Semianalytical study of excitons and quasiparticle band gap in two-dimensional insulators

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A theoretical study of the exciton binding energy in the two-dimensional hexagonal boron nitride monolayer is presented within the tight-binding approximation (TBA). A self-consistent equation for the interband electron-hole propagators is derived and in the long wavelength limit reduced to the standard hydrogen atom like Schrödinger equation. It is shown that inclusion of dynamically screened Coulomb interaction in ladder term is of crucial importance for proper description of exciton binding energy. This leads to the self-consistent eigenvalue problem with dynamical screening. The dependence of the exciton energy on the orbital quantum number is studied. It is predicted that for the fixed principal quantum number the states with higher orbital momentum have lower energy than the states with lower orbital momentum. Using the developed formulas and the experimental optical gap the quasiparticle gap is estimated. In the limit of high polarizability, a semiclassical procedure was used to obtain the exciton binding energy. The TBA parametrization is supported by ab initio calculations.

I. INTRODUCTION

For the last decade, the condensed matter physics has been dominated by experimental and theoretical investigation of the two-dimensional materials. One class of these materials are the direct gap two-dimensional insulators. The best known examples are monolayers (ML) of the members of transition-metal dichalcogenides and a hexagonal boron nitride monolayer (hBN-ML). hBN-ML, the simplest of the 2D insulators, exhibits a wide optical gap which in turn is responsible for a low electronic polarizability. With this electronic property comes the chemical inertness and mechanical stability, which originates from the strong σ bonds between the sp² hybrids. However, in spite of its simple structure, some basic problems still remain unsolved. The most significant is the inability to experimentally determine the single particle band gap, which numerous ab initio studies estimate to be between 7 and 9 eV. On the other hand, well established ab initio methodology which includes quasiparticle corrections (GW method) and solving the Bethe-Salpeter equation (BSE), so called GW-BSE method, is capable of giving accurate single particle and optical gap energies, including excitonic energy and their oscillator strength. However, the GW-BSE method is still computationally very heavy and time consuming (even for 2D crystals) while the method here proposed is semi-analytical and provides a fast estimation of excitonic energy and single particle gap.

In three-dimensional insulators, the exciton energies can be calculated using the simple Wannier hydrogen-like model in which the Coulomb interaction is screened by dielectric constant. In the optical absorption measurements the lowest exciton state appears as a well-defined isolated peak and higher exciton energies rapidly converge toward the single particle band gap. Therefore, the error in estimating the single particle band gap is relatively small.

However, in two-dimensional insulators the screening effects are large due to spatially depended dielectric function which screens the Coulomb potential in a nontrivial way. This modifies the hydrogen-like model substantially, resulting in (compared with the 3D case) a drastic change of quantized exciton energies and the absence of the degeneracy of the hydrogen-like orbitals, leading to their dependence not only on the principal quantum number n, but on the orbital quantum number ℓ as well. The ℓ-dependence of the exciton energies can be seen by probing the two-dimensional insulators with the two photon luminescence techniques.

