Theoretical Methods for Excitonic Physics in 2D Materials

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In this Perspective article, the reader is introduced to several theoretical methods of determining the exciton wave functions and the corresponding eigenenergies. The methods covered are either analytical, semianalytical, or numeric. All the details associated with the different methods are made explicit, thus allowing newcomers to do research on their own, without experiencing a steep learning curve. The Perspective starts with a variational method and ends with a simple semianalytical approach to solve the Bethe–Salpeter equation (BSE) in gapped 2D materials. For the first methods addressed in this Perspective, the authors focus on a single layer of hexagonal boron nitride (hBN) and of transition metal dichalcogenides (TMD), as these are exemplary materials in the field of 2D excitons. For explaining the Bethe–Salpeter method, the biased bilayer graphene, which presents a tunable bandgap is chosen. The system has the right amount of complexity (without being excessive). This allows the presentation of the solution in a context that can be easily generalized to more complex systems or to apply it to simpler models.

1. Introduction

The dawn of 2D materials occurred with the isolation of a single graphene layer on a silicon oxide substrate.[1] Around the same time, other 2D materials were isolated. Among these, we find hexagonal boron nitride (hBN),[2] transition metals dichalcogenides (TMD),[3] and 2D superconducting layers.[4]

The excitement about the new physics found in graphene layers, such as the half-integer quantum Hall effect (also found at room temperature),[5,6] Klein tunneling,[7] ballistic electronic transport,[8] high thermal conductivity,[9] constant optical absorption in the visible range of the electromagnetic spectrum,[10,11] and highly confined graphene plasmons with long propagation length,[12–15] shadowed for some time the interest in other 2D materials. As graphene physics matured, the interest in other 2D materials grew and novel physical properties were found. The existence of correlated phases in twisted graphene layers,[16–21] valley physics and excitons in TMDs,[3,22–27] 2D superconductivity,[28–32] 2D magnetic materials, and the myriad of heterostructures made of these materials has created a new and exciting research field in condensed matter physics and materials science alike.

Among the several correlated phases in 2D materials, excitons are of particular interest for a new class of optoelectronic devices. In the simplest possible picture, an exciton corresponds to a bound electron–hole pair, which is formed when an electron is promoted to the conduction band, thus leaving a hole in the valence band. These two particles, having opposite charges, interact via an electrostatic potential and may create bound states, similar to what one finds for the hydrogen atom due to the proton–electron interaction. Detailed experiments[31–35] revealed that the excitonic optical spectrum (characterized, for example, by how the system absorbs light) is rather different from what is predicted using the 2D Schrödinger equation with an attractive Coulomb potential.[36–38] Due to the reduced thickness of 2D materials, the electrostatic interaction between the electron and the hole is far less screened, and therefore stronger, than what is found for 3D systems. This allows for the emergence of stable excitons, which may be observed even at room temperature[39–43] (something harder to realize in conventional semiconductors). Besides excitons, other excitations may appear resulting from the interaction of one or more electrons, with one or more holes. The most prominent example of these are the trions observed in doped TMDs, resulting from the interaction of two electrons with one hole.[44,45]

The scope of the correlated phase in 2D materials is currently so vast that it is difficult to cover it within a single article. Therefore, in this perspective, we choose to focus our attention on the theoretical methods necessary to address the calculation of the properties of excitons in gapped 2D materials, with special emphasis on hBN, TMDs, and biased graphene bilayer. The latter example will be tackled using the Bethe–Salpeter equation.
its Brillouin zone.[3] This effect is responsible for the so-called optical response,[55] the most noticeable being the change in impurity density of states when the polarization is applied. Nonetheless, the interaction of unbound electrons and holes still introduces modifications to the density of states, as well as to the energy dispersion at the two nonequivalent vertices of the Brillouin zone.[3] This effect is responsible for the so-called valley-physics, which gave rise to the field of valleytronics.[3,53]

Despite its interesting features, single-layer graphene is a gapless material[54] and, therefore, hosts no bound electron–hole pairs. Nonetheless, the interaction of unbound electrons and holes still introduces modifications in high-energy part of the optical response,[55] the most noticeable being the change in energy of the van Hove singularity.

In stark contrast with its monolayer counterpart, biased bilayer graphene shows a tunable gap that can be as large as 150 meV.[56] The magnitude of this band gap can be controlled via an external electric field and dielectric environment, and allows the formation of tunable excitons, which have already been measured both experimentally[57] and described theoretically.[58] Contrarily to monolayer hBN and monolayer TMDs, the optical response of biased bilayer graphene is dominated by four bands, instead of just two. Despite being more intricate to describe theoretically, this type of multiband system is still tractable with simple methods.

As noted monolayer hBN presents a bandgap that allows the formation of bound electron–hole pairs in the gap, this is one of the simplest systems where excitons can be studied. The formation of energy levels in hBN is represented in a simplified manner in Figure 1, together with a schematic optical absorption spectrum inside the gap, clearly showcasing each excitonic resonance. These resonances become increasingly close as one reaches the top of the bandgap, as can be seen in the right panel of Figure 1.

The twisted graphene bilayer presents no gap under the application of an external electric field perpendicular to the layers, but its band structure can still be tuned by controlling the twist angle as well as the magnitude of the electric field.[59–61] On the same trend, Bernal stacking trilayer graphene (also known as ABA trilayer graphene) does not show a gap in the same conditions, with the electric field only modifying the effective mass of the electron–hole pairs, which, as in biased bilayer graphene, can be tuned through the magnitude of the electric field.

In this perspective, we will guide the reader through the determination of the excitonic properties in simple three-band systems. These are: monolayer hBN and monolayer TMDs, as well as biased bilayer graphene. The latter already shows the complexity of a multiband system without being exceedingly difficult to treat. The ABC trilayer graphene is left as an exercise for the adventurous reader.

### 3. General Formalism

In this section, we shall discuss the general equations that define the excitonic problem in 2D materials.

#### 3.1. The First Approach

The Wannier equation was first introduced in 1937 by Wannier[65] to describe the structure of electronic excitation levels of insulating crystals. It is, essentially, a Schrödinger equation for a 3D hydrogen atom with an effectively reduced mass. Such an approach clearly tries to capture the hydrogen-like nature of the electron–hole interaction in solids. Although first introduced for 3D systems, it can easily be expressed for 2D systems. Generically the Hamiltonian in such a description reads

$$H = -\frac{\hbar^2 V^2}{2\mu_{eh}} - V(r)$$  \hspace{1cm} (1)

where $\mu_{eh}$ is the reduced mass of the electron–hole pair and $V(r)$ is the electrostatic potential among electrons. The goal is to
determine the wave function and eigenenergies of the equation $H_{\nu}(\tau) = E_{\nu}(\tau)$, where $\tau$ is the relative position vector of the electron and hole, $E$ the exciton energy and $\psi(\tau)$ its wave function. When $V(\tau)$ is the Coulomb potential, the energy levels read in 3D

$$E_n = -\frac{\mu_e c^2 a^2}{2 e^2 n^2}$$

(2)

and $^{\text{[66,67]}}$

$$E_n = -\frac{\mu_a c^2 a^2}{2 e^2 (n - 1/2)^2}$$

(3)

in 2D, with $n = 1, 2, 3, \ldots$ the principal quantum number, $a \approx 1/137$ is the fine structure constant, $c$ the speed of light, and $e$, the relative permittivity of the semiconductor crystal (in 2D, $e_r$ is the environment dielectric constant). The Coulomb potential is appropriated for describing excitons in bulk semiconductors. However, due to screening, 3D excitons have binding energies of the order of tens of meV$^{[68]}$ (and are subject to thermal dissociation at room temperature). On the contrary, in 2D materials the screening is less efficient and as a consequence excitons are much more stable being observable at room temperature. Interestingly, however, the energy levels of the excitons in 2D materials are not given by Equation (3). This happens because this equation does not take into account the polarizability of 2D materials. Ahead we shall see how the Coulomb potential is modified for accounting with the aforementioned polarizability.

When transformed to momentum space, Equation (1) acquires the form

$$\frac{\hbar^2 k^2}{2\mu_{eh}} \phi(k) - \sum_k V_{k-k} \phi(k') = E_n \phi(k)$$

(4)

As we shall in the following, this equation is rather similar to the BSE, which accurately describes the excitonic properties in 2D materials, apart from a missing multiplicative term on the left-hand side. Here, $\phi(k)$ and $V_{k-k}$ are the Fourier transforms of $\psi(\tau)$ and $V(\tau)$, respectively, where $V(\tau)$ is the repulsive electron–electron interaction.

3.2. BSE

In this part of the text, we shall give the main steps to derive the BSE for a simple two-band model. In the end, we shall see how this equation compares with the Wannier model given above, and how it extends to the multiband case.

We start defining the exciton creation operator in a two-band system as

$$\hat{b}_\lambda^n = \frac{1}{\sqrt{A}} \sum_k \phi_\lambda^n(k) \hat{c}_k^n$$

(5)

where $A$ is the area of the monolayer, $\phi_\lambda^n(k)$ is the Fourier transform of the exciton wave function (unknown at this point), whose quantum numbers we label by $\nu$. For isotropic systems, and inspired by the problem of the Hydrogen atom, it is customary to separate the exciton wave function into a radial and an angular part, as $\phi_\lambda^n(k) = f^{(m)}_\lambda(k) e^{i m \theta}$, where $m = 0, \pm 1, \pm 2, \ldots$ stands for the angular quantum number of the exciton.$^{[69]}$ A similar type of solution is found when dealing with the real space wave function.

The operator $\hat{c}_k^n/\hat{c}_k^n$ creates/annihilates an electron in the conduction band, or, in other words, an electron is annihilated in the valence band, and one is created directly above it on the conduction band (we assume only vertical transitions due to the small momentum carried by photons). In principle, this transition between bands can occur at different points of the reciprocal space. Thus, to be general, we can express the exciton creation operator as a superposition of $\hat{c}_k^n \hat{c}_k^n$ in momentum space modulated by a given function, in this case $\phi_\lambda^n(k)$, which is yet to be determined.

