), i.e., where \( q_1 \neq -q_2 \). It was shown many years ago that this is possible, at least in principle, by using coherent standing waves.[70, 71]. In this approach, an x-ray standing wave is created by exciting

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1Electron dynamics underlie all fundamental phenomena in chemistry, biology and materials physics. Recent advances in attosecond laser sources have created widespread interest in studying such electronic processes in real time, particularly in cases where spatial information, e.g., about the detailed configuration of electron wave packets, can be inferred.[63–65]

2By reciprocity, the probability of propagating instead from \( r_2 \) to \( r_1 \) is the same.
a Bragg reflection in a crystal (or by using an external coherent source, such as a Bonse-Hart interferometer). Within a coherence volume, the x-ray photon lies in a superposition of two distinct momenta, $k_1$ and $k_2$. One then places the IXS detector (typically a backscattering analyzer) at some scattering angle, which defines two momentum transfers, $q_1$ and $q_2$. Under these conditions, due to interference between the two scattering channels, the cross section includes terms that are proportional to $\text{Im} \chi(q_1, q_2, \omega)$.

Could this approach be used to address the averaging problem in IXS imaging? It is not obvious that it can. In standing wave techniques one does not have complete freedom to choose the two momenta, $k_1$ and $k_2$. Because the wave field itself is created by a Bragg reflection, the momenta are always related by a reciprocal lattice vector, i.e., $k_2 = k_1 + G$. Hence, one’s access to reciprocal space is highly constrained, and it is unclear whether enough information is accessible to permit a full refinement of $\chi(x_1, x_2, t)$.

In this article we examine this issue by analyzing a simple model of a single quantum particle in a periodic potential. We find that whether enough reciprocal space is accessible depends on the dimensionality of the problem. We show that the standing wave approach fails in both one and two dimensions, because the dimensionality of the accessible momentum space is lower than the dimensionality of the data needed to perform a refinement. In three dimensions, however, the technique could in principle be viable.

### 5.1 Spatially-averaged IXS Imaging

We begin with a review of basic IXS imaging, as it has been carried out previously\[5, 66–68\]. In general, non-resonant IXS measures the dynamic structure factor $S(q, \omega)$, which is the fourier transform of the density-density correlation function\[66, 72\]. $S(q, \omega)$ is related to the charge response function (or charge propagator), $\chi(q_1, q_2, \omega)$, by the quantum mechanical version of the fluctuation-dissipation theorem

$$S(q, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\beta \hbar \omega}} \text{Im} \chi(q, -q, \omega). \quad (5.1)$$

Here, $q$ and $\omega$ are, respectively, the momentum and energy transferred into the sample by an incoming monochromatic beam of x-rays. Because we only have access to the imaginary part of $\chi$ (a constraint analogous to the phase problem in x-ray diffraction), we use the fact that $\chi$ is a causal function in time, and thus the real part of $\chi$ is related to its imaginary part through the Kramers-Kronig relation

$$\text{Re} \chi(q, -q, \omega) = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} d\omega' \omega' \frac{\text{Im} \chi(q, -q, \omega')}{(\omega')^2 - \omega^2}, \quad (5.2)$$

where $\mathcal{P}$ is the principal part. Inverse Fourier transforming $\chi(q, -q, \omega)$ (typically written simply as $\chi(q, \omega)$ in the literature) gives us $\chi(x, t)$, which reveals
the real space and time electronic response of the system to an idealized, point

The first factor \( \chi(x_1, x_2, t) \) is determined by the bandwidth. When \( t = 0 \), the disturbance is symmetric and no longer has the intrinsic, diffraction-limited Darwin width, \( \sigma_x \). As time progresses the disturbance propagates away from the source location, dispersing through the lattice in a manner dictated by the dispersion of the band (eq. 17), i.e., by integrating over a sufficiently large range of energies such that the dominant contributions to the integrand in Eq. 5.2 are captured, but also (2) spectra at sufficiently many values of \( q \) to confidently interpolate the response \( \chi(q, -q, \omega) \) for unmeasured regions of momentum space. In principle, this can be a time-consuming process. However, in practice, many crystalline materials have a high degree of symmetry which may be exploited to minimize the amount of momentum space that must be measured (see section VI).

5.2 IXS with standing waves

In the method we are proposing, the first experimental task is to create a coherent, x-ray standing wave. The most straightforward way to do this is to excite a Bragg reflection. Hence, the system of interest should be available in the form of high quality, single crystals. If the system is a molecule, rather than a solid, molecular crystals of the sort studied in protein crystallography must be synthesized. Further, the quality of the crystals must be high enough to support a standing wave, i.e., the mosaic spread of the crystal should be much narrower than the intrinsic, diffraction-limited Darwin width, \( \theta_W \), of the relevant Bragg reflection, \( G \).

Creating a standing wave requires the incident x-ray beam to be monochromatic and collimated. Because the phase of a Bragg-diffracted beam varies from 0 to \( \pi \) across its reflection profile, the angular divergence of the incident beam must be much less than \( \theta_W \) for the phase to be well-defined. Collimation can most easily be accomplished by reflecting the incident beam from a highly asymmetric reflection, preferably from a crystal that is identical to the crystal that will be creating the standing wave field.

Figure 5.1: \( \chi(x, t) \) at \( t = 400 \) as determined from a spatially-averaged IXS study of single crystal graphite, reproduced from [5].
Figure 5.2: (a) Layout of a standing wave IXS imaging experiment. Two identical crystals of the system of interest are required. The first, which is asymmetrically cut, collimates the beam, and the second produces the standing wave. \( k_1, k_2, \) and \( k_3 \) are the momenta of the incident, Bragg reflected, and inelastically scattered photons, respectively. \( \Psi \) describes rotations of the second crystal around \( G \). (b) Standing wave-field formed by incident photon \( k_1 \) and Bragg reflected photon \( k_2 \). Nodal planes of the standing wave-field are highlighted in blue (the nodal planes are shown to be coincident with the lattice planes here, but the phase of the standing wave-field is tunable in experiment and thus the position of the nodal planes is a free parameter).

Hence, the simplest arrangement for a standing wave IXS experiment would consist of two identical, nondispersively mounted, Bragg reflecting crystals of the system of interest (Fig. 5.2). The first should be asymmetrically cut, angularly compressing the x-ray beam. The second would be symmetrically cut, and would generate the standing wave field. This arrangement is widely used in standing wave techniques, which have been reviewed elsewhere.[52, 73] In the current case, however, the second crystal would serve as the “sample,” its scattered light being analyzed by the backscattering, IXS analyzer.

Once the standing wave condition is met, the photon field inside the crystal lies in a coherent superposition of the incoming momentum and the outgoing Bragg-diffracted momentum.[70, 71, 74] Under these circumstances, the initial and final states are given by

\[
|i\rangle = (g_1 a_{k_1\alpha_1}^\dagger + g_2 a_{k_2\alpha_2}^\dagger e^{i\gamma}) |m\rangle, \quad (5.3)
\]
\[
|f\rangle = a_{k_3\alpha_3}^\dagger |n\rangle. \quad (5.4)
\]

where \( a_{k\alpha} \) annihilates a photon with momentum \( k \) and polarization state \( \alpha \), and \( |m\rangle \) and \( |n\rangle \) are the initial and final many-body states of the valence electron system, respectively. \( g_1 \) and \( g_2 \) indicate the relative amplitudes of the incident and Bragg-reflected photons, and \( \gamma \) is their relative phase. All three parameters depend on the incident angle of the x-rays, and can be computed from dynamical diffraction theory[51, 73] and thus are assumed to be known. As discussed earlier, because the wave field is created by a Bragg reflection, \( k_2 = k_1 + G \), where \( G \) is a reciprocal lattice vector. Note that though \( k_1 \neq k_2 \), \( \omega_{k_1} = \omega_{k_2} \), so we define \( \omega_1 \equiv \omega_i = \omega_{k_1} = \omega_{k_2} \) and \( \omega_3 \equiv \omega_f = \omega_{k_3} \),

47
The Hamiltonian for a system of non-relativistic charged particles in an electromagnetic field is

\[
H = \sum_i \frac{p_i^2}{2m} + \sum_i V(x_i) + V_{\text{int}}^e
\]

\[
+ \int dx \left[ \rho(x) \frac{e^2 A^2}{2mc^2} - \frac{e}{2mc} \sum_i \left[ \delta(x - x_i) p_i \cdot A + \delta(x - x_i) A \cdot p_i \right] \right],
\]

where \(\rho(x) = \sum_i \delta(x - x_i)\) is the electron density operator, the sum being over the \(i\)th electron, and \(A\) is the quantized gauge field,

\[
A(x, t) = \left( \frac{2\pi \hbar}{V} \right)^{\frac{1}{2}} \sum_{k\alpha} \frac{c}{\sqrt{\omega_k}} \left( \hat{\epsilon}_{k\alpha} a_{k\alpha}^\dagger e^{-i(k \cdot x - \omega_k t)} + \hat{\epsilon}_{k\alpha} a_{k\alpha} e^{i(k \cdot x - \omega_k t)} \right).
\]