In this paper the single particle properties of the hBN-ML are calculated using the tight binding approximation. The TBA parameters are determined using the conductivity sum rule and from the difference of the bare atomic orbitals energies. The calculated TBA parameters are supported by the ab initio results such as DFT-LDA band gap and effective masses. The electronic polarizabilities have been calculated in both approaches and compared. Also within the TBA model the charge vertices have been derived explicitly. This will allows us to classify various contributions to the electron-hole propagator equation. The exciton energies are derived using the equation of motion techniques for the electron-hole pair propagator. A systematic derivation of the four contributions (in the leading order of Coulomb interaction) to the electron-hole propagator equation have been analyzed. In the ladder part, which governs the electron-hole dynamics, the dynamically screened Coulomb interaction is implemented. In the long wave limit approximation the electron-hole equation is reduced to Schrödinger equation for dynamical screened potential which is then solved self-consistently. The eigenvalues, i.e. the exciton ener-
gies, are calculated for the dynamical and statical case and compared. It will be argued that it is possible to obtain a realistic value of the single particle band gap using the experimentally obtained energy of the exciton ground state. This can be done by combining the DFT-LDA calculations of the static polarizability and the effective mass of the electron in the valence ($v$) and the conduction ($c$) band around the K point, which enter in to the Schrödinger equation with the screened Coulomb potential. Here it is assumed that hBN-ML sheet is free-standing. This way, various effects originating from the finite substrate polarization are deliberately avoided [16]. Particularly, the exciton ground state energy in the high polarizability limit is investigated by employing the Einstein-Brillouin-Keller (EBK) procedure [17] and compared with the solutions of the Schrödinger equation for the screened Coulomb potential. This leads to the analytical expression for the exciton ground state energy which is used to predict the quasiparticle band gaps of the selected two-dimensional insulators [18–20].

The extended calculations of the quasiparticle and exciton properties in hBN-ML followed by the ab initio parametrized TBA is given in Ref. [21]. But unlike the results presented in this paper, their results are too extensive but not applicable for a simple estimation of the exciton energies and the quasiparticle band gap.

This paper is organized as follows. In Sec. III the electronic band structure is determined using ab initio and tight binding approximation. A brief formulation of the ab initio calculation of the dielectric response and quasiparticle corrections in wide gap 2D crystals is presented. The band gap is estimated within the same ab initio formalism and using the conductivity sum rule. In Sec. III the equations that determine the dynamics of the electron-hole propagation are derived to the first order in Coulomb interaction. This equation is equivalent to the two-body Schrödinger equation and is solved for the case of bare and dynamically screened Coulomb interaction. The screened Coulomb interaction is calculated within the two-band TBA model. In Sec. IV the results are presented. The first ten exciton energy levels and their spatial extend are calculated. The exciton ground state energy in the high polarizability limit is investigated by using the EBK procedure and compared with the results of Sec. IV A.

II. BAND STRUCTURE

A. Ab initio studies of hBN-ML band structure and dielectric properties

In order to maintain the TBA parametrization in the framework of realistic crystal values the DFT calculation of the electronic ground state and the RPA dielectric function of hBN-ML are provided. Additionally, a brief quasiparticle $G_0W_0$ correction of DFT-LDA band gap around K point is provided, as discussed later.

At the DFT stage of the calculation the Kohn-Sham (KS) wave functions $\varphi_{Lk}(r)$ and energy levels $E_{Lk}^0$, i.e. the band structure of a hBN-ML is determined using the plane-wave DFT code QUANTUM ESPRESSO (QE) [22]. The core-electron interaction is approximated by the norm-conserving pseudopotentials [23], and the exchange correlation (XC) potential by the LDA Perdew-Zunger (PZ) functional [24]. For the hBN-ML primitive cell constant, $a = 4.746 \ \alpha_0$ ($\alpha_0$ is the Bohr radius) is used and the superlattice constant in the z direction is $L = 23.73 \ \alpha_0$. The ground state electronic densities of the hBN-ML are calculated using the $12 \times 12 \times 1$ Monkhorst-Pack k-point mesh [25] of the first Brillouin zone (BZ). For the plane-wave cut-off energy 60 Ry (816 eV). In order to obtain sharp Van Hove singularities the partial density of states (PDOS) are calculated using the $101 \times 101 \times 1$ Monkhorst-Pack k-point mesh.