When this operator acts on the excitonic ground state (or excitonic vacuum), which corresponds to the state with a filled valence band and an empty conduction band (no excitons present), we find

$$b_\lambda^n |GS\rangle = |\nu\rangle$$

(6)

where $|\nu\rangle$ represents the state of the exciton we have just created.

We write the energy of such a state as $E_\nu$.

To obtain the equation that gives both $E_\nu$ and $\phi_\lambda^n(k)$, we proceed in the following manner: 1) first, we introduce the fermionic Hamiltonian, $H$, of a system of interacting electrons written in second quantization; 2) then, we state that this Hamiltonian should be diagonal when expressed in terms of $b_\lambda^n$; 3) afterward, we compute the commutator $[H, b_\lambda^n]$ using the fermionic and bosonic definitions of the two operators; 4) finally, we demand both results to be the same and obtain the BSE.

We shall now follow the steps given above in a more detailed manner. The electronic Hamiltonian is composed of a kinetic and a potential contribution. The kinetic term can be readily quantized in terms of electron operators and reads

$$H_0 = \sum_{k,j} E_{kj} \hat{c}_k^\dagger \hat{c}_j$$

(7)

where the sum over $\lambda$ runs over the bands of the system, and $E_{kj}$ is the energy of an electron belonging to the band $\lambda$, with momentum $k$. The potential energy term (two-body interaction) reads

$$H_{\text{int}} = \frac{1}{2A} \sum_{k} \sum_{q_{k_{j_k}k_{j_\lambda}}(k_j, k_\lambda, q)} V_q F_{j_{\lambda j_{\lambda}}}(k_j, k_\lambda, q) \times \hat{c}_{k_j + q_1}^\dagger \hat{c}_{k_{j_1} - q_1} \hat{c}_{k_{j_\lambda} + q_2} \hat{c}_{k_\lambda - q_2}$$

(8)

where $V_q$ is the Fourier transform of the interaction potential among the electrons and

$$F_{j_{\lambda j_{\lambda}}}(k_j, k_\lambda, q) = \sum_{k} \sum_{q_{k_{j_k}k_{j_\lambda}}(k_j, k_\lambda, q)} V_{k_{j_k}q_{j_\lambda}} \hat{c}_{k_j}^\dagger \hat{c}_{k_\lambda} \hat{c}_{k_{j_1} - q_1} \hat{c}_{k_{j_\lambda} + q_2} \hat{c}_{k_{j_\lambda} - q_1} \hat{c}_{k_{j_\lambda} + q_2}$$

(9)
is a form factor with $\alpha_k$, the $\lambda$–band spinor, evaluated at $k$, which is obtained from the eigenvectors of the $k$-space model Hamiltonian (see discussion of the biased bilayer further ahead). We exclude the term $q = 0$ from the summation since it cancels with the background contribution due to ion–ion and electron–ion interaction in the solid.

To obtain the equation that defines the exciton wave functions, we will assume that the total Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}$, is diagonal when written in terms of the exciton operators $b^\dagger_k$, that is, $\hat{H} = \sum_k E_k b^\dagger_k b_k$. Then we will compute the commutator $\left[\hat{H}, b^\dagger_k\right]$ using the excitonic representation of the operator, as well as using their fermionic representation, Equation (5). In the end, we demand both results to be equal, and by doing so, an equation defining the exciton wave function emerges.

The computation of $\left[\hat{H}, b^\dagger_k\right]$ using the bosonic representation of the Hamiltonian is trivial, and its result reads

$$\left[\hat{H}, b^\dagger_k\right] = E_k b^\dagger_k = \frac{1}{\sqrt{A}} \sum_k \phi_k(k)c^\dagger_k c_k$$

Contrary to this commutator, computing $\left[\hat{H}, b^\dagger_k\right]$ using the fermionic representations of $\hat{H}$ and $b^\dagger_k$ is a rather cumbersome process. To compute this, we will break the commutator in two, separating contributions from $\hat{H}_0$ and $\hat{H}_{\text{int}}$. Starting with the evaluation of $\left[\hat{H}_0, b^\dagger_k\right]$, and using the following relations regarding commutators and anticommutators

$$[AB, C] = A[B, C] + [A, C]B$$
$$[AB, C] = A[B, C] - [A, C]B$$

one finds

$$\left[\hat{H}_0, b^\dagger_k\right] = \frac{1}{\sqrt{A}} \sum_k \phi_k(k)(E_k - E_k)c^\dagger_k c_k$$

To compute $\left[\hat{H}_{\text{int}}, b^\dagger_k\right]$, we start writing

$$\left[\hat{H}_{\text{int}}, b^\dagger_k\right] = \frac{1}{\sqrt{A}} \sum_{j, k} \sum_{q, k'} \phi_j(k') V_{j, k, l, q, k, k'}(k_j, k_q, k_k, k)$$

Using Equation (10) and (11), it is possible to show that the commutator can be transformed into

$$\left[\hat{c}^\dagger_{k_1 + q_1} c^\dagger_{k_2 - q_2} c_{k_3} b^\dagger_{k_4} c_{k_5}\right] = \left\{ c^\dagger_{k_1 + q_1} c^\dagger_{k_2 - q_2} c_{k_3} b^\dagger_{k_4} c_{k_5}\right\}$$

$$= \left\{ c^\dagger_{k_1 + q_1} c^\dagger_{k_2 - q_2} c_{k_3} b^\dagger_{k_4} c_{k_5}\right\}$$

where the Kronecker-$\delta$’s appear as a consequence of the anticommutation relation that the fermionic operators must obey. At this point in the calculation, we are faced with four terms containing the product of four-electron operators. Dealing with such terms is no easy task, and to simplify the calculation we introduce a mean-field approximation. This technique essentially allows us to transform the previous equation into one, where only products of two operators appear, by taking expectation values over pairs of operators. For clarity, we show how this mean-field approach is applied to the first term of the previous equation, and note that the other terms can be treated in an analogous manner. We write

$$\left\{ c^\dagger_{k_1 + q_1} c^\dagger_{k_2 - q_2} c_{k_3} b^\dagger_{k_4} c_{k_5}\right\} \approx \left( c^\dagger_{k_1 + q_1} c_{k_3}\right) \left( c^\dagger_{k_2 - q_2} c_{k_5}\right)$$

where $\langle \ldots \rangle$ refers to the expectation value taken over the homogeneous exciton ground state (fully occupied valence band and fully empty conduction band). Applying this technique to all the contributions, we find

$$\left[\hat{H}_{\text{int}}, b^\dagger_k\right] = -\sum_{p, k} \frac{1}{A \sqrt{2}} \sum_{q, q'} V_{p - k, q, q'}(k, p, k - p)c^\dagger_{k} c_{q}$$

Adding this expression with the result of the commutator with $H_0$ and demanding the result to be the same as the one obtained using the bosonic commutation relations, we find

$$E_k \phi_k(k) = \phi_k(k)(E_{k_1} - E_{k_2})$$

This is the BSE, and it determines the exciton energies $E_k$ and wave functions $\phi_k(k)$. It is clearly resembling Equation (4) apart from the term $F_{\text{coul}, \text{coul}}$. As noted, the exchange energy correction to the bare electronic bands was neglected in Equation (19). This correction turns out to be important at $k = 0$, as it renormalizes the bare bandgap. Also, the electron–hole exchange in the Coulomb potential was not included. This approximation...
introduces a correction of about 5% to the exciton binding energy, as shown in Ref. [73].

To clearly extract the Wannier equation from the BSE, let us introduce some approximations. To start, we use the approximation where the energy bands are parabolic near their bottom, i.e., \( E_{k_i} = E_0 + \frac{\hbar^2 k_i^2}{2m_i} \) (with \( m_i \) the effective mass on the band \( i \)), and write

\[
E_{k_i} - E_{k_i'} \approx E_0 + \frac{\hbar^2 k_i^2}{2\mu_{eh}}
\]

(20)

where \( \mu_{eh} \) has been defined before as the reduced mass of the electron–hole pair and \( E_0 \) is the energy difference between the top and bottom of the valence and conduction bands, respectively. Then, the form factor on the second term on the right-hand side is approximated to 1, which is a good approximation for a large band gap. Using these three approximations, one finds

\[
E_{\text{bind}} \phi_i(k) = \frac{\hbar^2 k_i^2}{2\mu_{eh}} \phi_i(k) - \frac{1}{A} \sum_p \phi_i(p) V_{k-p}
\]

(21)

with \( E_{\text{bind}} = E_v - E_c \). It is now a simple task to recognize a convolution integral on the last term of the right-hand side. Thus, Fourier transforming the whole equation to real space, we obtain

\[
E_{\text{bind}} \psi_v(r) = -\frac{\hbar^2 \gamma^2}{2\mu_{eh}} \psi_v(r) - \psi_v(r) V(r)
\]

(22)

which is the Wannier equation.

Thus, we see that to obtain the energies and wave functions of excitons in 2D systems two approaches can be followed. One either solves an integral equation in momentum space, or a differential equation in real space. The latter is easier to deal with and more suitable for analytical approaches. The shortcomings of the real space approach are a general loss of accuracy due to the approximation used, and the loss of some physical phenomena associated with the form factor \( F_{\text{2D}} \) (in particular, the real-space approach fails to capture the lack of degeneracy between states with symmetric angular quantum numbers).

3.3. Extension to Multiband Systems

In the derivation we just presented, it was assumed that we were working with a system with a single pair of bands. However, one may be interested in studying multiband systems, where more than one valence/conduction band should be considered.

For brevity, we shall only state the modified versions of the equations for the multiband case, and refer the reader to Refs. [74,75] for more details.