To lowest order in the interaction \(H_{\text{int}} = \int dx \rho(x) e^2 A^2 / 2mc^2\), the scattering matrix element \(\langle f | H_{\text{int}} | i \rangle\) becomes

\[
\langle f | H_{\text{int}} | i \rangle = \frac{2\pi \hbar e^2}{mV} \frac{q_1^2}{\sqrt{\omega_1 \omega_2}} (\hat{\epsilon}_1 \cdot \hat{\epsilon}_2) \langle n | \rho(-q_1) | m \rangle + \frac{2\pi \hbar e^2}{mV} \frac{g_2 e^{i\gamma}}{\sqrt{\omega_3 \omega_2}} (\hat{\epsilon}_2 \cdot \hat{\epsilon}_3) \langle n | \rho(-q_2) | m \rangle.
\]

where we have defined \(q_1 = \mathbf{k}_1 - \mathbf{k}_3\) and \(q_2 = \mathbf{k}_2 - \mathbf{k}_3\) (the two momenta transferred to the sample by inelastic scattering). The transition rate \(\Gamma_{i \rightarrow f}\) at finite temperature \(T\) is given by Fermi’s golden rule

\[
\Gamma_{i \rightarrow f} = \frac{4\pi^2 \hbar}{\omega_1 \omega_3} \left( \frac{e^2}{mV} \right)^2 \sum_{n,m} b_m \left[ g_1^2 |\hat{\epsilon}_1 \cdot \hat{\epsilon}_2|^2 \langle n | \rho(q_1) | m \rangle \right]^2
\]

\[
+ g_1 g_2 e^{i\gamma} (\hat{\epsilon}_1 \cdot \hat{\epsilon}_2)(\hat{\epsilon}_3 \cdot \hat{\epsilon}_4) \langle m | \rho(q_1) | n \rangle \langle n | \rho(-q_2) | m \rangle
\]

\[
+ g_1 g_2 e^{-i\gamma} (\hat{\epsilon}_3 \cdot \hat{\epsilon}_4)(\hat{\epsilon}_1 \cdot \hat{\epsilon}_2) \langle m | \rho(q_2) | n \rangle \langle n | \rho(-q_1) | m \rangle
\]

\[
\times \delta(E - E_n + E_m),
\]

where \(E_m = e^{-\beta E_m} / Z\) is the Boltzmann factor and \(E\) is the energy transferred to the sample.

The physically relevant quantity is the doubly-differential cross section

\[
\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{1}{\Phi} \frac{\partial^2 N}{\partial \Omega \partial E}.
\]

where \(\partial^2 N / \partial \Omega \partial E\) is the density of final states and \(\Phi\) is the incident flux. In standing wave IXS one detects a single photon in the final state, so for a photon of polarization \(\alpha\) we have \(\partial^2 N / \partial \Omega \partial E = V \omega_3^2 / 8\pi^3 \hbar c^3\) and \(\Phi = c / V\). Substitut-
ing into Eq. 5.9, we have

\[
\frac{d^2 \sigma}{dE' d\Omega} = \left( \frac{e^2}{mc^2} \right)^2 \frac{\omega_3}{\omega_1} \sum_{n,m} b_m \left[ g_1^2 |\epsilon_3^* \cdot \epsilon_1|^2 + |\langle n | \rho(q_1) | m \rangle|^2 + g_2^2 |\epsilon_3^* \cdot \epsilon_2|^2 + |\langle n | \rho(q_2) | m \rangle|^2 \right] \\
+ g_1 g_2 e^{i\gamma} \langle \epsilon_3^* \cdot \epsilon_1 \rangle \langle \epsilon_3^* \cdot \epsilon_2 \rangle \langle m | \rho(q_1) | n \rangle \langle n | \rho(q_1) | m \rangle \langle m | \rho(q_2) | n \rangle \langle n | \rho(q_2) | m \rangle \\\n\times \delta(E - E_n + E_m). \tag{5.10}
\]

Upon inspection of Eq. 5.10, we note that the expressions

\[
\sum_{n,m} b_m |\langle n | \rho(q_1) | m \rangle|^2 \delta(E - E_n + E_m) \\
\sum_{n,m} b_m |\langle n | \rho(q_2) | m \rangle|^2 \delta(E - E_n + E_m)
\]

are the standard diagonal dynamic structure factors \(S(q_1, \omega)\) and \(S(q_2, \omega)\), respectively, so we can rewrite the equation more compactly as

\[
\frac{d^2 \sigma}{dE' d\Omega} = \left( \frac{e^2}{mc^2} \right)^2 \frac{\omega_3}{\omega_1} \left[ g_1^2 |\epsilon_3^* \cdot \epsilon_1|^2 S(q_1, \omega) + g_2^2 |\epsilon_3^* \cdot \epsilon_2|^2 S(q_2, \omega) \right] \\
+ g_1 g_2 e^{i\gamma} \langle \epsilon_3^* \cdot \epsilon_1 \rangle \langle \epsilon_3^* \cdot \epsilon_2 \rangle S(q_1, q_2, \omega) \\
+ g_1 g_2 e^{-i\gamma} \langle \epsilon_3^* \cdot \epsilon_1 \rangle \langle \epsilon_3^* \cdot \epsilon_2 \rangle S(q_2, q_1, \omega), \tag{5.11}
\]

where \(\omega = \omega_1 - \omega_3\), the energy transferred to the sample, and we have defined a nondiagonal, generalized dynamic structure factor

\[
S(q_1, q_2, \omega) = \sum_{n,m} b_m \langle m | \rho(q_1) | n \rangle \langle n | \rho(-q_2) | m \rangle \times \delta(h\omega - E_n + E_m). \tag{5.12}
\]

This quantity, which we will see is related to the desired off-diagonal components of the susceptibility, \(\chi(q_1, -q_2, \omega)\), in principle can be extracted from the scattered intensity by taking measurements at multiple values of the phase shift, \(\gamma\), subtracting the diagonal structure factor terms, and properly normalizing.\,[70, 74] It should therefore be possible in this manner to fully isolate the nondiagonal response of the system.

### 5.3 Generalized Fluctuation Dissipation Theorem

We now wish to make a connection between the generalized dynamic structure factor, \(S(q_1, q_2, \omega)\), and the response function, \(\chi(q_1, q_2, \omega)\), for an inhomogeneous but periodic system, which is defined in real space as a quantum
mechanical thermal average,
\[
\chi(x_1, x_2, t_1, t_2) = -\frac{i}{\hbar} \sum_m b_m \langle m | [\rho(x_1, t_1), \rho(x_2, t_2)] | m \rangle \theta(t_1 - t_2). \tag{5.13}
\]

Here, \(\theta(t)\) is the Heaviside step function. Transforming into momentum and frequency space, we have
\[
\text{Im} \chi(p_1, p_2, \omega) = -\pi \sum_{n,m} b_m \langle m | \rho(p_1) | n \rangle \langle n | \rho(p_2) | m \rangle \delta(-\hbar \omega + E_n - E_m)
\]
\[
-\langle m | \rho(p_2) | n \rangle \langle n | \rho(p_1) | m \rangle \delta(-\hbar \omega - E_n + E_m) \tag{5.14}
\]
where \(\omega = \omega_1 - \omega_2\) (note that in Eq. 5.14, \(\omega_1\) and \(\omega_2\) are the frequency representations of, respectively, \(t_1\) and \(t_2\), and we will show their relationship to the \(\omega_1\) and \(\omega_2\) of Section 5.2) and the \(|m\rangle\) are again many-body eigenstates of the electronic system. We can compare Eq. 5.14 with Eq. 5.12 and substitute in \(S\) to get
\[
\text{Im} \chi(q_1, q_2, \omega) = -\pi S(q_1, -q_2, \omega)
\]
\[
+\pi \sum_{n,m} b_m \langle m | \rho(q_2) | n \rangle \langle n | \rho(q_1) | m \rangle \delta(-\hbar \omega - E_n + E_m). \tag{5.15}
\]

Switching the indices \(n\) and \(m\) in the second term and noting that \(b_n = b_m e^{-\beta \hbar \omega}\), we arrive at
\[
S(q_1, q_2, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\beta \hbar \omega}} \text{Im} \chi(q_1, -q_2, \omega). \tag{5.16}
\]
This expression is a generalized form of the fluctuation-dissipation theorem, and is very similar to the usual fluctuation-dissipation theorem Eq. 5.1. Note that the standing wave constraint \(k_2 = k_1 + G\) implies the constraint \(p_2 = G - p_1\) on the accessible components of \(\chi(p_1, p_2, \omega)\). From now on, we will use \(q\)'s when referring to the momentum transfers in an actual experiment, and \(p\)'s when referring to the momentum variables in the Fourier transform of \(\chi(x_1, x_2, \omega)\), with \(q_1 = p_1\) and \(q_2 = -p_2\).