If hBN-ML is approximated as fully 2D system its dielectric function is given by [19] with the independent electrons response function $\chi^0(q, \omega) = L\lambda_{g_z=0,g_z'=0}(q, \omega)$ given by (4.10). However, if the dispersivity of the dielectric response in the direction perpendicular to crystal lattice plane (the z direction) is included, the response function matrix becomes

$$\chi_{g_z, g'_z}(q, \omega) = \chi^0_{g_z, g'_z}(q, \omega) + \frac{1}{V} \sum_{kLL'} G^LL'_{k,k+q}(g_z) \frac{f^L_{k} - f^L'_{k+q}}{\hbar \omega + i \eta + E_{L}^k - E_{L'}^{k+q}} G^{*LL'}_{k,k+q}(g'_z),$$

where $f^L_{k}$ is the Fermi-Dirac distribution at temperature $T$ and the charge vertices are

$$G^LL'_{k,k+q}(g_z) = \int_V \mathrm{d}^3r \varphi^*_{Lk}(r)e^{-iq\cdot r} e^{-iqz} \varphi_{L'k+q}(r).$$

Here $q$ is the momentum transfer vector parallel to the $x - y$ plane and $r = (\rho, z)$ is a 3D position vector and $g_z$ is the reciprocal lattice vector in the perpendicular (z) direction. Integration in (2.2) is performed over the normalization volume $V = S \times L$, where $S$ is the normalization surface. The independent electron response function (2.1) is calculated using $201 \times 201 \times 1$ k-point mesh sampling which corresponds to 40405 Monkhorst-Pack special k-points in the Brillouin zone. This k-point mesh sampling enables the minimum transfer wave vector $q_{min} = 0.0076 \ \alpha_0^{-1}$. The damping parameter used is $\eta = 50$ meV and the temperature is $k_B T = 10$ meV. The band summation is performed over 40 bands, which proved to be sufficient for proper description of the electronic excitations up to 30 eV.

It is shown that in the long wavelength limit ($q \approx 0$) the hBN-ML 2D static dielectric function can be approximated as:

$$\epsilon(q \approx 0, \omega = 0) = 1 + \lambda_{DFT}|q|$$

where the DFT screening length is $\lambda_{DFT} = 10.5 \ \alpha_0$. Considering wide hBN-ML band gap, the static approximation [26] is valid in the dynamical limit, even up to
relation energy is Here XC is LDA exchange correlation energy, COH correlation energy is

\[ \Sigma_{\text{XC}} = \frac{1}{2} \sum_{L'} \int \frac{dq}{(2\pi)^2} w^{\text{ind}}_{g_z,g_z'}(q, \omega = 0)G^{LL'}_{k,k+q}(g_z - g_z') \]  

and static SEX energy is

\[ \Sigma_{\text{SEX}} = - \sum_{L'} \int \frac{dq}{(2\pi)^2} f^{L'} L'_{k,k+q} \times \]

\[ w^{\text{ind}}_{g_z,g_z'}(q, \omega = 0)G^{LL'}_{k,k+q}(g_z)G^{LL'}_{k,k+q}(g_z') \]

The induced Coulomb interaction matrix \( \hat{w}^{\text{ind}} = \hat{v}\hat{\chi} \hat{v} \) is determined by solving Dyson-equation \( \chi = \hat{\chi}_0 + \hat{\chi}\hat{\phi}\hat{\chi} \) for the screened response matrix \( \hat{\chi} \). The bare Coulomb interaction matrix elements are given by

\[ v_{g_z,g_z'}(q) = \frac{e^2}{L} \int_{-L/2}^{L/2} dz dz' e^{-q|z-z'|} e^{ig_zz} e^{-ig_z'z'} \]

and total, screened Coulomb interaction matrix is \( \hat{w} = \hat{v} + \hat{w}^{\text{ind}} \).

The hBN-ML is a direct gap insulator with the conduction band minimum (CBM) and the valence band maximum (VBM) located at the K point of the Brillouin zone. The DFT band gap obtained in this calculation is 2Δ_{DFT} = 6 eV and after the quasiparticle correction [2.1, 2.0] (this is for purpose provided just in K point of the Brillouin zone) it increases to 2Δ_{GW} = 9 eV.