For a multiband system, we define the state of an exciton as

\[
\vert \nu \rangle = \frac{1}{\sqrt{A}} \sum_{k_i} \sum_{s} \phi_{s} \phi_{s'} (k_e) e_{s, e_{s'}} | GS \rangle
\]

(23)

which differs from the previous definition on the sum over the bands, which was previously absent. The BSE is also modified and reads

\[
E_i \phi_{s', s} (k) = \phi_{s', s} (k) (E_{k_e} - E_{k_i}) - \frac{1}{A} \sum_{s', s''} \phi_{s', s''} (p) V_{k-p}
\]

(24)

\[
F_{s', s''} (k, p, k - p)
\]

where once again we see the sum over the bands of the system.

Next, we shall derive the form of the electrostatic potential that should be used to solve either the BSE or the Wannier equation in 2D systems.

3.4. The Rytova–Keldysh Potential

2D semiconductors are characterized by a 2D polarization. This, together with the fact that the electrostatic field lines are for the most of it outside the semiconductor makes the electrostatic potential different from the Coulomb interaction between two charges in the bulk, as we now shall see [76].

The key to the derivation of the Rytova–Keldysh potential is the fact that the charge fluctuations are proportional to the Laplacian of the potential evaluated at the plane of the 2D material, which is assumed to be surrounded by vacuum for simplicity. Such a fact comes from the following considerations: the induced charge density, \( \delta n_{2D}(r) \), due to a point charge located at a distance \( r \) from the system is given by the 2D polarization in the usual way \( \delta n_{2D}(r) = -\nabla \cdot \mathbf{P}_{2D} \), where the 3D position vector is given by \( r = (r_x, r_z) \), and \( \delta n_{2D} \) has units of charge per unit area. The polarization itself is proportional to the total electric field \( \mathbf{P}_{2D} = -\epsilon_0 \chi_{2D} \nabla V(r_x, z = 0) \), with \( \chi_{2D} \) having dimensions of length. Therefore

\[
\delta n_{2D}(r) = \epsilon_0 \chi_{2D} \nabla^2 V(r_x, z = 0)
\]

(25)

Let us write Poisson’s equation as \( \nabla^2 V(r) = -\varepsilon [n_{2D}\varepsilon + n(r)]/\varepsilon_0 \), where \( n_{2D} \) is the background positive charge density due to the atomic nuclei (in units of particles per area). We now write the electronic density (in units of particles per area) as \( n(r) = n_{2D} + \delta(n) + \delta(z) \Delta \sigma(r) \), where \( n_{2D} \) is the neutralizing density of negative charge, \( \delta(n) \) represents the density of a localized charge at position \( r \), and \( \delta(z) \Delta \sigma(r) \) is the induced charge density fluctuation in the 2D material. With these definitions, Poisson’s equation reads

\[
\nabla^2 V(r) = -\frac{\varepsilon}{\varepsilon_0} \delta(n) - \frac{\varepsilon}{\varepsilon_0} \delta(z) \chi_{2D} \nabla^2 V(r_x, z = 0)
\]

(26)

where \( \varepsilon \Delta \sigma(r) = \delta n_{2D}(r) \). Fourier transforming the previous equation we obtain \( [k = (k_x, k_z)] \)

\[
-(k_x^2 + k_z^2) V(k) = -\frac{\varepsilon}{\varepsilon_0} + k_x^2 \chi_{2D} \nabla V(k_x, z = 0)
\]

(27)

Solving for \( V(k) \), we find

\[
V(k) = \frac{\varepsilon}{\varepsilon_0} \left[ \frac{1}{k_x^2 + k_z^2} - \frac{k_x^2}{k_x^2 + k_z^2} \right] \chi_{2D} \nabla V(k_x, z = 0)
\]

(28)

Fourier transforming the previous equation in the \( k_z \) coordinate to real space (and taking \( z = 0 \)) we obtain
\[ V(k_i) = \frac{e}{2\pi \epsilon_0 \epsilon_{\parallel}} \frac{k_{\parallel}}{k_{\parallel}} \chi_{2D} V(k_i) \]  
(29)

where

\[ V(k_i) = \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} V(k_i, k_z) \]  
(30)

Solving for \( V(k_i) \), we obtain

\[ V(k_i) = \frac{e}{2\pi \epsilon_0 \epsilon_{\parallel}} k_{\parallel} \]  
(31)

where \( 1/k_{\parallel} = \chi_{2D}/2 \). This potential can be written with a dielectric function depending on \( k_{\parallel} \) as

\[ V(k_i) = \frac{e}{2\pi \epsilon_0 \epsilon_{\parallel}} 1 \]  
(32)

with

\[ \epsilon(k_{\parallel}) = \epsilon_0 \left( 1 + \frac{k_{\parallel}}{k_{\parallel}} \right) \]  
(33)

A more rigorous treatment\(^{(77)}\) can be performed to obtain a dielectric function that does not diverge as \( k_{\parallel} \to \infty \). The Fourier transform of the potential to real space on the 2D material reads\(^{(78)}\)

\[ V(r_j) = \frac{e}{2\pi} \int dkd_{ij} e^{ik \cdot r_{ij}} \epsilon_{\parallel} \]  
(34)

where \( r \equiv r_{ij} \) now stands for the in-plane radial position, \( r_0 = 1/k_{\parallel} \), and \( H_0(x) \) and \( Y_0(x) \) are the Struve function and the Bessel function of the second kind, respectively. The repulsive potential represents the interaction among the electrons in a polarizable 2D semiconductor reads \( V_\text{R-K}(r) = eV(r_j) \). Despite its complicated analytical form, this potential approaches the Coulomb potential at large distances, but diverges logarithmically near the origin. We note in passing that the generalization of the Rytova–Keldysh potential to a multilayer system has been recently computed\(^{(79)}\).

In the following sections, we will show different methods to solve the excitonic problem, both in real and momentum spaces, using the Rytova–Keldysh potential.

### 4. Real Space Solution

In this section, we will present different methods to solve the excitonic problem in real space. For each method, we shall focus on a concrete system, and give the results for the binding energies and wave functions of the associated excitons. We start discussing the tight-binding model of an hBN monolayer, from where we derive the eigenvalues and eigenfunctions used in the calculation of the optical conductivity using the BSE.

#### 4.1. Tight-Binding Model of hBN Monolayer: From Real Space to Momentum Space

In this section, we aim to briefly discuss the tight-binding model used to describe the single-particle electronic properties of gaped Dirac systems. We shall focus on the case of hBN, and explain how to extend the model to describe TMDs.

The basic premise of a tight-binding model is that an electron in a given orbital is located in the vicinity of its parent ion, but may experience a transition, or hopping, to an orbital of a nearby ion. The likelihood of these transitions is characterized by the so-called hopping integrals. In order for us to construct the tight-binding Hamiltonian of hBN (or TMDs), we must first choose which orbitals and which hoppings we wish to consider; obviously, increasing the number of orbitals and the number of hoppings yields a more accurate model, but also a more complex one.

In a minimal approach, we consider only the \( p_z \) orbitals of the atoms located on the two sublattices of the hBN layer, which we label as \( A \) and \( B \) (see Figure 2). Considering only hoppings between nearest neighbors, we write the Hamiltonian in real space as

\[
H = \frac{E_g}{2} \sum_{j=1}^{N} [r_i, A] [r_i, A] - \frac{E_g}{2} \sum_{j=1}^{N} [r_i, B] [r_i, B] + \sum_{j=1}^{N} \sum_{i=1}^{3} [r_i, A] [r_i + d_j, B] + \text{h.c.}
\]

(35)

where \( E_g/2 \) is the on-site energy of the \( p_z \) orbitals, \( t \) is the hopping integral between an orbital at \( r_i \) (corresponding to the \( A \)-sublattice), and an orbital at \( r_i + d_j \) (corresponding to the \( B \)-sublattice), where the \( d_j \) are the three vectors connecting a site of the \( A \)-sublattice to its three nearest neighbors (all belonging to the \( B \)-sublattice). Introducing the Fourier representation of \([r_i, A] = \sum_{p} \chi_{\text{p}}^{A} e^{ip \cdot r_i} [p, A]\), we are able to write the Hamiltonian as \( H = \sum_{p} \Psi^{\text{p}} H_{\text{p}} \Psi^{\text{p}} \), with \( \Psi^{\text{p}} = ([p, A], [p, B]) \), where the momentum space Hamiltonian reads

\[
H_{\text{p}} = \begin{pmatrix}
\frac{E_g}{2} & t \phi_{\text{p}} \\
-t \phi_{\text{p}}^* & -\frac{E_g}{2}
\end{pmatrix}
\]

(36)

Figure 2. Lattice and Brillouin zone of hBN. (Left) Real space lattice of hBN, showing the nonequivalent \( A \) and \( B \) lattice sites, and the lattice vectors connecting these two sites. (Right) Electronic Brillouin zone of hBN, showing the \( \Gamma \)-point at the zone center and the nonequivalent \( K_+ \) and \( K_- \) points.
with $\phi_p = \sum_{j=1}^3 e^{-ipd_j}$. The energy bands and eigenvectors associated with this Hamiltonian can be obtained through the diagonalization of $H_k$. The minimum gap between the valence and conduction bands occurs at the points $K_{\pm} = \frac{2\pi}{a} \left( \pm \frac{1}{\sqrt{3}}, 0 \right)$, with $a$ the distance between nearest neighbors. Since we will be interested in the low energy response alone, we can expand $\phi_k$ near these points, thus obtaining an effective low-energy Hamiltonian. Writing $p = rK + k$, with $r = \pm 1$, and considering $|k|$ to be small, we find $\phi_k \approx \frac{1}{2} \left( r_k \pm ik_y \right)$. Within this approximation, the effective Hamiltonian takes the form of a Dirac Hamiltonian

$$H^{\text{eff}} = \frac{E_g}{2} \sigma_z - \hbar v_F(r_k \sigma_x - k_y \sigma_y)$$

(37)

where $\hbar v_F = 3a/2$ is termed the Fermi velocity, and $\sigma_i$, $i = \{x, y, z\}$ are the Pauli matrices. Diagonalizing $H^{\text{eff}}$, we obtain the energy dispersion

$$E_{\pm k} = \pm \sqrt{\frac{E_g^2}{4} + \hbar^2 v_F^2 k^2}$$

(38)

where $+/–$ refers to the conduction/valence band. The eigenvectors read

$$|u_{+,k}\rangle = \left( \cos \frac{\tilde{k}_x}{2}, -\sin \frac{\tilde{k}_x}{2} e^{i\xi_0} \right)^T$$

(39)

$$|u_{-,k}\rangle = \left( \sin \frac{\tilde{k}_x}{2} e^{i\xi_0}, \cos \frac{\tilde{k}_x}{2} \right)^T$$

(40)

where $\theta = \arctan k_y/k_x$ and $\tilde{k}_x = \arctan(2\hbar v_F k/E_g)$. We note in passing that where the complex exponentials $e^{i\xi_0}$ are located is important when the excitonic problem is treated in momentum space.