### 5.4 Quantum particle in a periodic potential

We now address the question of whether standing wave IXS can provide, at least in principle, enough information to carry out a full refinement of the charge propagator, \(\chi(x_1, x_2, t)\). We begin by pointing out that the experimental constraint for standing waves of \(k_2 = k_1 + G\) is not, upon closer consideration, as severe
a restriction as it may seem. First, we expand $\chi$ in its Fourier components,

$$\chi(x_1, x_2, t) = \int \frac{dp_1 dp_2}{(2\pi)^6} \chi(p_1, p_2, t)e^{ip_1 \cdot x_1 + ip_2 \cdot x_2}.$$  

(5.17)

If one imposes the constraint that the system is periodic

$$\chi(x_1, x_2, t) = \chi(x_1 + R, x_2 + R, t),$$  

(5.18)

where $R$ is a Bravais vector of the real space lattice, one finds

$$p_2 = G - p_1.$$  

(5.19)

Because $-G$ is also a reciprocal lattice vector, we can also write $p_2 = -G - p_1$, which then exactly reproduces the standing wave condition $k_2 = k_1 + G$ using our definitions of the momentum variables from Eq. 5.16. In other words, while not all combinations of vectors $p_1$ and $p_2$ are experimentally accessible in a standing wave approach, all combinations that are independent in terms of crystal symmetry are accessible.

The question, then, is whether there is enough experimental flexibility in the variable $k$, given a fixed value of $G$. To answer this question, we consider the specific case of a single quantum particle traveling in a periodic array of harmonic potential wells of strength $\nu$,

$$V(x) = \sum_R \nu |x - R|^2 \theta(r_0 - |x - R|),$$  

(5.20)

where $\theta(r)$ is again the Heaviside step function. For simplicity we assume the system is simple cubic with lattice parameter $a$, i.e., $R = (n_x a, n_y a, n_z a)$, but our conclusions should apply much more generally. $r_0$ is the radius of each well. The lowest tight-binding band in this model exhibits the dispersion

$$\omega(k) = 2t_h(1 - \cos(k_x a) - \cos(k_y a) - \cos(k_z a))$$  

(5.21)

where $t_h$ is the hopping parameter between wells. The electron field operator for this case is

$$\Psi(x) = \frac{1}{\sqrt{N}} \sum_k c_k \psi_k(x)$$  

(5.22)

where $\psi_k(x) = \sum_R \phi(x - R)e^{ik \cdot R}$ is the tight-binding wavefunction of momentum $k$, with $k = 0$ corresponding to the wave vector of the zero-temperature ground state $|0\rangle$. $c_k$ is the annihilation operator for the single electron state $\psi_k$. $N$ is the number of wells in our model. For sufficiently deep wells, the tight binding orbitals for the potential from Eq. 5.20 are

$$\phi(x) = (\pi\sigma^2)^{-\frac{d}{4}} e^{-\frac{|x|^2}{2\sigma^2}}$$  

(5.23)
where $d$ is the dimensionality of the system.

What we wish to determine are the values of $q_1$ and $q_2$ at which it is necessary, in this model, to measure the generalized dynamic structure factor, $S(q_1, q_2, \omega)$, to perform a reconstruction of the complete $\chi(x_1, x_2, t)$. Because the bands disperse, the scattered intensity depends not just on $q_1$ and $q_2$, but also on the value of the transferred energy, $\omega$, resulting in a problem that is in principle seven dimensional. To simplify the analysis, we define an auxiliary quantity

$$\xi(p_1, p_2) = \hbar \int_0^\infty d\omega \sum_{n,m} b_m \langle m | \rho(p_1) | n \rangle \langle n | \rho(p_2) | m \rangle \delta(-\hbar \omega + E_n - E_m)$$

$$(5.24)$$

where we have taken the zero-temperature limit ($b_0 = 1$ and $b_m \neq 0 = 0$) for simplicity. The quantity $\xi$ is a measure of the total amount of spectral weight to be found at a given combination of $p_1$ and $p_2$, irrespective of the value of $\omega$. In terms of the momentum states

$$\xi(p_1, p_2) = \sum_k \langle 0 | \rho(p_1) | k \rangle \langle k | \rho(-p_2) | 0 \rangle,$$

$$(5.25)$$

where $|k\rangle$ denotes the electron in a momentum eigenstate $\psi_k(x)$.

In momentum space, the density operator $\rho(x) = \Psi^\dagger(x)\Psi(x)$ is

$$\rho(p) = \frac{\tilde{\Phi}(p)}{N} \sum_{p'p''G} c^\dagger_{p'} c_{p''} e^{-i(p'-p''+p) \cdot R},$$

$$(5.26)$$

where $\tilde{\Phi}(p)$ is the fourier transform of $|\phi(x)|^2$. Note that because $|\phi(x)|^2$ is real, $\tilde{\Phi}(p) = \tilde{\Phi}^\dagger(-p)$. Because we have a periodic system, $\sum_R e^{-i(p'-p''+p) \cdot R}$ is non-zero only if the quantity $(p' - p'' + p) = G$, where $G$ is a reciprocal lattice vector. Eq. 5.26 reduces to

$$\rho(p) = \frac{\tilde{\Phi}(p)}{N} \sum_{p'p''G} c^\dagger_{p'} c_{p''} N \delta_{p'-p''+p,G}$$

$$(5.27)$$

Substituting Eq. 5.27 into Eq. 5.25

$$\xi(p_1, p_2) = \frac{\tilde{\Phi}(p_1) \tilde{\Phi}(p_2)}{N} \sum_{G_1, G_2} \delta_{G_1-G_2} \delta_{p_1-G_1, k}$$

$$(5.28)$$

Because any linear combination of reciprocal lattice vectors $G$ is itself a reciprocal lattice vector, the Kronecker delta term in Eq. 5.28 reproduces the
constraint \( p_2 = -p_1 - G \) for the auxiliary quantity \( \xi \) to be non-zero. Replacing the appropriate terms in Eq. 5.14, we get

\[
\text{Im} \chi(p_1, p_2, \omega) = \frac{\hat{\Phi}(p_2) \hat{\Phi}(p_1)}{\hbar} \left[ \sum_{G_1, G_2} \delta_{-p_1 - p_2, G_1 + G_2} \delta(\omega + \omega_{-p_1 - G}) - \sum_{G_1, G_2} \delta_{-p_1 - p_2, G_1 + G_2} \delta(\omega - \omega_{-p_1 - G}) \right].
\]

(5.29)

5.4.1 One-Dimensional Case

In the one-dimensional case, Eq. 5.20 describes a chain of harmonic wells. This case is not experimentally realizable, since it requires all the vectors in Fig. 5.2 to be collinear, which is impossible except in the limit of infinite energy. We can, however, draw several important conclusions about the functional form of \( \xi \) from this case.

In one dimension the momenta \( q_1 \) and \( q_2 \) are scalars, and the reciprocal lattice vectors \( G = 2\pi h/a \) are described by a single index, \( h \). The resulting value of \( \xi(q_1, -q_2) \) is illustrated in Fig. 5.3. In an aperiodic system, \( \xi \) is in principle nonzero for all values of \( q_1 \) and \( q_2 \). In a periodic system, however, the constraint \( q_2 = q_1 + G \) implies that \( \xi \) is nonzero only along the set of lines depicted in Fig. 5.3a.

Fig. 5.3b shows how the magnitude of \( \xi(q_1, -q_1 - G) \) varies, as a function of \( q_1 \), along a selection of these lines. Two important observations can be made from this plot. First, the intensity along a given line is not uniform, but has the shape of a Gaussian centered half-way between \( q_1 = 0 \) and \( q_1 = -G \), whose momentum width \( \Delta q_1 = \sigma^{-1} \). Second, the intensity varies from one line to the next, decaying with increasing \( |G| \), again with a Gaussian envelope with width \( \sigma^{-1} \).

From this simple case we see an important relationship between the degree of inhomogeneity of the system and the range of momenta that must be sampled experimentally to reconstruct \( \chi(x_1, x_2, t) \). The narrower the wells, i.e., the more inhomogeneous the system, the larger the number of \( G \) values that must be sampled, and the larger the range of \( q_1 \) that must be sampled for each \( G \). Hence, the number of \( G \) values that must be sampled is not infinite, but is of order \( a/\sigma \), which is a measure of the strength of local field effects. For the parameters chosen here, one need only sample up to \( h = 2 \) to acquire \( > 99\% \) of the spectral weight that is available. In the limiting case of a homogeneous system, \( \sigma \to \infty \), \( \xi \) is nonzero only for \( G = 0 \), and conventional IXS may be considered a complete parameterization of the response, as expected.
Figure 5.3: (a) Lines in the \((q_1, q_2)\) plane along which \(\xi(q_1, q_2)\) may be non-zero in the one-dimensional case. (b) Value of \(\xi(q_1, G - q_1)\) for a few selected values of \(G\).

\[
G = \frac{2\pi}{a}(2, 0)
\]

Figure 5.4: Relative magnitude and orientation for the experimental geometry in the two-dimensional, co-planar case. Here \(G = 2\pi(2, 0)/a\).
5.4.2 Two-Dimensional Case

In two dimensions, a standing wave experiment is physically realizable, and corresponds to all the rays in Fig. 5.2 lying in a single plane, i.e., $\Psi = 0$. In this case Eq. 5.20 describes a square, planar array of harmonic wells, the quantities $q_1$ and $q_2$ are two-component vectors, and the reciprocal lattice vectors $G = 2\pi(h,k)/a$ are described by two indices, $h$ and $k$.