The hBN-ML band structure and PDOS are shown in Fig. (1b) with an emphasis on the conduction and the valence band. The primary and secondary minima in the conduction band are only 0.115 eV apart. In the 3D case the Van der Waals interaction shifts this second minimum below the first one, thus making hBN an indirect gap insulator [28].

In order to better understand the electronic properties, the orbital decomposition of the valence bands through the PDOS calculation is also provided, shown in Fig. (1b). It can be seen that in the vicinity of the K point, the valence band is formed entirely from the boron 2p_z orbital while the conduction band is formed entirely from the nitrogen 2p_z orbital. The calculated effective masses of the conduction and the valence band at K point are \( m^*_c = 0.8m_e \) and \( m^*_v = 0.75m_e \), respectively. The effective mass of the valence band at the Γ point is found to be approximately equal to the electron mass \( m_e \).

B. The tight binding approximation

The band structure of hBN-ML can be easily obtained using the TBA model, which is here presented in the second quantization representation. The fermionic field operator in the basis of localized atomic orbitals labeled by index \( n \) is

\[ \Psi^\dagger(r) = \sum_{n \sigma} c_{n \sigma}^\dagger \phi_{n \sigma}^* (r - R). \]  

In the case of hBN-ML the two 2p_z orbitals on nitrogen and boron atoms are labeled as \( n = N \) or \( B \), respectively with the spin index \( \sigma \). Vectors \( R \) describe an absolute position of the atomic orbital \( n \) in the crystal and are usually decomposed as \( R = R_0 + r_n \), with \( R_0 \) being the primitive lattice vector and the \( r_n \) the position of the orbital \( n \) within the primitive cell. It is assumed that the atomic orbitals are localized such that

\[ \int d\mathbf{r} \phi_{n \sigma}^*(\mathbf{r} - \mathbf{R}) \phi_{n' \sigma'}(\mathbf{r} - \mathbf{R}') = \delta_{nn'}\delta_{\sigma\sigma'}\delta_{\mathbf{RR'}}. \]

The bare Hamiltonian operator is defined as

\[ \hat{H}_0 = \int d\mathbf{r} \Psi^\dagger(\mathbf{r}) \hat{H}(\mathbf{r}) \Psi(\mathbf{r}). \]

where the real space Hamiltonian \( \hat{H}(\mathbf{r}) \) consists of the bare atomic Hamiltonian and the contribution from the residual two-particle interaction. The latter is described by an effective single particle interaction called the crystal potential [29] or the effective potential, from the DFT point of view. Implementing (2.7) and (2.8) in (2.9), yields

\[ \hat{H}_0 = \sum_{nn'\sigma} \sum_{R_j} H^{nn'}_{\sigma}(R_j)c_{nR\sigma}^\dagger c_{n'R\sigma} \delta_{R+R_j}. \]  

Since the matrix elements of the Hamiltonian depend on the distance between atomic orbitals, a set of vectors \( \{R_j\} \) are introduced which represent the relative positions of the first neighbors, with the zero vector \( (r = 0) \) formally included, as shown in Fig. (1a). Thus the diagonal elements in (2.10) are the atomic orbital energies \( \varepsilon_n, H^{NN}(0) = \varepsilon_N, H^{BB}(0) = \varepsilon_B \) and the off-diagonal elements \( H^{NB}(R_j) = H^{BN}(R_j) = -t_0, \) give the
electron hopping parameter $t_0$. Next, the Hamiltonian (2.10) is written in the delocalized orbitals representation \{nk\} by transforming the fermion operators

$$c_{n,k \sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_{R} e^{i \mathbf{k} \cdot \mathbf{R}} c_{n,R \sigma}^\dagger.$$  \hfill (2.11)