Near the bottom of the conduction band and near the top and of the valence band, the spectrum of hBN can be approximated by Equation (38). The effective mass follows as

$$\frac{1}{m} \frac{d^2 E_{\pm k}}{d^2 k^2} |_{k=0} = \pm \frac{2v_F^2}{E_g}$$

(41)

which leads to a reduced electron–hole mass $\mu_{\pm} = E_g/(4v_F^2)$.

Although the previous derivation focused on hBN, the broad strokes remain the same to describe the single-particle electronic structure of TMDs. The two main differences for TMDs are the orbitals that must be accounted for, and the necessity to account for spin-orbit coupling. The effective Hamiltonian for such a system can be obtained by adding to Equation (37) the term $^{[80,81]}$

$$H^{\text{SOC}} = \lambda r \sigma_z \frac{\sigma_x}{2} - \frac{1}{2}$$

(42)

where $\mathbf{I}$ is the identity matrix, $\sigma_z = \pm 1$ labels the spin projection of the bands, and $\lambda$ quantifies the spin–orbit coupling.

### 4.1.1. Optical Matrix Element

An important quantity to compute, and that often appears when studying the optical response, is the matrix element of the position operator. We shall now find an analytical expression for that quantity. Consider the matrix element

$$\langle u_{+,k}|r|u_{-,k} \rangle$$

(43)

We now note that

$$\langle u_{+,k}|[H, r]|u_{-,k} \rangle = (E_{k} - E_{-k}) \langle u_{+,k}|r|u_{-,k} \rangle$$

(44)

Focusing on the commutator $[H, r]$, we write

$$[H, r] = i\hbar v_F(\tau \sigma_x - \sigma_y)$$

(45)

We thus find [see Ref. [82]] for the oscillator strength of excitons in Dirac materials

$$\langle u_{+,k}|r|u_{-,k} \rangle = i\hbar v_F \frac{\langle u_{+,k}|(\tau \sigma_x - \sigma_y)|u_{-,k} \rangle}{E_{+k} - E_{-k}}$$

$$= \frac{i\hbar v_F}{E_{+k} - E_{-k}} \left( \cos \frac{\tilde{k}_x}{2} - e^{i\xi_0} \sin \frac{\tilde{k}_x}{2} \right)(rk + iy)$$

(46)

From the previous matrix element, we see that only the $s$ and $d$ angular momenta couple to the electromagnetic field. This is clear from the $(\cos^2 \tilde{k}_x - e^{i\xi_0} \sin^2 \tilde{k}_x)$ factor in Equation (46), which upon angular integration lead to nonzero coupling for only $s$ (the term with the cosine) and $d$ (the term with the sine) angular momenta states.

### 4.2. Variational Method

The variational method$^{[83,84]}$ is the simplest technique of choice for addressing the problem of finding the exciton low-lying states, corresponding to the least energetic excitons which appear further away from the conduction band edge. The method consists in proposing a trial wave function with unknown parameters, computing the expectation value of the Hamiltonian, $H$, and minimizing it relatively to the unknowns. Formally, we define a function $\langle \psi_{\alpha}(r) \rangle$, where $\alpha$ represents the set of unknowns. The average $E_{\alpha} = \langle \psi_{\alpha}(r) | H | \psi_{\alpha}(r) \rangle$ is then computed and the $\alpha$’s are obtained from $\partial E_{\alpha}/\partial \alpha = 0$. Once the $\alpha$’s are known, this allows us to obtain the minimum value of $E_{\alpha}$.

This method has been used to describe excitons in black phosphorus$^{[85]}$ and in TMDs$^{[85–90]}$ providing good results when benchmarked against the solution of the Bethe-Salpeter equation and the measured excitonic spectrum. We note in passing that perturbative methods (not described in this work) have also been applied with success to the description of black phosphorus.$^{[91]}$

The exciton Stark shift electron absorption is another problem that can also be computed using variational wave functions in real space$^{[92]}$ as well as the possibility of using fractional dimensions.$^{[93]}$ The study of black phosphorus using a numerical method where the Wannier equation is discretized in a finite mesh has also been performed.$^{[94,95]}$
Let us consider excitons in an hBN monolayer and model the effective potential with the Rytova–Keldysh potential

$$V_{R-K}(r) = \frac{\varepsilon}{4\pi \varepsilon_0 r, \kappa} H_0 \left( r \right) - Y_0 \left( r \right)$$

(47)

where $\varepsilon$ is the average relative permittivity of the two media surrounding the monolayer, and the minus sign accounts for the attractive interaction between the electron and the hole in the exciton.

As Equation (47) diverges as $r \to 0$, we consider variational wave functions inspired by the solution of the 2D Coulomb potential. The ansatz for the ground state wave function reads

$$\Psi_{10} = C_{10} e^{-r/\beta_{10}}$$

(48)

where $\beta_{10}$ is a variational parameter and $C_{10}$ a normalization constant. This represents an approximation to the excitonic ground-state wave function. The wave functions for excited states can then be written as

$$\Psi_{20} = C_{20} \left( 1 - d \frac{r}{\beta_{20}} \right) e^{-r/\beta_{20}}$$

(49)

$$\Psi_{2x} = C_{2x} e^{-r/\beta_{2x}}$$

$$\Psi_{2y} = C_{2y} e^{-r/\beta_{2y}}$$

where all three functions are orthogonal to each other by symmetry. $C_i$ is a normalization constant, the $\beta$s are variational parameters, and the $d$ parameter is obtained imposing orthogonality between $\Psi_{10}$ and $\Psi_{20}$, and is given by

$$d = \frac{\beta_{10} + \beta_{20}}{2\beta_{10}}$$

(50)

Next, we give the eigenenergies of the four variational states ($\Psi_{2x}$ and $\Psi_{2y}$ are degenerated) introduced above as well as a plot of the corresponding wave functions.

Focusing on the ground state for simplicity, we can then compute the expectation value of the Hamiltonian on the variational wave function as

$$E(\beta_{10}) = \left\langle \Psi_{10} \left| -\frac{\hbar^2 \nabla^2}{2m_e} + V_{R-K}(r) \right| \Psi_{10} \right\rangle$$

(51)

The previous average has an analytical solution in terms of elementary functions. Having computed this expectation value, we then find its minimum to determine the variational parameter $\beta_{10}$. An analogous methodology is also applied to $\Psi_{20}$ and $\Psi_{2x}$ (or $\Psi_{2y}$, as the two states are degenerate). The energies of the first three excition states in hBN are presented in Table 1, where the parameters used were $\varepsilon_r = 1$ and $r_0 = 10\AA$. The reduced mass $\mu_{eh}$ has been obtained directly from the hBN band structure near the $K$ points and it is given by Equation (35).

Table 1. Excitonic states in hBN are presented in

| $\beta_{10}$ | $\Psi_{10}$ | $\Psi_{20}$ |
|--------------|-------------|-------------|
| $E^w$        | $-1.27$     | $-0.547$    | $-0.402$    |
| $\beta_{2x}$ | $6.796$     | $8.304$     | $11.84$     |

Figure 3. Variational wave functions for hBN monolayer. Radial probability density $|R(r)|^2 r$ of the 1s, 2s, and 2p states obtained using the variational method with the functions of Equation (42) and (43) for hBN monolayer.

The radius is given in units of the Bohr radius $\alpha_0$.

4.3. Analytical Expression for the Optical Subgap Conductivity of hBN Single Layer

In this section, we take advantage of knowing the analytical form of the variational wave functions to obtain an analytical expression for the optical conductivity following the general definition introduced ahead [see Equation (85)]. Knowing the wave functions, however, is not enough to determine the optical conductivity due to selection rules introduced by the matrix element of the dipolar operator. As a consequence, some transitions are allowed (termed bright excitons) while others are not (termed dark excitons). A detailed study of the matrix element of the dipolar operator reveals that the bright excitons correspond to the $s$ and $d$ transitions [see Equation (46)]. A study of the oscillator strength reveals that the dominant transition is the 1s. In the analytical expression given layer, we include the contribution from this transition only, as it dominates the sub-gap optical response of the monolayer.

For writing an analytical expression for the optical conductivity of hBN, we need the Fourier transform to momentum space of the exciton wave function in real space. We take advantage of the existence of a simple variational wave function for the exciton. Beginning with the variational ansatz of Equation (48), we take the 2D Fourier transform

$$\psi_{1s}(k) = 2\pi \int_0^\infty |\Psi_{10}(kr)f_0(kr)| dr = \frac{2\sqrt{2\pi} \beta_{10}}{(1 + k^2 \beta_{10})^{3/2}}$$

(52)

where $f_0(x)$ is the cylindrical Bessel function of order zero. As we previously noted, Equation (40), only $s$ and $d$ angular momenta couple to the electromagnetic field. As the oscillator strength for $d$-series transitions proves itself to be several orders of magnitude smaller than that of the $s$-series states, we approximate the dipole matrix element as
\[
\langle u_{+k}|u_{-k}\rangle \approx \frac{i h \nu_F}{E_{+k} - E_{-k}} \cos^2 \left( \frac{\xi_k}{2} \right) (\tau k + i\bar{y})
\] (53)

Focusing on x-polarized light, we write Equation (86) as

\[
\sigma^{(1)}(\omega) = \frac{e^2}{8\pi^2 i\hbar} \frac{E_{1s}}{E_{1s} - (\hbar \omega + i\Gamma_{1s})} \left| \Omega_{1s} \right|^2 \times \frac{\hbar^2 v_f^2 - \hbar \nu_F E_{2\beta}}{E_{2\beta}^2 - 4\hbar^2 v_f^2} \left( \frac{\hbar v_F}{2m_e} \right)^2
\] (54)

where the non-resonant term was excluded. \(\Gamma_{1s}\) controls the line width of the excitonic absorption peak. \(\psi_{1s}(r)\) is the variational parameter entering in Equation (48) (the 1s state), and \(E_{1s} = E_{\text{bind.1s}} + E_g\) is the energy of the excitonic state. The optical conductivity above the gap requires the use of unbounded states.