The quantity $\xi(q_1, -q_2)$ is now a scalar function in four-dimensional space and is not easily illustrated. Extending reasoning from the one-dimensional case, however, we expect $\xi$ to be nonzero only along discrete, two-dimensional sections through this space, again defined by the constraint $q_2 = q_1 + G$. Moreover, we expect the magnitude of $\xi$ to decrease with increasing $|G|$, and to be substantial only for $\sqrt{h^2 + k^2} \leq 2$. By analogy with Fig. 5.3b, we plot in Fig. 5.5 several sections of $\xi(q_1, -q - G)$ for selected values of $G$. As in Fig. 5.3b, $\xi$ is a Gaussian function centered at the midpoint between $q_1 = 0$ and $q_1 = -G$, whose width is isotropic and equal to $\sigma^{-1}$.

Because the two-dimensional case is experimentally realizable, it is now possible to address the fundamental question of whether enough information is accessible with standing wave IXS to reconstruct $\chi(x_1, x_2, t)$. To do so, one must experimentally parameterize a set of two-dimensional surfaces, such as those illustrated in Fig. 5.5, each defined by a distinct $G$. For the experimental geometry defined in Fig. 5.2, the various momenta in sample coordinates are illustrated in Fig. 5.4 and are given by

$$q_2 = q_1 + G, \quad (5.30)$$

$$q_{1x} = -k_1 \sin(\eta) - k_3 \sin(\phi - \eta), \quad (5.31)$$

$$q_{1y} = k_1 \cos(\eta) - k_3 \cos(\phi - \eta), \quad (5.32)$$

$$q_{2x} = q_{1x} + G, \quad (5.33)$$

$$q_{2y} = q_{1y}, \quad (5.34)$$

where the $x$ and $y$ axes are defined with respect to the crystal axes of the sample (Fig. 2).

For a given choice of $G$, the angle of the beam with respect to the crystal is fixed by the Bragg condition. Hence, the only means of adjusting the momenta is to adjust the scattering angle of the IXS analyzer. Applying Eqs. 5.30-5.34, we see that this has the effect of tracing out a circular trajectory in momentum space, that has radius $k_1$ and intersects both the origin and $-G$. For illustrative purposes we display in Fig. 5.5 (black lines) each of these trajectories, for the specific case of an x-ray beam energy $E = 15.5 \, hc/a$.

Without any further examination, a serious problem is already evident. One

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$^3$Generally speaking, in $d$ dimensions $\xi$ is a scalar function residing in a $2d$-dimensional space, and the constraint $q_2 = q_1 + G$ defines a discrete set of $d$-dimensional sections through this space.
Figure 5.5: $\xi(q_1, G - q_1)$ plotted for the two-dimensional case against the two components $q_{1x}$ and $q_{1y}$ for several values of $G$. $\xi$ has the form of a Gaussian centered at the half-way point between $q_1 = 0$ and $q_1 = -G$. The solid lines are the contours traced out by rotating the IXS analyzer through 360°.

must experimentally parameterize two-dimensional surfaces such as those shown in Fig. 5.5, however the set of experimentally accessible points is only one-dimensional, corresponding to a cut through each of the needed surfaces. Hence, we are faced with a crisis of dimensionality: The set of accessible information is of lower dimensionality than what is needed to refine the susceptibility.

The dimensionality could be increased, of course, by adjusting also the beam energy, as illustrated in Fig. 5.6. This changes the radius of the circular section, in principle allowing one to sweep out a two-dimensional surface. Unfortunately, the nature of IXS is such that each incident energy (apart from modest amounts of tunability) requires a distinct experimental setup with a distinct energy analyzer. We conclude that the two-dimensional case of standing wave IXS imaging, while experimentally realizable, lacks the momentum flexibility to be useful for imaging.

5.4.3 Three-Dimensional Case

Finally, we address the three-dimensional case, in which Eq. 5.20 describes a cubic lattice of harmonic wells. All momenta now have three components, and
Figure 5.6: Contour shown in Fig. 5(b) for several values of the beam energy. Red, dashed green, and dotted blue contours correspond to $E = 12.3 \hbar c/a$, $E = 15.5 \hbar c/a$, and $E = 20.4 \hbar c/a$, respectively. Continuously tuning the beam energy in this manner can in principle trace out a two-dimensional surface, though doing so is prohibitively difficult experimentally.

the $G$ vectors are described by three indices, $h$, $k$, and $l$. $\xi(q_1, -q_2)$ is a scalar function in six-dimensional space, but periodicity dictates that it is nonzero only along discrete, three-dimensional contours parameterized by $q_2 = q_1 + G$. By analogy with the previous two cases, we expect the function $\xi(q_1, -q_1 - G)$ to be a Gaussian with width $\sigma^{-1}$ centered on the point $q_1 = -G/2$.

In terms of the measurement itself, two types of motions are now possible that were not available in either of the previous cases: (1) The analyzer may now be rotated in two directions, i.e., both parallel and perpendicular to the Bragg plane. (2) The sample may be rotated around an axis parallel to $-G$, changing the sample angles while maintaining the Bragg condition. The latter motion is usually referred to as a “$\Psi$ rotation”.

The analyzer motion, which is now two-dimensional, traces out a spherical shell in $q_1$ space. As in the two-dimensional case, this sphere has radius $k_1$ and intersects both the origin and the point $q_1 = -G$. As before, this section is of lower dimensionality than the space spanned by the function $\xi(q_1, -q_1 - G)$. An additional degree of freedom is needed to make the dimensionality of the measurement match the that of the $\xi$ function.

This degree of freedom is supplied by the $\Psi$ rotation. Rotating the crystal around the Bragg vector (i.e., maintaining the Bragg condition) has the effect of sweeping the spherical shell around an axis defined by the line connecting the origin and $q_1 = -G$. In this manner, the shell sweeps out a three-dimensional volume in momentum space. The volume swept out is a torus, with major radius $\sqrt{k_1^2 - G^2}$ and minor radius $k_1$, as illustrated in Fig. 7. A plot of the intersection of this torus with a constant-contour plot of $\xi(q_1, -q_1 - G)$ is shown in Fig. 5.8. We conclude that the crisis of dimensionality encountered in the two-dimensional case does not take place here, and that standing wave IXS imaging – in principle – should be a viable technique in the real world of three dimensions.
Figure 5.7: Toroidal volume swept out by combined rotation of the two detector motions and the sample azimuth, Ψ, in the three-dimensional case. The center contains a blind spot whose shape is a vesica piscis swept through its major symmetry axis. This blind spot may be made arbitrarily small by increasing the beam energy.

While the dimensionality of the experiment is adequate, the three-dimensional case has some blind spots. As one might expect, information outside the torus shown in Fig. 5.8 is not accessible. This is the standing-wave manifestation of the well-known diffraction limit, which says that it is not possible in a scattering experiment to extract information about features smaller than half a wavelength.

Second, and less intuitively, there is a blind spot in the center of the torus (see Fig. 5.7) whose shape is a three-dimensional vesica piscis with axis length $|G|$ and major radius $k_1 - \sqrt{k_1^2 - G^2}$. It remains to be determined whether this inner blind spot poses a serious limitation on using standing wave IXS for imaging. We note, however, that the radius of the blind spot goes to zero as $k_1 \to \infty$, so it can always be made arbitrarily small experimentally by raising the beam energy.

5.5 Conclusions

To summarize, we have found that standing wave measurements are, in principle, a viable approach to overcoming the translational averaging problem[69] in IXS imaging.[66, 67] If successfully implemented, this approach would reveal the complete density response, $\chi(x_1, x_2, t)$, which describes the electron disturbance created by a source placed at any arbitrary location, $x_2$, in a spatially inhomogeneous but periodic system – typically with Angstrom spatial and attosecond time resolution. This technique can be thought of as a generalization of x-ray crystallography that allows refinement of the excited states of a periodic system, rather than just its ground state, and represents the maximum that can be learned by interaction of light with matter in the regime of linear response. This technique would be most useful for imaging excitations in very inhomogeneous systems, such as molecular crystals, in which local field effects
are significant and transverse excitations, such as transverse plasmons, can be important.

Analyzing a simple model of a single quantum particle in a periodic potential, we have shown that standing wave IXS imaging is an innately three-dimensional measurement, in the sense that both out-of-plane analyzer motions and sample Ψ-rotations are required to achieve a complete data set. Such an experiment would require (at the minimum) two copies of the crystal of interest: one that is asymmetrically cut to collimate the beam, and a second to create the standing wave field and function as the “sample”. The scattering experiment would then require six rotation axes: a conventional three-axis sample goniometer, a single-axis, two-theta rotation supporting an energy-integrating detector for measuring the Bragg diffracted beam, and a second two-theta rotation, with both in- and out-of-plane degrees of freedom, supporting a backscattering, IXS analyzer.