Thus, the Hamiltonian transforms as

$$\hat{H}_0 = \sum_{n,n'} \sum_{k \sigma} H_{k}^{n,n'} c_{n,k \sigma}^\dagger c_{n',k \sigma},$$  \hfill (2.12)

where the matrix elements are

$$H_{k}^{NN} = \varepsilon_N, \quad H_{k}^{NB} = t_k, \quad H_{k}^{BB} = \varepsilon_B,$$  \hfill (2.13)

and the term $t_k$ is defined as

$$t_k = -t_0 \sum_{j=1,2,3} e^{-i k \cdot \mathbf{r}_j}.$$  \hfill (2.14)

The transition from the delocalized orbital representation \{nk\} to the diagonal Bloch representation \{Lk\} is obtained by a unitary transformation

$$c_{L,k \sigma}^\dagger = \sum_{n} U_{k}(L,n)c_{n,k \sigma}^\dagger.$$  \hfill (2.15)

The inverse transformation of (2.15) can be defined as

$$c_{n,k \sigma}^\dagger = \sum_{L} V_{k}(n,L)c_{L,k \sigma}^\dagger,$$  \hfill (2.16)

where $V = U^{-1}$ is unitary matrix inverse. The elements of matrices $U$ and $V$ are presented in Appendix A. The diagonalization of (2.12) is straightforward. Introducing $2\Delta = \varepsilon_B - \varepsilon_N$ and choosing $\varepsilon_B + \varepsilon_N = 0$, gives

$$\varepsilon_{k}^{c,v} = \pm \sqrt{\Delta^2 + |t_k|^2},$$  \hfill (2.17)

It can be noted that in the spatial case of two identical atoms in the base, $\Delta = 0$, and the eigenvalues (2.17) reduce to graphene dispersions \cite{30}. After the diagonalization, the Hamiltonian (2.12) has the simple form

$$\hat{H}_0 = \sum_{L,k \sigma} \varepsilon_{L,k \sigma} c_{L,k \sigma}^\dagger c_{L,k \sigma}.$$  \hfill (2.19)

C. Determination of the TBA band parameters

The electron hopping parameter $t_0$ can be determined by fitting the dispersions (2.17) to the \textit{ab initio} results shown in Fig.1(b), or using the conductivity sum rule \cite{31,32}. This rule is applicable to all cases in which the electron states at the bottom or at the top of the band (Gamma point of the Brillouin zone in our case) have the quadratic dispersion and do not exhibit hybridization with the states from other bands. This is clearly the case for the valence band, since the low-lying bands are formed from the $\sigma$ bonds between the planar $sp^2$ hybrids. Hence, any matrix element containing transition between the planar hybrid and the $2p_z$ orbitals vanishes due to symmetry.

The conductivity sum rule states that the total spectral weight of the total conductivity tensor with Cartesian indices $\alpha \alpha$ can be connected with the plasmon dispersion relation $\Omega_{pl}(\mathbf{q})$ as

$$4 \int_{-\infty}^{\infty} \Re \sigma_{\alpha \alpha}(\omega, \mathbf{q}) d\omega = \Omega_{pl}^2(\mathbf{q}) \approx \frac{2\pi n_{tot}(\mathbf{q})}{m_e}. \hfill (2.20)$$
The \( n_{\alpha}^{tot} = (1/V) \sum_{Lk\sigma} f_k^L \) is the total concentration of the conducting electrons and can be decomposed as \( n_{\alpha}^{tot} = n_{\alpha}^{inter} + n_{\alpha}^{intra} \). The effective intraband concentration of conducting electrons \( n_{\alpha}^{intra} \) is defined as \( n_{\alpha}^{intra} = (1/V)(m_e/h^2) \sum_{Lk\sigma}(\partial^2 \varepsilon_k^L/\partial k_\sigma^2) f_k^L \). For vanishing low electron concentration in the valence band, by definition \( n_{\alpha}^{intra} \leq n_{\alpha}^{tot} \) and from their explicit forms follows

\[
\frac{1}{m_{\alpha}^*} = \left| \frac{\partial^2 \varepsilon_k^L}{\partial k_\sigma^2} \right| \leq \frac{1}{m_e}. \tag{2.21}
\]