### 4.4. Expansion in a Complete Set of Basis Functions

A common approach in physics for determining the spectrum and respective eigenfunctions of a system is to expand the unknown wave functions into a convenient complete set of basis functions, with unknown coefficients, that is

\[
\psi_{n,l}(r) = \lim_{N \to \infty} \sum_{n=0}^N a_{n,n}\psi_{n,l}(r)
\] (55)

where \(l\) is the angular quantum number (assuming a system with polar symmetry), \(n\) is the principal quantum number, \(\psi_{n,l}(r)\) are the functions of the chosen basis, and \(a_{n,n}\) are the unknown coefficients. The problem is then reduced to one in linear algebra, that is, to the determination of \(a_{n,n}\).

Here, opt to expand the exciton wave functions in terms of cylindrical Bessel functions, which form a complete basis on a disk of radius R. To obtain the eigenfunctions and eigenenergies of an infinite system, R is chosen sufficiently large, such that the exponential tail of the wave functions is accurately captured. If this requirement is not satisfied, one is effectively solving the Wannier equation on a finite disk, which yields different solutions than those of the infinite (at least approximately) system. Just like in the variational methods, we focus on an hBN monolayer.

We begin considering the exact solution to the Schrödinger equation in polar coordinates for a particle confined by a circular infinite potential well. In this system, separation of variables can be immediately applied and a generic eigenstate reads\(^{100}\)

\[
\psi_{n,l}(r,\varphi) = C_{n,l} \frac{\Omega_{n,l}}{\sqrt{2\pi}} J_\nu J_l \left( \frac{z_{n,l} r}{R} \right)
\] (56)

where \(J_l(x)\) is the Bessel function of the first kind of order \(l\), \(z_{n,l}\) is the \(n\)th zero of \(J_l(x)\), and \(C_{n,l}\) is a normalization constant given by

\[
C_{n,l} = \frac{2}{R^2 \int_{0}^{\infty} |J_l(x)|^2 dx}
\] (57)

As the Rytova–Keldysh potential, Equation (47), is invariant under rotations, the quantum number \(l\) in Equation (56) is well-defined. As such, the Hamiltonian (Equation (1)) will be diagonal in blocks of fixed \(l\), which significantly lowers the computational complexity, effectively reducing the integration to a 1D problem. We can then compute the matrix elements of the Hamiltonian using two different functions \(\psi_{n,l}(r,\varphi)\)

\[
H_{n,m}^{(1)} = \left\langle \psi_{n,l} \left| -\frac{\hbar^2}{2m_e} \nabla^2 + V_{R-K}(r) \right| \psi_{m,l} \right\rangle
\] (58)

With the matrix element computed, we write a matrix for a chosen basis size \(N\). Diagonalizing this \(N \times N\) matrix, we obtain an approximation of the eigenstates and eigenenergies of the Wannier equation with the Rytova–Keldysh potential. The eigenvectors of the matrix will give the coefficients \(a_{n,n}\) of the expansion of the excitonic wave function on a basis of Bessel functions.

Focusing on an hBN monolayer, with the same parameters as before, we consider the 1s, 2s, and 2p excitonic states with a basis size of \(N = 120\) and \(R/a_0 = 200\).

The wave functions of the 1s, 2s, and 2p states are depicted in Figure 4 and the eigenenergies are given in Table 2, both showing a very good agreement with the variational calculation. Note how the wave functions already vanish for \(r = 100a_0\), justifying

![Figure 4. Bessel function expansion wave functions for hBN monolayer. Radial probability density \(|R(r)|^2\) of the 1s, 2s, and 2p states obtained using the finite basis approximation for hBN monolayer.](image)

Table 2. Energies from the basis-expansion method and from BSE for the hBN monolayer. Energies, in eV, of the excitonic ground state and first excited states for hBN obtained with the finite basis approach. The last line of the table are the results of the variational calculation, which have a slightly larger value, as demanded by the variational theorem. Also note that the solution via the BSE predicts different energy values for 2p\(_+_z\) and 2p\(_-_z\), which is not predicted by the Wannier equation.

| State | 1s  | 2s  | 2p\(_+_z\) | 2p\(_-_z\) |
|-------|-----|-----|------------|------------|
| \(E_n\) | -1.31 | -0.426 | -0.551 | -0.551 |
| \(E^{\text{BSE}}_n\) | -1.27 | -0.445 | -0.549 | -0.635 |
| \(E^{\alpha}_n\) | -1.27 | -0.402 | -0.547 | -0.547 |
the use of a disk radius of \( R = 200a_0 \). Increasing the value of \( R \)
would not produce any appreciable change on the final results. Reducing \( R \),
however, could significantly decrease the binding energies as a consequence of increased confinement. Also, note
that in Table 2, we give the result obtained via the solution of the BSE
calculation (how to solve the BSE is described later in the text). This equation takes the spinorial structure of
the wave function into account via the term \( F_{\varepsilon,k}\kexp{k,p-k,p} \), whereas the Wannier equation makes the approximation
\( F_{\varepsilon,k}\kexp{k,p-k,p} = 1 \). Therefore, one should not expect a complete agreement between the calculation
using the BSE and using the expansion in the Bessel function’s basis. In any case, the
energies found using an expansion in the Bessel function’s basis are smaller (more negative) than those found using the variational
calculation, as expected. Also, note that including the spinorial structure into account leads to a degeneracy breaking
between the states 2p\(_+\) and 2p\(_-\).

4.5. Shooting Method

The shooting method is a simple numerical approach for determining the eigenstates and the eigenvalues of the Wannier
equation. In broad strokes, this method is based on the discretization of the Wannier equation, which is then integrated for different values of the exciton energy until a smooth wave function is obtained. In the following, we give a more detailed description of this procedure.

As we mentioned earlier, the Rytov–Keldysh potential has a logarithmic divergence at the origin. Because of this, to optimize the numerical calculation, the differential equation should be discretized over a logarithmic grid, allowing for a sufficiently dense mesh near the origin, where the wave functions vary more abruptly. Hence, we first transform the radial Wannier equation using a logarithmic transformation and then apply an appropriate mesh of points for an accurate representation of the eigenstates over the full radial range. Here, we address this method in the context of a TMD monolayer.

The basic premise of this method lies in the fact that the Wannier equation only yields continuous wave functions with a continuous derivative for specific energy values, which correspond to the binding energies of the excitonic states. Our task is thus to find what energy values produce smooth wave functions. The shooting method is generally implemented in the following manner: i) first, an initial guess for the binding energy is chosen; ii) using this energy the Wannier equation is integrated from left to right, and from right to left, matching the two results somewhere far away from the edges of the domain. This can be done explicitly by discretizing the differential equation, or by using an appropriate numerical package. Also, one can choose to match the wave functions themselves, or their logarithmic derivative; iii) next, the wave functions are scaled in the matching point, forcing the continuity of the complete wave function (this step is not necessary if one works with the logarithmic derivatives); iv) afterward, the continuity of the derivative of the resulting function must be verified; if it is a smooth function, then the initial guess for the binding energy was correct, if not the process must be repeated with a new guess for the binding energy until the continuity condition is satisfied.

In a more detailed way, we start with the Wannier equation, and write the wave function as \( \psi(r) = R(r)\Phi(\theta) \), with \( \Phi(\theta) \propto e^{\text{in}m} \) where \( m = 0, \pm 1, \pm 2, \ldots \) is the angular quantum number. Using this, the Wannier equation is transformed into a differential equation defining the radial function \( R(r) \). Performing the substitution \( u(r) = R(r)/\sqrt{r} \), one finds

\[
\frac{1}{2\mu_{eh}} \frac{d^2 u}{dr^2} + \left[ \frac{4m^2 - 1}{8\mu_{eh}r^2} + V_{R^-K}(r) \right] u(r) = Eu(r)
\]

where the term proportional to \( m^2 \) is the well-known centrifugal potential, and the boundary conditions are \( u(r = 0) = 0 \) and \( u(r \to \infty) = 0 \). To facilitate numerical calculations it is convenient to consider the boundary conditions \( u(r = \epsilon) = \epsilon \) and \( u(r = R) = R \) instead, where \( \epsilon \) is a small, yet finite, quantity and \( R \) is chosen sufficiently deep into the region where \( u(r) \) decays monotonically to zero, such that \( u(R) \sim 0 \). Working with \( u(r) \) instead of \( R(r) \) has the advantage of eliminating terms with a first derivative in the radial coordinate. Note that transforming the problem from \( R(r) \) to \( u(r) \) is a natural modification since \( |u(r)|^2 = |R(r)|^2/r \) corresponds to the radial probability density. The shooting algorithm can be directly applied to Equation (52), however, to improve the efficiency of the calculation we can introduce the change of variable \( x = \ln r \), and the new function \( u(x) = f(x)e^{x/2} \), leading to the differential equation

\[
- \frac{1}{2\mu_{eh}} \frac{d^2}{dx^2} f(x) + \left[ \frac{m^2}{2\mu_{eh}} + e^{2x} V_{R^-K}(e^x) \right] f(x) = e^{2x} f(x) E
\]

The advantage of working with a logarithmic grid lies in the improved description of the region near \( r = 0 \), which is critical when the differential equation is integrated from left to right. Note that it is more important to have a detailed description near \( r = 0 \) than in the region \( r \to \infty \), since in the former the wave function and its derivative vary abruptly, while in the latter the changes are more gradual due to the slow decaying behavior of the wave functions at large distances. Numerically, we define a minimum value of \( x \) as \( x_{\text{min}} = e^{x_M} \), with \( x_M \) a negative number and a maximum value of \( x \) as \( x_{\text{max}} = e^{x_N} \), where \( x_M \) is a positive number. These two numbers, \( x_{\text{min}} \) and \( x_{\text{max}} \), define the lower and upper limits of the spatial grid, respectively. As noted, \( x_{\text{max}} \) is chosen such that the wave functions are essentially zero in an appreciable position range in the grid of points. The value of \( x_{\text{min}} \) is chosen such that the wave function near the origin is well represented.