One might at first glance think that the data collection time required to refine, for example, the three-dimensional $\chi(x_1, x_2, t)$ for a molecular crystal would be enormous. Specifically, suppose one were studying a molecular crystal whose ground state density had been refined with conventional x-ray crystallography, to a resolution providing $N$ cartesian voxels in each unit cell. Such a refinement would have required of order $N$ independent Bragg measurements (unless other information about the structure, such as its symmetry, were known). To refine $\chi(x_1, x_2, t)$ for this structure with the same resolution, because the response is a function of both source and observation coordinates, would require of order $N^2$ measurements at a single time slice. To construct the complete dynamics, then, requires $N^2 N_t$ measurements, where $N_t$ is the number of points in the time series. This number is, without a doubt, impractically large nearly all conceivable cases.

Figure 5.8: Intersection of the toroidal measurement volume shown in Fig. 7 with a constant-contour plot of $\xi(q_1, -q_1 - G)$.
The time considerations, however, need not be so severe. For example, if one fixes $x_2$, i.e., if one decides before the measurement where to “strike” the molecule, the number of unknowns reduces to $NN_i$. Further, as in x-ray crystallography, knowledge of symmetry further reduces the number of unknowns. For example, all four of the independent measurements in Fig. 5.6, which are related by symmetry, would reveal the same experimental result; this could have been anticipated ahead of time from the crystal symmetry. Other tricks, such as taking one- or two-dimensional projections, compromising the resolution by probing only small order $G$ values, etc., are always possible in specific cases. Hence, we expect the data collection time to be no more intensive than the spatially-averaged IXS imaging, which has already been demonstrated.[5, 67, 68]

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Appendix A

Graphene Band Structure

We consider wavefunctions of the form
\[ |\psi^A_{n}\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot R^A_n} |\psi^A_k\rangle, \]
\[ |\psi^B_{n}\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot R^B_n} |\psi^B_k\rangle \quad (A.1) \]

with their inverses
\[ |\psi^A_k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R^A_n} |\psi^A_n\rangle, \]
\[ |\psi^B_k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R^B_n} |\psi^B_n\rangle \quad (A.2) \]

where \(|\psi^A_n\rangle\) is the localized Wannier orbital at site \(R^A_n\). The lattice vectors can be written as
\[ \mathbf{a}_1 = \frac{a}{2} (3, \sqrt{3}) \quad , \quad \mathbf{a}_2 = \frac{a}{2} (3, -\sqrt{3}), \quad (A.3) \]

and the reciprocal lattice vectors are given by
\[ \mathbf{b}_1 = \frac{2\pi}{3a} (1, \sqrt{3}) \quad , \quad \mathbf{b}_2 = \frac{2\pi}{3a} (1, -\sqrt{3}). \quad (A.4) \]

The hamiltonian for this system considering nearest-neighbor interactions can be written as
\[ \hat{H} = -t \sum_{(i,j)} (\hat{a}^+_i \hat{b}_j + \hat{b}^+_j \hat{a}_i) \quad (A.5) \]

where the operators \(\hat{a}_i(\hat{b}_j)\) annihilate the states \(|\psi^A_i\rangle (|\psi^B_j\rangle\). In tight binding, we assume eigenfunctions of the form
\[ H |\psi_k\rangle = \epsilon(k) |\psi_k\rangle \quad (A.6) \]

where \(|\psi_k\rangle = c^A(k) |\psi^A_k\rangle + c^B(k) |\psi^B_k\rangle\). Taking the matrix elements \(\langle \psi^A_B | H | \psi_k \rangle\), we get the eigenvalue equation
\[ \begin{pmatrix} \langle \psi^A_k | H | \psi^A_k \rangle & \langle \psi^A_k | H | \psi^B_k \rangle \\ \langle \psi^B_k | H | \psi^A_k \rangle & \langle \psi^B_k | H | \psi^B_k \rangle \end{pmatrix} \begin{pmatrix} c^A(k) \\ c^B(k) \end{pmatrix} = \epsilon(k) \begin{pmatrix} c^A(k) \\ c^B(k) \end{pmatrix}, \quad (A.7) \]
In graphene, there are three nearest neighbor vectors $\mathbf{R}^A - \mathbf{R}^B = \delta_i$
\[ \delta_1 = \frac{a}{2}(1, \sqrt{3}) \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}) \quad \delta_3 = -a(1, 0). \] (A.8)

If we consider the matrix element $\langle \psi_A^k | H | \psi_B^k \rangle$, we see that
\[ \langle \psi_A^k | H | \psi_B^k \rangle = -t \sum_{(i,j), n,m} e^{-ik \cdot (\mathbf{R}^A_n - \mathbf{R}^B_m)} \langle \Omega | e^{ik \cdot \mathbf{R}^A_n a_n a_i \mathbf{b}_j b_m e^{ik \cdot \mathbf{R}^B_m} | \Omega \rangle = -t \sum_{i=1}^3 e^{-ik \cdot \delta_i}. \] (A.9)

For simplicity, we define the quantity
\[ \phi_I(k) = \sum_{i=1}^3 e^{-ik \cdot \delta_i}, \] (A.10)

which allows us to write eigenvalue equation as
\[ \begin{pmatrix} 0 & -t \phi_I(k) \\ -t \phi_I(k)^* & 0 \end{pmatrix} \begin{pmatrix} c^A(k) \\ c^B(k) \end{pmatrix} = \epsilon(k) \begin{pmatrix} c^A(k) \\ c^B(k) \end{pmatrix}, \] (A.11)

which gives us the following expression for the conduction and valence bands:
\[ \epsilon_c(k) = +t|\phi_I(k)| \quad |\psi_c(k)\rangle = \frac{1}{\sqrt{2}} \left( \frac{\phi_I(k)}{|\phi_I(k)|} |\psi_A^k\rangle + |\psi_B^k\rangle \right), \]
\[ \epsilon_v(k) = -t|\phi_I(k)| \quad |\psi_v(k)\rangle = \frac{1}{\sqrt{2}} \left( \frac{\phi_I(k)}{|\phi_I(k)|} |\psi_A^k\rangle - |\psi_B^k\rangle \right). \] (A.12)

More explicitly, the energy can be written as
\[ \epsilon(k) = \pm \sqrt{3 + 2 \cos(\sqrt{3}k_y a) + 4 \cos \left( \frac{3k_x a}{2} \right) \cos \left( \frac{\sqrt{3}k_y a}{2} \right)}. \] (A.13)
Appendix B

Graphite Band Structure

The Hamiltonian of ABA graphite is simply

\[
H = -t \sum_{l,(i,j)} \left[ a_{i,l}^\dagger b_{j,l} + b_{j,l}^\dagger a_{i,l} \right] \\
- \gamma_1 \left[ \sum_{l_{even},\langle j,j \rangle} \left[ a_{j,l}^\dagger b_{j',l+1} + b_{j',l+1}^\dagger a_{j,l} \right] \right] \\
+ \sum_{l_{odd},\langle j,j \rangle} \left[ b_{j,l}^\dagger a_{j',l+1} + a_{j',l+1}^\dagger b_{j,l} \right] \\
- \gamma_3 \left[ \sum_{l_{even},\langle (j,j') \rangle} \left[ b_{j,l}^\dagger a_{j',l+1} + a_{j',l+1}^\dagger b_{j,l} \right] \right] \\
+ \sum_{l_{odd},\langle (j,j') \rangle} \left[ a_{j,l}^\dagger b_{j',l+1} + b_{j',l+1}^\dagger a_{j,l} \right] 
\]  

(B.1)

where the sum is taken over nearest neighbors \( \langle i, j \rangle \) and the layers \( l \). The hopping parameter \( \gamma_1 \) is the vertical hopping between the A and B sublattice points (indicated by the double brackets), and \( \gamma_3 \) is the nearest A and B interlayer coupling (indicated by the triple brackets).