The effective mass tensor is diagonal and isotropic for the TBA dispersions, i.e. \( m_{\alpha}^* = m^* \), where

\[
\frac{1}{m^*} = \frac{3}{2\hbar^2} \sqrt{\Delta^2 + g_0^2}. \tag{2.22}
\]

From the assumption that the orbital energies of boron and nitrogen are equal to the bare atomic ones \( \varepsilon_n \approx \varepsilon_n^0 \), follows \( 2\Delta \approx 6 \text{ eV} \). If the lower limit of \( 2.22 \) is taken, i.e. \( m^* \approx m_e \), with the lattice parameter \( a = 4.746 \text{ å} \), the expression \( 2.22 \) gives \( t_0 \approx 2.6 \text{ eV} \).

The TBA bands \( 2.17 \) with the derived parameters \( t_0 \) and \( \Delta \) are shown in the Fig.4(b). The agreement between the TBA bands and the ones obtained from many-body DFT calculations (which includes Hartree-Fock contribution) may come as a surprise. Here, these many particle correlation effects have been phenomenologically incorporated in the simple single particle TBA model by choosing the adequate value of the atomic orbital energies \( \varepsilon_n \) and the lower limit of \( 2.21 \).

The TBA effective masses of the valence and conductive bands at the K point (which will be used in the following calculations) are

\[
m_{\alpha}^* = m_{\beta}^* = 4\Delta \hbar^2/(3\mu_0^2 a^2), \tag{2.23}
\]

or \( m_e^* = m_c^* = 0.75m_e \).

**D. The charge density operator**

The charge density operator

\[
\hat{\rho}(\mathbf{r}) = e \Psi^\dagger(\mathbf{r}) \Psi(\mathbf{r}) \tag{2.24}
\]

can be derived within the simple two-band TBA model presented in the section 1113. Using condition \( 2.8 \) and Fourier transformations \( 2.24 \), the charge density operator in \( \mathbf{q} \approx 0 \) becomes

\[
\hat{\rho}(\mathbf{q}) = \sum_{\mathbf{RR}} \sum_{\sigma'\sigma} \sum_{\sigma''} c_{\mathbf{R} \sigma}^\dagger c_{\mathbf{R} \sigma' \sigma''} e^{-i\mathbf{q} \cdot \mathbf{R}} e^{-i\mathbf{q} \cdot \mathbf{R}'},
\]

\[
\times e \int d\mathbf{r} \phi_{n\sigma}^* (\mathbf{r} - \mathbf{R}) e^{-i\mathbf{q} \cdot \mathbf{r}} \phi_{n'\sigma'}(\mathbf{r} - \mathbf{R}')
\]

\[
\approx \sum_{\mathbf{R}} e^{-i\mathbf{q} \cdot \mathbf{R}} \sum_{\sigma} \sum_{\sigma'\sigma''} e^{i\mathbf{q} \cdot \mathbf{R}} \phi_{n\sigma}^* c_{\mathbf{R} \sigma' \sigma''} e^{-i\mathbf{q} \cdot \mathbf{R}}. \tag{2.25}
\]

With an aide of \( 2.11 \), the above expression can be written in the representation of the delocalized atomic orbitals \{n\k}\n
\[
\hat{\rho}(\mathbf{q}) = \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} e^{i\mathbf{q} \cdot \mathbf{k}'} G_{\mathbf{k},\mathbf{k}+\mathbf{q},\sigma} \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{\mathbf{k}+\mathbf{q},\sigma'} \tag{2.26}
\]

with \( G_{\mathbf{k},\mathbf{k}+\mathbf{q}} \approx \delta_{\mathbf{n},\mathbf{n}'} \). In a similar way, the charge density operator \( \hat{\rho}(\mathbf{q}) \) can be defined in the Bloch representation, using transformation \( 2.16 \)

\[
\hat{\rho}(\mathbf{q}) = \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} e^{i\mathbf{q} \cdot \mathbf{k}'} G_{\mathbf{k}',\mathbf{k}+\mathbf{q},\sigma} \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{\mathbf{k}+\mathbf{q},\sigma'} \tag{2.27}
\]