In Figure 5a, we depict the wave functions obtained with the shooting method for the 1s state \( (m = 0) \) of the TMD WSe\(_2\), using three distinct guesses for the binding energy. Comparing the three results it is clear that \( E = -0.0094 \) a.u. (255 meV) corresponds to the correct binding energy, since it produces a smooth wave function, as opposed to the other two guesses, whose wave functions present a sharp kink in the matching point (implying that the used energy is not physically meaningful). The binding energy of other \( s \)-states can be obtained by changing the initial guess for the binding energy. To obtain the solutions of other exciton states, e.g., the 2p state, we modify the centrifugal potential (which now becomes finite), and introduce new guesses for the binding energy. The plot of the radial probability density of the 1s, 2p, and 3p states is
depicted in Figure 5b. There, we observe that the wave functions follow the same qualitative traits as their counterpart for the 2D hydrogen atom, with the difference of being more spread out in space as a consequence of the reduced interaction strength (in r in 2D instead of 1/r in 3D, when r → 0). The dashed lines mark the exciton Bohr radius of each state, corresponding to 23a₀, 72a₀ and 200a₀, with a₀ = 0.53 Å the Bohr radius of the Hydrogen atom, for the 1s, 2p and 3p states, respectively.

5. Momentum Space Solution

In the previous section, we described three possible approaches to solve the excitonic problem in real space, i.e., to solve the Wannier equation. Now, in the current section, we will present two methods to solve the excitonic problem directly in momentum space, i.e., to solve the Wannier and BSE equations. As we mentioned when both equations were introduced, the BSE should be more accurate than the Wannier equation, since the latter is obtained from the former after the introduction of a series of approximations. This increased accuracy comes at the cost of a reduced number of approaches to solve the BSE (for a seminal analytical approach see\[101,102\]).

In Section 5.1, we develop a method to solve the Wannier equation directly in momentum space. The method explores the expansion of the excitonic wave function in polar coordinates and the transformation of the integral equation in a generalized eigenvalue problem. We apply this method to the calculation of the ground-state energy of the 2D Hydrogen atom.

In Section 5.3, we shall describe how to treat the BSE by first converting it from a 2D to a 1D integral equation, followed by its discretization and numerical diagonalization. To be specific, we shall consider the case of a biased bilayer graphene. The energies and wave functions of its excitons will be computed, and its optical conductivity determined.

5.1. Solution of the Wannier Equation in Momentum Space

In this section, we present a fast semianalytical method of solving the Wannier Equation (4) in momentum space (which is an approximation to the BSE) based on an expansion in Chebyshev polynomials. The starting point is Equation (4). The next step is the expansion of the exciton wave function in polar coordinates as

$$\psi_n(k) = \psi_n(k, \theta) = \sum_{l=-\infty}^{\infty} \psi_{n,l}(k) e^{il\theta}$$

(61)

where n denotes the principal quantum number. Introducing the angular average of the potential

$$V_l(k, q) = \int_0^{2\pi} \frac{d\theta}{2\pi} V(k - q) e^{il\theta}$$

(62)

we obtain

$$\frac{\hbar^2}{2\mu_0} k^2 \psi_{n,l}(k) - \int_0^\infty dq d\theta V_l(k, q) \psi_{n,l}(q) = E_{nl} \psi_{n,l}(k)$$

(63)

To apply the Chebyshev method, the limits of integration must coincide with the domain in which the Chebyshev polynomials are defined, \(x \in [-1, 1]\). To this end, a conformal hyperbolic map is applied, reading

$$x = \frac{\xi k - 1}{\xi k + 1}$$

(64)

with \(\xi\) a scaling parameter (later chosen to be 1). This transforms the Wannier equation into

$$\frac{\hbar^2}{2\mu_0 \xi^2} \left( \frac{1 + x}{1 - x} \right)^2 \psi_{n,l}(x) - \frac{1}{\xi^2} \int_{-\infty}^{\infty} dt \frac{1 + t}{\pi (1 - t)^3} V_l(x, t) \psi_{n,l}(t)$$

$$= E_{nl} \psi_{n,l}(x)$$

(65)

We then expand the wave function coefficients in terms of Chebyshev polynomials, \(T_l(x)\), while considering a weight function \(f(x)\) as

$$\psi_{n,l}(x) = f(x) \sum_{m} \psi_{n,l}^{(m)} T_m(x).$$

(66)

The weight function \(f(x)\) is used to assure the convergence of the method. Upon replacing Equation (65) in (64) and looking at the integral in Equation (64) alone we find


\[ \int_{-1}^{1} \frac{1 + t}{\pi (1 - t)} V_i(t) f(t) T_m(t) = \int_{-1}^{1} \frac{d}{dt} K_i(x, t) T_m(t) \]

and choosing \( f(x) = (1 - t)^{1/2} / (1 + t) \), the integration kernel \( K_i(x, t) \) acquires a very simplified form, reading

\[ K_i(x, t) = \frac{x - t}{\pi} V_i(x, t) \]  

To be able to efficiently compute this kernel, we consider its expansion in terms of Chebyshev polynomials as

\[ K_i(x, t) \approx \sum_{m} b_{m,i}(x) T_m(t) \]  

where the integral can now be done analytically using

\[ \int_{-1}^{1} \frac{d}{dt} T_j(t) T_m(t) = \frac{1}{2} \left[ \delta_{j+m} + \lambda_{j-m}(x) \right] \]

where \([103] \)

\[ \lambda_{0}(x) = \log \left| \frac{1 + x}{1 - x} \right| \]

\[ \lambda_{1}(x) = -2 + x\lambda_{0}(x) \]

and the recursion relation for higher order terms is

\[ \lambda_{k+1}(x) = 2x\lambda_{k}(x) - \lambda_{k-1}(x) + 2 \frac{1 + \cos(kx)}{k^2 - 1} \]

where \( k = 1, 2, \ldots \) The kernel integral then reads \([103] \)

\[ I_{m,i} = \int_{-1}^{1} \frac{d}{dt} K_i(x, t) T_m(t) \]

\[ = \frac{1}{2} \sum_{j} b_{j,i}(x) \left[ \delta_{j+m} + \lambda_{j-m}(x) \right] \]

Defining a grid of points coincident with the zeros of the Chebyshev potential of order \( N \)

\[ x_i = \cos \left( \frac{2i - 1}{2N} \pi \right) \]

with \( i = 1, 2, \ldots, N \), Equation (57) is transformed to

\[ \frac{\hbar^2}{2\mu_0} \frac{1}{2E} \left( \frac{1 + x_i^2}{1 - x_i^2} f(x_i) \right) \sum_{m} T_m(x_i)c_{m,i} = \frac{1}{2E} \sum_{m} I_{m,i} c_{m,i} \]

\[ = E^i f(x_i) \sum_{m} T_m(x_i)c_{m,i} \]  

which defines a generalized eigenvalue problem (with \( x_i \) and \( m \) the matrix entries). This concludes the presentation of the method. As a simple example, we show results for the 2D hydrogen atom in Table 3, where the convergence of the method is studied with the number of Chebyshev polynomials. In atomic units, the repulsive Coulomb potential reads \( V(q) = 2\pi/\hbar^2 \) and the ground state energy is \( E^{1,0} = -2 \).

In Figure 6, we depict the linear scaling of the ground state energy of the 2D hydrogen atom as a function of the number \( N \) of Chebyshev polynomials used, in the interval \( N \in [10, 100] \). The exact value for the ground state energy is \( E^{1,0} = -2 \) whereas the finite-size scaling gives \( E^{1,0} = -1.991 \). The result could be improved if larger \( N \)’s are included in the fitting.

Although we have used the method for solving the Wannier equation, its extension to the solution of the BSE is elementary since it amounts to the multiplication of the electrostatic potential by the structure factor coming from the spinorial nature of the wave functions. This extension will be addressed somewhere else.\([104]\)

### 5.2. Tight-Binding Model of Biased Bilayer Graphene

Before describing how to solve the BSE for a multiband system, we shall briefly go over a tight-binding model for biased bilayer graphene. This has been treated in other references where more detailed discussions can be found.\([105–108]\)

In Figure 7, we show the lattice of biased bilayer graphene. It essentially corresponds to two graphene layers in the AB (or Bernal) stacking configuration subject to an external electric field...
which creates a potential difference between the bottom and top layers. To characterize this system we shall employ a tight-binding Hamiltonian written directly in momentum space, where we account for nearest neighbors intralayer hoppings ($\gamma_0$), as well as nearest neighbors ($\gamma_1$) and next nearest neighbors ($\gamma_3$, $\gamma_4$, and $\gamma_5$) interlayer hoppings. Doing so, one finds the Hamiltonian to be

$$H_{TB} = V\begin{bmatrix} \gamma_0\phi(k) & \gamma_1 & \gamma_4\phi^*(k) \\ \gamma_0\phi^*(k) & V & \gamma_3\phi(k) \\ \gamma_1 & \gamma_3\phi(k) & -V & \gamma_0\phi^*(k) \\ \gamma_4\phi(k) & \gamma_5\phi^*(k) & \gamma_0\phi^*(k) & -V \end{bmatrix}$$

(78)

when written in the basis \{a, b, c, d, e, f\}, where b/t denotes bottom and top layers, and 1, 2 denotes the different sub-lattices in each layer (see Figure 7). Also $\phi(k) = \sum_{i=1}^{3} e^{ikd_i}$, with $d_i$ are the vectors connecting a given site with its three nearest neighbors. The top layer is at a potential of $+V$, and the bottom layer at $-V$, meaning that the total potential difference between the top and bottom layers is $2V$. Although we have considered several hopping parameters, we shall set $\gamma_3 = \gamma_4 = 0$ when computing the band structure and eigenvectors, due to their low impact on those results. However, when computing the optical response later in the text, these hoppings will be included in the definition of the dipole matrix element to more accurately capture the optical selection rules.