Instead of just two species of wavefunctions as in graphite, we now have four kinds of wavefunction, each associated with either the A or B sublattice.
on either an odd- or even-numbered layer. Thus we have the wavefunctions

\[
|\psi^{A}_{n,2l}\rangle = \frac{1}{\sqrt{N_{\text{even}}}} \sum_{k} e^{-i k \cdot R^{A}_{n,2l}} |\psi^{A}_{k,\text{even}}\rangle,
\]
\[
|\psi^{A}_{n,2l+1}\rangle = \frac{1}{\sqrt{N_{\text{odd}}}} \sum_{k} e^{-i k \cdot R^{A}_{n,2l+1}} |\psi^{A}_{k,\text{odd}}\rangle,
\]
\[
|\psi^{B}_{n,2l}\rangle = \frac{1}{\sqrt{N_{\text{even}}}} \sum_{k} e^{-i k \cdot R^{B}_{n,2l}} |\psi^{B}_{k,\text{even}}\rangle,
\]
\[
|\psi^{B}_{n,2l+1}\rangle = \frac{1}{\sqrt{N_{\text{odd}}}} \sum_{k} e^{-i k \cdot R^{B}_{n,2l+1}} |\psi^{B}_{k,\text{odd}}\rangle
\]

with their inverses

\[
|\psi^{A}_{k,\text{even}}\rangle = \frac{1}{\sqrt{N_{\text{even}}}} \sum_{n,l} e^{i k \cdot R^{A}_{n,2l}} |\psi^{A}_{n,2l}\rangle,
\]
\[
|\psi^{A}_{k,\text{odd}}\rangle = \frac{1}{\sqrt{N_{\text{odd}}}} \sum_{n,l} e^{i k \cdot R^{A}_{n,2l+1}} |\psi^{A}_{n,2l+1}\rangle,
\]
\[
|\psi^{B}_{k,\text{even}}\rangle = \frac{1}{\sqrt{N_{\text{even}}}} \sum_{n,l} e^{i k \cdot R^{B}_{n,2l}} |\psi^{B}_{n,2l}\rangle,
\]
\[
|\psi^{B}_{k,\text{odd}}\rangle = \frac{1}{\sqrt{N_{\text{odd}}}} \sum_{n,l} e^{i k \cdot R^{B}_{n,2l+1}} |\psi^{B}_{n,2l+1}\rangle
\]

where the \(l\)'s are summed over a range that covers all the layers. \(N\) is still the total number of \(A\) or \(B\) sites in each layer, and \(L_{\text{even(odd)}}\) is the number of layers of the even or odd subsystem (total layers are counted from 1 to \(L\) from the bottom to the top of the stack as in Fig. B.1). For simplicity, we will abbreviate \(|\psi^{A/B}_{k,\text{even}}\rangle\) as \(|\psi^{A/B}_{k,e}\rangle\) and \(|\psi^{A/B}_{k,\text{odd}}\rangle\) as \(|\psi^{A/B}_{k,o}\rangle\). The lattice vectors can be written as

\[
a_{1} = \frac{a}{2}(3, \sqrt{3}, 0) \quad , \quad a_{2} = \frac{a}{2}(3, -\sqrt{3}, 0) \quad , \quad a_{3} = c(0, 0, 1)
\]

with the basis \((0,0,0)\) and \((a,0,c/2)\) for the \(B\) sublattice and \((-a,0,0)\) and \((0,0,c/2)\) for the \(A\) sublattice. and the reciprocal lattice vectors are given by

\[
b_{1} = \frac{2\pi}{3a}(1, \sqrt{3}, 0) \quad , \quad b_{2} = \frac{2\pi}{3a}(1, -\sqrt{3}, 0) \quad , \quad b_{3} = \frac{2\pi}{c}(0,0,1)
\]

The lattice constants are \(a = 1.42\text{Å}\)and \(c = 6.7\text{Å}\). In tight binding, we assume eigenfunctions of the form

\[
H |\psi_{k}\rangle = \epsilon(k) |\psi_{k}\rangle
\]

where

\[
|\psi_{k}\rangle = \epsilon^{A}(k) |\psi^{A}_{k,e}\rangle + \epsilon^{B}(k) |\psi^{B}_{k,e}\rangle + \epsilon^{A}_{o}(k) |\psi^{A}_{k,o}\rangle + \epsilon^{B}_{o}(k) |\psi^{B}_{k,o}\rangle
\]
the matrix elements \( \langle \psi_{k,c/e}^A/B | H | \psi_k \rangle \), we get the eigenvalue equation

\[
\begin{pmatrix}
\langle \psi_{k,c}^A | H | \psi_{k,c}^A \rangle & \langle \psi_{k,c}^A | H | \psi_{k,e}^A \rangle & \langle \psi_{k,c}^A | H | \psi_{k,o}^A \rangle & \langle \psi_{k,e}^A | H | \psi_{k,c}^A \rangle & \langle \psi_{k,e}^A | H | \psi_{k,e}^A \rangle & \langle \psi_{k,e}^A | H | \psi_{k,o}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,c}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,e}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,o}^A \rangle \\
\langle \psi_{k,e}^A | H | \psi_{k,c}^A \rangle & \langle \psi_{k,e}^A | H | \psi_{k,e}^A \rangle & \langle \psi_{k,e}^A | H | \psi_{k,o}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,c}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,e}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,o}^A \rangle \\
\langle \psi_{k,o}^A | H | \psi_{k,c}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,e}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,o}^A \rangle & \langle \psi_{k,c}^B | H | \psi_{k,c}^B \rangle & \langle \psi_{k,c}^B | H | \psi_{k,e}^B \rangle & \langle \psi_{k,c}^B | H | \psi_{k,o}^B \rangle & \langle \psi_{k,e}^B | H | \psi_{k,c}^B \rangle & \langle \psi_{k,e}^B | H | \psi_{k,e}^B \rangle & \langle \psi_{k,e}^B | H | \psi_{k,o}^B \rangle \\
\langle \psi_{k,o}^A | H | \psi_{k,o}^A \rangle & \langle \psi_{k,o}^A | H | \psi_{k,e}^B \rangle & \langle \psi_{k,o}^A | H | \psi_{k,e}^B \rangle & \langle \psi_{k,c}^B | H | \psi_{k,c}^B \rangle & \langle \psi_{k,c}^B | H | \psi_{k,e}^B \rangle & \langle \psi_{k,c}^B | H | \psi_{k,o}^B \rangle & \langle \psi_{k,e}^B | H | \psi_{k,c}^B \rangle & \langle \psi_{k,e}^B | H | \psi_{k,e}^B \rangle & \langle \psi_{k,e}^B | H | \psi_{k,o}^B \rangle
\end{pmatrix} \times
\begin{pmatrix}
c_c^A(k) \\
c_c^B(k) \\
c_o^A(k) \\
c_o^B(k)
\end{pmatrix} = \epsilon(k) \begin{pmatrix}
c_c^A(k) \\
c_c^B(k) \\
c_o^A(k) \\
c_o^B(k)
\end{pmatrix},
\tag{B.7}
\]

Within a single graphene layer, there are three nearest neighbor vectors \( \mathbf{R}^A - \mathbf{R}^B = \delta_i \)

\[
\delta_1 = \frac{a}{2}(1, \sqrt{3}, 0) \quad , \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}, 0) \quad , \quad \delta_3 = -a(1, 0, 0). \tag{B.8}
\]

The relevant interlayer nearest neighbor vectors are

\[
\mathbf{R}_{j,c/e}^B - \mathbf{R}_{j,o}^A = \pm \left(0, 0, \frac{c}{2}\right) + \delta_i \quad , \quad \text{(coupled by } \gamma_3),
\]

\[
\mathbf{R}_{j,c/e}^A - \mathbf{R}_{j,o}^B = \pm \left(0, 0, \frac{c}{2}\right) \quad , \quad \text{(coupled by } \gamma_1) \tag{B.9}
\]

as shown in Fig. B.1. In essence, the \( \gamma_1 \) coupling relates a \( B \) atom of layer \( l \) to the \( A \) atom directly below it in the \( l+1 \) layer, and the \( \gamma_3 \) coupling relates an \( A \) atom of layer \( l \) to the 3 \( B \) atoms that are closest to it in the \( l+1 \) layer. Because the \( A \) atom in layer \( l \) is directly above the center of the hexagon in layer \( l+1 \), these relations are simple to see.

We now need to compute the matrix elements in Eq. B.7, and we need only compute the upper or lower diagonal due to the hermiticity of the matrix. The on-diagonal terms are again all zero because we ignore the on-site potential. We also already know the intralayer terms like \( \langle \psi_{k,c}^A | H | \psi_{k,c}^A \rangle \) because they are just the graphene matrix elements (there are no next-nearest layer hoppings to consider in addition to the graphene terms) in the approximation that the graphene sheets are infinitely large. Lastly, it is clear from the hamiltonian that we ignore interlayer hopping from \( A \) to \( A \) sublattices and similarly for \( B \), so we can ignore the matrix elements like \( \langle \psi_{k,c}^A | H | \psi_{k,c}^B \rangle \). We therefore need only compute the matrix elements that involve interlayer hopping between \( B \) and \( A \) sublattices. Here are all the relevant non-zero interlayer matrix elements for an even, odd, and infinite number of layers \( L \) (ignoring creation/annihilation
operator combinations that return 0): 