Similar to what was done when the tight-binding model for hBN was introduced, we can expand this Hamiltonian near the points $K_{\pm} = \left(\frac{\pi}{3a}, 0\right)$, leading to an effective low-energy Hamiltonian. In Figure 8, we depict the bands obtained from the diagonalization of such an Hamiltonian, for different values of V.

Clearly, when $V \neq 0$, a gap opens; this is the key ingredient to exploring excitonic effects. From the diagonalization of the low-energy Hamiltonian, we also find the eigenvectors associated with each band. We label these vectors as $|\phi_k^{\eta}\rangle$ and $|\phi_k^{\eta'}\rangle$, where the index $\eta$ is defined as in Figure 8, i.e., the bands closer to the middle of the gap have $\eta = -1$, while the other two have $\eta = 1$. The eigenvectors read...
\[ |\psi_{k}^{(p)}\rangle = \begin{cases} |a_{1}^{-1}e^{i\theta}, a_{2}^{-1}e^{i\theta}, a_{3}^{-1}e^{2i\theta}\rangle & (79) \\
|\alpha_{k}^{p}\rangle = \begin{cases} |a_{1}^{+}, a_{2}^{+}e^{-i\theta}, a_{3}^{+}\rangle, \alpha_{a_{4}}^{+e}\rangle & (80) \\
|\alpha_{k}^{p}\rangle = \begin{cases} |a_{1}^{-}, a_{2}^{-}e^{-i\theta}, a_{3}^{-}, a_{4}^{-}\rangle, \alpha_{a_{4}}^{-}\rangle & (81) \\
|\alpha_{k}^{p}\rangle = \begin{cases} |a_{1}^{+}, a_{2}^{+}e^{-i\theta}, a_{3}^{+}, a_{4}^{+}\rangle, \alpha_{a_{4}}^{+}\rangle & (82) \\
\end{cases}
\end{cases}
\]

where \(\theta = \arctan(k_{y}/k_{x})\), with \(k = (k_{x}, k_{y})\) the wave vector measured relatively to the point \(K_{c}\), where \(r = \pm 1\). The specific form of each entry is of not particularly interesting for the current discussion due to their complicated analytical expressions. However, we note that for small \(k\) one finds \(|a_{1}^{-}\rangle, |a_{1}^{+}\rangle |a_{2}^{-}\rangle, |a_{2}^{+}\rangle |a_{3}^{-}\rangle, |a_{3}^{+}\rangle |a_{4}^{-}\rangle, |a_{4}^{+}\rangle \approx |a_{1}^{-}\rangle, |a_{1}^{+}\rangle |a_{2}^{-}\rangle, |a_{2}^{+}\rangle \approx |a_{3}^{-}\rangle, |a_{3}^{+}\rangle \approx |a_{4}^{-}\rangle, |a_{4}^{+}\rangle\).

\section{5.3. Solution of the BSE}

In this part of the section, we shall describe how to solve the BSE, to obtain the energies and wave functions of the excitons in biased bilayer graphene. As we saw earlier, the BSE for a multi-band system can be expressed as \(\psi_{k}^{(p)}(k) = (E_{k} - E_{k}^{(p)})\psi_{k}^{(p)}(k) + \sum_{q} V(k - q) \times \left\langle \psi_{k}^{(p)}(q) \right\rangle \psi_{k}^{(p)}(q)
\)

\(\psi_{k}^{(p)}(k)\) is the excitonic wave function that we wish to obtain, \(\psi_{k}^{(p)}(q)\) and \(E_{k}^{(p)}\) are the single-particle electronic wave functions and energies of each band (which we obtained earlier), and \(V(k)\) is the Fourier transform of the Rytova–Keldysh potential coupling different bands and thus capturing many-body effects including the intrinsic many-body nature of excitons.

As previously noted, we consider the electrostatic potential to be the Rytova–Keldysh potential \(\tau_{\theta}/\alpha\) (usually employed to describe excitonic phenomena in mono- and few-layer materials), whose derivation is available in Section 3.4. In momentum space, this potential is given by

\[ V(k) = \frac{2\pi\hbar e}{\epsilon_{r} k(1 + r_{0}k)} \]

where \(\alpha \approx 1/137\) is the fine-structure constant, \(\epsilon_{r}\) the mean dielectric constant of the medium above/below the bilayer graphene. The parameter \(r_{0}\) corresponds to an in-plane screening length related to the 2D polarizability of the material. It can be calculated from the single-particle Hamiltonian of the system, although \(ab\) initio calculations might be necessary for accurate computation of \(r_{0}\) depending on the material.\(^{113}\) This screening parameter varies with the bias potential \(V\) (since the band structure is also modified), and its numerical value is of the utmost importance if the excitonic properties of a specific system are to be studied accurately.\(^{113,114}\) An in-depth discussion of the in-plane screening length in bilayer graphene has been done in Ref. [116]. In our biased bilayer graphene system, with \(V = 52\text{meV}\), the value of this effective screening length is \(r_{0} \approx 107.\AA\).

To solve the BSE, we first decompose the exciton wave function into the product of an angular and a radial part. Therefore, the wave function can be written as \(\psi_{k}^{(p)}(k) = \int \psi_{k}^{(p)}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}\)

with \(m = 0, \pm 1, \pm 2, \ldots, \pm 6\). Then, the phases of the eigenvectors \(\psi_{k}^{(p)}\) must be chosen in such a way that the form factor \(\left\langle \psi_{k}^{(p)}\right|\psi_{q}\left|\psi_{k}^{(p)}\right\rangle\) always leads to angular dependences of the form \(e^{i\mathbf{q}\cdot\mathbf{r}}\), with \(\lambda\) an integer, for every combination of valence and conduction bands. If this is the case, then the sum over \(q\) can be converted into an integral, and through a change of variable, the angular integral can be evaluated. This effectively transforms the initial 2D integral equation into a simple 1D problem, which can then be numerically diagonalized. More details on how to achieve this are discussed in Section 7.

Due to its particular band structure, the excitonic properties of biased bilayer graphene are dominated by the two bands closer to the middle of the gap, with the other two introducing only small corrections. As a result, to simplify the following analysis, we restrict our problem to those two bands. We note, however, that our description to solve the BSE could be equally applied if the 4 four bands were to be accounted for; in fact, in some systems, such as bilayer hBN, the complete four-band model has to be used.\(^{117,118}\)

Based on these considerations, we solve the BSE, and obtain the binding energies displayed in Table 4. The states were labeled following the notation of the hydrogen atom, with s-states having \(m = 0\), p-states having \(m = \pm 1\), etc. We note the energy difference between states with symmetric \(m\), something not captured by the Wannier equation, and that can be interpreted as a modification of the kinetic energy of the carriers due to the finite Berry curvature near the K points in this type of material.\(^{119}\)

Furthermore, it is important to note that Equation (83) is actually a separate equation for each pair of bands \(c, \eta_{i}, \nu, \eta_{k}\). This implies that there are four equations (two valence times two conduction) that must be solved simultaneously, stemming from the two valence and two conduction bands. Additionally, as mentioned previously, a careful choice of the phases of the single-particle spinors allows us to transform the BSE into a 1D integral equation. Details of this procedure are given in the Appendix of Ref. [38]. In 7, a summary overview of this methodology is discussed, as well as the numerical method for 1D integration of the BSE.

\section{5.4. Optical Conductivity}

Now, as the final part of this section, we shall use the solution of the BSE to compute the optical conductivity of biased bilayer graphene due to excitons.

| \(E_{\text{BSE}}\) | 1s | 2s | 2\(p_{+}\) | 2\(p_{-}\) |
|---|---|---|---|---|
| -16.3 | -5.36 | -9.35 | -10.3 |
Considering that the system is excited by an external time-dependent electric field, and working in the dipole approximation, the optical conductivity of the system is given by\(^\text{[54,120,121]}\) (generalizations to nonlinear optics of 2D materials are also available\(^\text{[58]}\))

$$\sigma^{(1)}(\omega) = \frac{e^2}{8\pi^2\hbar^2} \sum_{n} E_n \frac{\Omega_n \Omega_n^*}{E_n + \hbar\omega} + (\omega \rightarrow -\omega)^*$$  \(\text{(85)}\)

where the sum over \(n\) represents the sum over excitonic states with energy \(E_n\) and wave function \(\psi_{n,\text{exc}}\). Additionally, a phenomenological broadening parameter \(\Gamma_n\) is included via the usual substitution \(\omega \rightarrow \omega + i\Gamma_n\). This parameter is considered to be \(n\)-dependent\(^\text{[58]}\) In Equation (85), \(\Omega_n\) is defined as

$$\Omega_n = \sum_{\ell, r} \langle \psi_{n,\text{exc}}(\mathbf{k}) | \mathbf{u}_\ell^\dagger | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{u}_\ell | \psi_{n,\text{exc}}(\mathbf{k}) \rangle$$  \(\text{(86)}\)

with \(\langle \mathbf{u}_\ell^\dagger | \mathbf{r} \rangle | \mathbf{u}_\ell | \psi_{n,\text{exc}}(\mathbf{k}) \rangle\) the interband dipole operator matrix element; \(\mathbf{r}\) is the position operator and \(\mathbf{e}\) the polarization vector of the external time-dependent electric field. To compute this matrix element, we invoke the relation

$$\langle \mathbf{u}_\ell^\dagger | \mathbf{r} \rangle | \mathbf{u}_\ell | \psi_{n,\text{exc}}(\mathbf{k}) \rangle = \frac{\langle H, \mathbf{r} \rangle | \mathbf{u}_\ell \rangle}{E^\mathbf{u} - E^\mathbf{k}}$$  \(\text{(87)}\)

Evaluating the commutator and transforming the sum over \(k\) into a 2D integral, selection rules are imposed from the angular integration, i.e., the values of \(m\) which lead to finite results are determined. As mentioned when the tight-binding model of this system was introduced, we consider the hoppings \(\gamma_1, \gamma_4,\) and \(\gamma_5\) when evaluating this commutator. Although this approach is not entirely self-consistent, it is an excellent approximation that significantly simplifies the calculations.

For a linearly polarized electric field, we reproduce the same optical selection rules as those found in\(^\text{[58]}\) with the \(\gamma_0\) hopping parameter allowing transitions to states with \(m = -\tau\) and \(m = -3\tau\) (\(p\)- and \(f\)-states, respectively, when hydrogenic labels are used). Transitions to states with \(m = 0\) (the \(s\)-states) are allowed only by the next nearest neighbors hopping parameter \(\gamma_5\), as obtained in\(^\text{[58]}\).

Fixing the external bias potential at \(V = 52\text{meV}\),\(^\text{[58]}\) we obtain Figure 9 for the full xx linear optical conductivity. In this figure, we can clearly distinguish three resonances, namely those associated with 1s, 2p\(_{-}\), and 3p\(_{-}\) states, with a plateau forming close to the bandgap value as the excitonic resonances become ever closer to each other.

6. Conclusion

In this perspective, we have addressed different theoretical methods for computing the excitonic wave function and corresponding eigenenergies. The methods vary. Starting with the simpler variational method in real space and closing with the solution of the BSE in momentum space, we hope to arm the reader with a multitude of techniques that allow them to start doing research on this topic. Putting together in a single paper the different methods scattered in the literature and making the text as self-contained as possible, the reader may find this reference quite useful for daily research work. One of the topics of this article was the application of the BSE to biased graphene bilayer. This system can also be doped with a dual gate architecture, leading to the possibility of controlling excitons excitation by inducing residual carriers in the conduction band of the bilayer.\(^\text{[122]}\)

The methods described in this article can also be applied to more difficult systems, such as interlayer excitons in multi-layer materials or by considering spin–valley couplings. Additionally, a relevant system for future research is ABC–trilayer graphene, with a bandgap controlled externally by an electric field perpendicular to the layers, and which displays various many-body phenomena recently considered in both experimental and theoretical articles. Also interesting to explore is the opening of a gap in twisted bilayer graphene due to Coulomb interactions\(^\text{[123]}\) and well as excitons in the metallic regime, a very unconventional situation.\(^\text{[124]}\) Finally, the extension of the methods discussed in this perspective for studying excitons in Moiré TMD and hBN is worth pursuing.

Appendix

Methodology for Integration of Bethe-Salpeter Equation with Rytova-Keldysh Potential: The Case of Biased Graphene Bilayer

Taking the thermodynamic limit, Equation (83) can be written as

$$E f_{c,\eta_{\mathbf{k}}, \eta_{\mathbf{q}}} (k) = (E^\mathbf{k} - E^\mathbf{q}) f_{c,\eta_{\mathbf{k}}, \eta_{\mathbf{q}}} (k) - \frac{1}{4\pi^2} \sum_{\eta_{\mathbf{q}}} \int q dq d\theta q V(k - q) \langle \mathbf{u}_{\mathbf{k}} | \mathbf{u}_{\mathbf{q}} \rangle \langle \mathbf{u}_{\mathbf{q}} | \mathbf{u}_{\mathbf{k}} \rangle$$  \(\text{(A1)}\)

$$\times \langle \mathbf{u}_{\mathbf{q}} \rangle \langle \mathbf{u}_{\mathbf{k}} \rangle f_{c,\eta_{\mathbf{k}}, \eta_{\mathbf{q}}} (q) e^{im(\theta q - \theta k)}$$

\(\text{Figure 9. Optical conductivity of biased graphene bilayer. Real part of the excitonic xx-conductivity for biased Bernal-stacked bilayer graphene encapsulated in hBN with a bias potential } V = 52\text{meV, broadening parameters } \Gamma_{\eta_{\mathbf{q}}} = 0.3\text{meV and } \Gamma_{\eta_{\mathbf{q}}} = 0.1\text{meV, and a } N = 450\text{ point Gauss–Legendre quadrature. The first ten states of each excitonic series were considered for the total conductivity. Vertical dashed lines represent the bandgap of the system. The different } \eta_{\mathbf{q}} \text{ in the legend symbolize the hopping term that leads to specific resonances. The quantity } \sigma_0 = \pi e^2 / (2h).\)
This problem can be simplified further as
\[
\langle \phi_{m}^{0} \rvert \phi_{q}^{0} \rangle \langle \phi_{q}^{0} \rvert \phi_{k}^{0} \rangle = \sum_{j=0}^{4} A_{j}^{m,q_{j},q_{j}}(k, q) \theta^2(d_{j} - d_{j+1})
\]  
(A2)

where the angular dependence has been extracted from \( A_{j}^{m,q_{j},q_{j}}(k, q) \).

Regarding the radial integral of the potential term, it can be written as
\[
I_{m}(k, q) = \int_{0}^{2\pi} \frac{\cos(m\theta)}{\kappa(k, q, \theta)} d\theta - \int_{0}^{2\pi} \frac{\cos(m\theta)}{1 + \rho_{0}(k, q, \theta)} d\theta
\]

(A3)

where \( \kappa(k, q, \theta) = \sqrt{k^2 + q^2 - 2kq\cos\theta} \) and only the even term is nonzero due to parity. Inspecting the integrand, it is clear that the \( I_{m} \) function will be numerically ill-behaved when \( k = q \). For this effect, we decompose the integrand in terms of partial functions as
\[
I_{m}(k, q) = \sum_{j=0}^{4} \int_{0}^{2\pi} \frac{\cos(m\theta)}{\kappa(k, q, \theta)} d\theta - \int_{0}^{2\pi} \frac{\cos(m\theta)}{1 + \rho_{0}(k, q, \theta)} d\theta
\]

(A4)

With this decomposition, it is clear now that only the \( I_{m}(k, q) \) integral will be problematic when \( k = q \). Substituting \( I_{m}(k, q) \) into Equation (A1), we write
\[
E_{f,C_{R},\eta_{1},\eta_{2}}(k) = (E_{k}^{m} - E_{k}^{q}) \sum_{j=1}^{4} m_{j}^{m,q_{j},q_{j}}(k, q) A_{j}^{m,q_{j},q_{j}}(k, q)
\]

(A5)

Writing (where the possible values of \( \lambda = 0, \ldots, 4 \) is specific of the biased graphene bilayer)
\[
\mathcal{J}_{m,q_{j},q_{j}}(k, q) = \sum_{j=0}^{4} m_{j}^{m,q_{j},q_{j}}(k, q) A_{j}^{m,q_{j},q_{j}}(k, q)
\]

(A6)

\[
E_{f,C_{R},\eta_{1},\eta_{2}}(k) = (E_{k}^{m} - E_{k}^{q}) \sum_{j=1}^{4} m_{j}^{m,q_{j},q_{j}}(k, q) A_{j}^{m,q_{j},q_{j}}(k, q)
\]

(A7)

the BSE can now be compactly written as
\[
E_{f,C_{R},\eta_{1},\eta_{2}}(k) = (E_{k}^{m} - E_{k}^{q}) \sum_{j=1}^{4} m_{j}^{m,q_{j},q_{j}}(k, q) A_{j}^{m,q_{j},q_{j}}(k, q)
\]

(A8)

We now focus our attention on the problematic \( \mathcal{J}_{m,q_{j},q_{j}}(k, q) \) object. To treat the divergence at \( q = k \), an auxiliary function \( g_{m}(k, q) \) is introduced. This function obeys the limit
\[
\lim_{q \rightarrow k} \mathcal{J}_{m,q_{j},q_{j}}(k, q) - g_{m}(k, q) = 0
\]

(A9)

and it modifies the integrals as
\[
\int_{0}^{\infty} \mathcal{J}_{m,q_{j},q_{j}}(k, q) f_{C_{R},\eta_{1},\eta_{2}}(k, q) dq
\]

(A10)

Following,[125,67,58] this auxiliary function is chosen as
\[
g_{m}(k, q) = \mathcal{J}_{m,q_{j},q_{j}}(k, q) \frac{2k^2}{k^2 + q^2}
\]

(A11)

Having finished outlining the analytical procedure, we now proceed to the numerical solution of the BSE. This is performed using the same methodology as,[58] which we will quickly outline. A variable change is introduced to convert the integration limits from \([0, +\infty)\) to a finite limit, in this case \([0, 1]\), defined as \( q = \tan(\pi t) \). With this variable change, we proceed by discretizing \( x \), writing the numeric problem as
\[
\int_{0}^{b} f(x) dx \approx \sum_{i=1}^{N} f(x_{i}) w_{i}
\]

(A13)

\[
where
\]

(A14)

with \( \xi_{i} \) the \( i \)th zero of the Legendre polynomial \( P_{N}(x) \).
Finally, it is important to realize that Equation (A8) can be written as the eigenvalue problem of a $tN \times tN$ matrix (i.e., a $t \times t$ matrix of $N \times N$ matrices). The $i^\text{th}$ blocks come from the different combinations of band indices (i.e., $t$ conduction bands times $t$ valence bands), and each $N \times N$ matrix comes from the numerical discretization of the integral. Specifically, in biased bilayer graphene Equation (A8) would be written as a $2N \times 2N$ matrix. Solving this eigenvalue problem for a sufficiently large quadrature, one obtains the excitonic eigenvalues and eigenfunctions.

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**Conflict of Interest**

The authors declare no conflict of interest.

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