\[
\langle \psi_{k,e}^A | H | \psi_{k,o}^B \rangle_{L_o} = - \frac{\gamma_1}{N \sqrt{L_2 l_2 L_{2l+1}}} \sum_{n,l',n''} \langle \Omega | e^{-ik \cdot R^A_{n,2l'}} a_{n,2l'} \\
\times \left( a_{j,l}^\dagger b_{j',l''} + a_{j',l''}^\dagger b_{j,l} \right) b_{m,2l'+1}^\dagger e^{ik \cdot R^B_{m,2l'+1}} | \Omega \rangle \\
- \frac{\gamma_1}{N \sqrt{L_2 l_2 (L_2 l_2 + 1)}} \left[ \sum_{(j,j'),l''} \langle \Omega | e^{-ik \cdot R^A_{j,2l''}} e^{ik \cdot R^B_{j',2l'+1}} | \Omega \rangle \\
+ \sum_{(j,j'),l''} \langle \Omega | e^{-ik \cdot R^A_{j,2l''+2}} e^{ik \cdot R^B_{j',2l'+1}} | \Omega \rangle \right] \\
= - \frac{N \gamma_1}{N \sqrt{L_2 l_2 (L_2 l_2 + 1)}} \left[ \sum_{l''=1}^{L_2 l_2} \langle \Omega | e^{ik_z c/2} | \Omega \rangle + \sum_{l''=0}^{L_2 l_2 - 1} \langle \Omega | e^{-ik_z c/2} | \Omega \rangle \right] \\
= - \frac{\gamma_1 (L - 1) \cos(k_z c/2)}{\sqrt{L_2 l_2 (L_2 l_2 + 1)}}, \tag{B.10}
\]

\[
\langle \psi_{k,e}^A | H | \psi_{k,o}^B \rangle_{L_o} = - \frac{\gamma_1}{N \sqrt{L_2 l_2 L_{2l+1}}} \sum_{n,l',n''} \langle \Omega | e^{-ik \cdot R^A_{n,2l'}} a_{n,2l'} \\
\times \left( a_{j,l}^\dagger b_{j',l''} + a_{j',l''}^\dagger b_{j,l} \right) b_{m,2l'+1}^\dagger e^{ik \cdot R^B_{m,2l'+1}} | \Omega \rangle \\
= - \frac{2N \gamma_1}{NL} \left[ \sum_{l''=1}^{L_2 l_2} \langle \Omega | e^{ik_z c/2} | \Omega \rangle + \sum_{l''=0}^{L_2 l_2 - 1} \langle \Omega | e^{-ik_z c/2} | \Omega \rangle \right] \\
= - \frac{2 \gamma_1}{L} \left[ \left( \frac{L - 2}{2} \right) e^{ik_z c/2} + \left( \frac{L - 2}{2} + 1 \right) e^{-ik_z c/2} \right] \\
= - \frac{2 \gamma_1}{L} \left[ (L - 2) \cos \left( \frac{k_z c}{2} \right) + e^{-ik_z c/2} \right], \tag{B.11}
\]
\begin{align}
\langle \psi_{k,e}^A | H | \psi_{k,o}^B \rangle_{L_\infty} &= - \frac{\gamma_1}{N L^{2L} | L^{2L} + 1 \rangle \sum_{n,j',m,l''} \langle \Omega | e^{-ik R_{n,2l'}} a_{n,2l'} \\
&\quad \times \left( a_{j',l'}^\dagger b_{j,l'+1} + a_{j,l'+1} | b_{j',l}^\dagger \right) b_{m,2l''+1}^\dagger e^{ik R_{m,2l''+1}} | \Omega \rangle \\
&= - \frac{2N\gamma_1}{NL} \left[ \sum_{\mu'=1}^{2} \langle \Omega | e^{ik z c/2} | \Omega \rangle + \sum_{\mu'=0}^{2} \langle \Omega | e^{-ik z c/2} | \Omega \rangle \right] \\
&= - \frac{2\gamma_1}{L} \left( \frac{L}{2} e^{ik z c/2} + \frac{L}{2} e^{-ik z c/2} + e^{-ik e c/2} \right) \frac{1}{2} \rightarrow 0 \\
&= - 2 \cos \left( \frac{k_z c}{2} \right) \gamma_1, \tag{B.12}
\end{align}

\begin{align}
\langle \psi_{k,e}^B | H | \psi_{k,o}^A \rangle_{L_0} &= - \frac{\gamma_3}{N L^{2L} | L^{2L} + 1 \rangle \sum_{n,j',m,l''} \langle \Omega | e^{-ik R_{n,2l'}^B} b_{n,2l'} \\
&\quad \times \left( b_{j',l'}^\dagger a_{j,l'+1} + b_{j,l'+1} | a_{j',l}^\dagger \right) a_{m,2l''+1}^\dagger e^{ik R_{m,2l''+1}^A} | \Omega \rangle \\
&= - \frac{\gamma_3}{N L^{2L} | L^{2L} + 1 \rangle \sum_{\langle (j,j') \rangle, l'} \langle \Omega | e^{-ik R_{2l'},2l''} e^{ik R_{2l',2l''+1}} | \Omega \rangle \\
&\quad \sum_{\langle (j,j') \rangle, l''} \langle \Omega | e^{-ik R_{2l'},2l''} e^{ik R_{2l',2l''+1}} | \Omega \rangle \\
&= - \frac{N\gamma_3}{N L^{2L} | L^{2L} + 1 \rangle \sum_{\langle (j,j') \rangle, l'} \langle \Omega | e^{ik z c/2} e^{-ik z c} | \Omega \rangle \\
&\quad \sum_{\langle (j,j') \rangle, l''} \langle \Omega | e^{ik z c/2} e^{-ik z c} | \Omega \rangle \\
&= - \frac{\gamma_3}{L^{2L} | L^{2L} + 1 \rangle \left[ \left( \frac{L-1}{2} \right) e^{ik z c/2} \right. \\
&\quad + \left. \left( \frac{L-3}{2} + 1 \right) e^{-ik z c/2} \right] \sum_i e^{-ik \delta_i} \\
&= - \frac{\gamma_3 (L-1) \cos(k_z c/2)}{\sqrt{L^{2L} | L^{2L} + 1 \rangle}} \sum_i e^{-ik \delta_i}, \tag{B.13}
\end{align}
We can further simplify these expressions by defining a quantity related to the number of layers $L$ and $k$:

$$f(k, L) = \begin{cases} 
(L - 1) \cos(k_z c/2) \left[ \frac{L - 1}{2} \left( \frac{k_z c}{2} + 1 \right) \right]^{-\frac{1}{2}}, & L \text{ odd} \\
\frac{2}{L} \left[ (L - 2) \cos \left( \frac{k_z c}{2} \right) + e^{-ik_z c/2} \right], & L \text{ even} \\
2 \cos \left( \frac{k_z c}{2} \right), & L \to \infty.
\end{cases}$$

We can further simplify these expressions by defining a quantity related to the number of layers $L$ and $k$:

$$\langle \psi_{k,c}^B | H | \psi_{k,o}^A \rangle_{L_o} \quad = - \frac{\gamma_3}{N \sqrt{L_2} L_{2l+1}} \sum_{n_{l'},m_{l''}} \langle \Omega \rangle \left[ e^{-ik \cdot R_{n_{l'},2l'}} b_{n_{l'},2l'} ight. \\
\times \left. \left( \hat{b}_{j,l}^\dagger a_{j',l'+1} + \hat{b}_{j',l'+1}^\dagger a_{j,l} \right) \hat{a}_{m_{l''},2l''+1}^\dagger e^{ik \cdot R_{m_{l''},2l''+1}} \right] | \Omega \rangle \\
= - \frac{2N \gamma_3}{L} \left[ \sum_{l'=0,i=1}^{L-3} e^{ik_z c/2} e^{-ik \cdot \delta_i} + \sum_{l''=0,j=1}^{L-2} e^{-ik_z c/2} e^{-ik \cdot \delta_i} \right] | \Omega \rangle \\
= - \frac{2\gamma_3}{L} \left[ \left( \frac{L - 2}{2} \right) e^{ik_z c/2} + \left( \frac{L - 2}{2} + 1 \right) e^{-ik_z c/2} \right] \sum_i e^{-ik \cdot \delta_i}, \quad (B.14)
$$

$$\langle \psi_{k,c}^B | H | \psi_{k,o}^A \rangle_{L_\infty} \quad = - \frac{\gamma_3}{N \sqrt{L_2} L_{2l+1}} \sum_{n_{l'},m_{l''}} \langle \Omega \rangle \left[ e^{-ik \cdot R_{n_{l'},2l'}} b_{n_{l'},2l'} ight. \\
\times \left. \left( \hat{b}_{j,l}^\dagger a_{j',l'+1} + \hat{b}_{j',l'+1}^\dagger a_{j,l} \right) \hat{a}_{m_{l''},2l''+1}^\dagger e^{ik \cdot R_{m_{l''},2l''+1}} \right] | \Omega \rangle \\
= - \frac{2N \gamma_3}{L} \left[ \sum_{l'=0,i=1}^{L-3} e^{ik_z c/2} e^{-ik \cdot \delta_i} + \sum_{l''=0,j=1}^{L-2} e^{-ik_z c/2} e^{-ik \cdot \delta_i} \right] | \Omega \rangle \\
= - \frac{2\gamma_3}{L} \left[ \left( \frac{L}{2} \right) e^{ik_z c/2} + \left( \frac{L}{2} + 1 \right) e^{-ik_z c/2} \right] \sum_i e^{-ik \cdot \delta_i} \\
= - 2 \cos \left( \frac{k_z c}{2} \right) \gamma_3 \sum_i e^{-ik \cdot \delta_i}, \quad (B.15)
Recalling that $\phi_I(k) = \sum_i e^{-i k \cdot \delta_i}$, we can rewrite Eq. B.7 as

$$
\begin{pmatrix}
0 & -t\phi_I(k) & 0 & -\gamma_1 f(k, L) \\
-t\phi_I^*(k) & 0 & -\gamma_3 f(k, L)\phi_I(k) & 0 \\
0 & -\gamma_3 f^*(k, L)\phi_I^*(k) & 0 & -t\phi_I(k) \\
-\gamma_1 f^*(k, L) & 0 & -t\phi_I^*(k) & 0
\end{pmatrix}
\begin{pmatrix}
c^A_e(k) \\
c^B_e(k) \\
c^A_o(k) \\
c^B_o(k)
\end{pmatrix}
= \epsilon(k)
\begin{pmatrix}
c^A_e(k) \\
c^B_e(k) \\
c^A_o(k) \\
c^B_o(k)
\end{pmatrix},
$$

(B.17)

### B.1 Bilayer Graphene

This method should be exact for bilayer graphene. We consider the wave functions

$$
|\psi_{n,2}^A\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot R_{n,2}^A} |\psi_{k,2}^A\rangle,
$$

$$
|\psi_{n,1}^A\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot R_{n,1}^A} |\psi_{k,1}^A\rangle,
$$

$$
|\psi_{n,2}^B\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot R_{n,2}^B} |\psi_{k,2}^B\rangle,
$$

$$
|\psi_{n,1}^B\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot R_{n,1}^B} |\psi_{k,1}^B\rangle
$$

(B.18)

with their inverses

$$
|\psi_{k,2}^A\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_{n,2}^A} |\psi_{n,2}^A\rangle,
$$

$$
|\psi_{k,1}^A\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_{n,1}^A} |\psi_{n,1}^A\rangle,
$$

$$
|\psi_{k,2}^B\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_{n,2}^B} |\psi_{n,2}^B\rangle,
$$

$$
|\psi_{k,1}^B\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_{n,1}^B} |\psi_{n,1}^B\rangle.
$$

(B.19)

The lattice vectors can be written as

$$
a_1 = \frac{a}{2} (3, \sqrt{3}, 0) \quad , \quad a_2 = \frac{a}{2} (3, -\sqrt{3}, 0)
$$

(B.20)
with the basis \((0, 0, 0)\) for the \(B\) sublattice and \((-a, 0, 0)\) for the \(A\) sublattice, and the reciprocal lattice vectors are given by
\[
b_1 = \frac{2\pi}{3a} (1, \sqrt{3}, 0) \quad , \quad b_2 = \frac{2\pi}{3a} (1, -\sqrt{3}, 0)
\] (B.21)
The lattice constants are \(a = 1.42\text{Å}\) and \(c = 6.7\text{Å}\). In tight binding, we assume eigenfunctions of the form
\[
H |\psi_k\rangle = \epsilon(k) |\psi_k\rangle
\] (B.22)
where \(|\psi_k\rangle = c^A_2(k) |\psi^A_{k,2}\rangle + c^B_2(k) |\psi^B_{k,2}\rangle + c^A_1(k) |\psi^A_{k,1}\rangle + c^B_1(k) |\psi^B_{k,1}\rangle\). Taking the matrix elements \(\langle \psi^A_{k,1/2} | H | \psi_k \rangle\), we get the eigenvalue equation
\[
\begin{pmatrix}
\langle \psi^A_{k,2} | H | \psi^A_{k,2}\rangle & \langle \psi^A_{k,2} | H | \psi^B_{k,2}\rangle & \langle \psi^A_{k,2} | H | \psi^A_{k,1}\rangle & \langle \psi^A_{k,2} | H | \psi^B_{k,1}\rangle \\
\langle \psi^B_{k,2} | H | \psi^A_{k,2}\rangle & \langle \psi^B_{k,2} | H | \psi^B_{k,2}\rangle & \langle \psi^B_{k,2} | H | \psi^A_{k,1}\rangle & \langle \psi^B_{k,2} | H | \psi^B_{k,1}\rangle \\
\langle \psi^A_{k,1} | H | \psi^A_{k,2}\rangle & \langle \psi^A_{k,1} | H | \psi^B_{k,2}\rangle & \langle \psi^A_{k,1} | H | \psi^A_{k,1}\rangle & \langle \psi^A_{k,1} | H | \psi^B_{k,1}\rangle \\
\langle \psi^B_{k,1} | H | \psi^A_{k,2}\rangle & \langle \psi^B_{k,1} | H | \psi^B_{k,2}\rangle & \langle \psi^B_{k,1} | H | \psi^A_{k,1}\rangle & \langle \psi^B_{k,1} | H | \psi^B_{k,1}\rangle \\
\end{pmatrix}
\times
\begin{pmatrix}
c^A_2(k) \\
c^B_2(k) \\
c^A_1(k) \\
c^B_1(k) \\
\end{pmatrix}
= \epsilon(k)
\begin{pmatrix}
c^A_2(k) \\
c^B_2(k) \\
c^A_1(k) \\
c^B_1(k) \\
\end{pmatrix}, \quad \text{(B.23)}
\]
Within a single graphene layer, there are three nearest neighbor vectors \(R^A - R^B = \delta_i\)
\[
\delta_1 = \frac{a}{2} (1, \sqrt{3}, 0) \quad , \quad \delta_2 = \frac{a}{2} (1, -\sqrt{3}, 0) \quad , \quad \delta_3 = -a(1,0,0).
\] (B.24)
The relevant interlayer nearest neighbor vectors are
\[
R^B_{ij,2} - R^A_{ij,1} = \left(0, 0, \frac{c}{2}\right) + \delta_i \quad , \quad \text{(coupled by } \gamma_3\text{)},
\]
\[
R^A_{ij,2} - R^B_{ij,1} = \left(0, 0, \frac{c}{2}\right) \quad , \quad \text{(coupled by } \gamma_1\text{)} \quad \text{(B.25)}
\]
as shown in Fig. B.1.

We now need to compute the matrix elements in Eq. B.7, and we need only compute the upper or lower diagonal due to the hermiticity of the matrix. The on-diagonal terms are again all zero because we ignore the on-site potential. We also already know the intralayer terms like \(\langle \psi^A_{k,2} | H | \psi^B_{k,2}\rangle\) because they are just the graphene matrix elements (there are no next-nearest layer hoppings to consider in addition to the graphene terms) in the approximation that the graphene sheets are infinitely large. Lastly, it is clear from the hamiltonian that we ignore interlayer hopping from \(A\) to \(A\) sublattices and similarly for \(B\), so we can ignore the matrix elements like \(\langle \psi^A_{k,2} | H | \psi^A_{k,1}\rangle\). We therefore need only
compute the matrix elements that involve interlayer hopping between B and A sublattices. Here are all the relevant non-zero interlayer matrix elements for an even, odd, and infinite number of layers \( L \) (ignoring creation/annihilation operator combinations that return 0):

\[
\langle \psi_A^{k,2} | H | \psi_B^{k,1} \rangle = -\frac{\gamma_1}{N} \sum_{n,m} \langle \Omega | e^{-ikz_c/2} [ a_{n,2}^\dagger b_{j',1}^\dagger b_{m,1}^{\dagger} e^{ikR_{m,1}^A}] | \Omega \rangle \\
= -\frac{\gamma_1}{N} \sum_{j} \langle \Omega | e^{-ikz_c/2} | \Omega \rangle \\
= -\gamma_1 e^{-ikz_c/2},
\]
(B.26)

\[
\langle \psi_B^{k,2} | H | \psi_A^{k,1} \rangle = -\frac{\gamma_3}{N} \sum_{n,m} \langle \Omega | e^{-ikz_c/2} [ b_{n,2} a_{j,1}^{\dagger} a_{m,1}^{\dagger} e^{ikR_{m,1}^B}] | \Omega \rangle \\
= -\frac{N\gamma_3}{N} \sum_{i=1}^3 \langle \Omega | e^{-ikz_c/2} e^{-ik\delta_i} | \Omega \rangle \\
= -\gamma_3 e^{-ikz_c/2} \sum_{i} e^{-ik\delta_i} \\
= -\gamma_3 e^{-ikz_c/2} \phi I(k),
\]
(B.27)

We can now rewrite Eq. B.23 as

\[
\begin{pmatrix}
0 & -t\phi I(k) & 0 & -\gamma_1 e^{-ikz_c/2} \\
-t\phi I^*(k) & 0 & -\gamma_3 e^{-ikz_c/2} \phi I(k) & 0 \\
0 & -\gamma_3 e^{ikz_c/2} \phi I^*(k) & 0 & -t\phi I(k) \\
-\gamma_1 e^{ikz_c/2} & 0 & -t\phi I(k) & 0
\end{pmatrix} \times 
\begin{pmatrix}
c_2^A(k) \\
c_2^B(k) \\
c_4^A(k) \\
c_4^B(k)
\end{pmatrix} = \epsilon(k) 
\begin{pmatrix}
c_2^A(k) \\
c_2^B(k) \\
c_4^A(k) \\
c_4^B(k)
\end{pmatrix},
\]
(B.28)
References