The operator \( \hat{G}_{\mathbf{k}+\mathbf{q}}^{\mathbf{LL}'} \) is called the electron-hole propagator and it plays a pivotal role in the equations describing the charge density excitations. The charge vertex \( G_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\mathbf{LL}'} \) is given by

\[
G_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\mathbf{LL}'} = \sum_{\mathbf{n},\mathbf{n}'} G_{\mathbf{n},\mathbf{n}'} V_{\mathbf{k}}(\mathbf{n},\mathbf{L}) V_{\mathbf{k}'}^{\dagger}(\mathbf{n}',\mathbf{L}') \tag{2.28}
\]

and its explicit form is derived in Appendix C. These matrix elements are a trivial simplification of the matrix elements \( 2.22 \), obtained by setting \( g_2 = 0 \) and restricting the number of Bloch bands to two.

**III. EQUATION OF MOTION FOR THE ELECTRON-HOLE PROPAGATOR**

Here an analysis is presented of the charge density fluctuations in a electron subsystem described by a single particle Hamiltonian \( 2.10 \) to which a long-range electron-electron interaction is added. Therefore in the context of the expression \( 2.27 \), it is clear that the dynamics of the electron-hole propagator \( \hat{G}_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\mathbf{LL}'} \) has to be determined in the presence of the \( v \) and \( c \) bands only, since at the point of interest (K point of the Brillouin zone) the other bands are far enough away in energy (Fig.4(b)). Hereafter, the spin index in the electron-hole propagator, whose dynamic is described by the Heisenberg equation

\[
i\hbar \frac{\partial}{\partial t} \hat{\rho}_{\mathbf{k},\mathbf{k}+\mathbf{q}} = \left[ \hat{\rho}_{\mathbf{k},\mathbf{k}+\mathbf{q}}, \hat{H} \right], \tag{3.1}
\]

is omitted.

The Hamiltonian in \( 3.1 \) consists of the bare Hamiltonian \( 2.10 \) and the Coulomb interaction term

\[
\hat{H}_{\text{e-e}} = \frac{1}{2} \sum_{\mathbf{q} \neq 0} v_{\mathbf{q}} \hat{\rho}_{\mathbf{q}}^{\dagger}(\mathbf{q}) \hat{\rho}(\mathbf{q})
\]

\[
= \frac{1}{2\mathbf{V}} \sum_{\mathbf{k}',\mathbf{k},\mathbf{q},\mathbf{q}',\mathbf{s}'} \mathcal{W}(\mathbf{L}_1,\mathbf{L}_2,\mathbf{L}_3,\mathbf{L}_4) \times
\]

\[
\sum_{\mathbf{L}_1,\mathbf{L}_2,\mathbf{L}_3,\mathbf{L}_4} c_{\mathbf{l}_{1},\mathbf{k},\mathbf{\sigma}'} c_{\mathbf{l}_{2},\mathbf{k}+\mathbf{q},\mathbf{\sigma}'} c_{\mathbf{l}_{3},\mathbf{k},\mathbf{\sigma}'} c_{\mathbf{l}_{4},\mathbf{k}-\mathbf{q},\mathbf{\sigma}'} \tag{3.2}
\]
The two-particle Coulomb matrix elements in (3.2) are given in terms of charge vertices:

\[ \mathcal{W}(L_k L_{k'} L_{q} L_{q'}) = v_q e^2 G_{k,k-q} G_{k',k'+q} \]  

(3.3)

with \( v_q = 2\pi/|q| \) being the Fourier transform of the bare Coulomb interaction in two dimensions. In the following sections, \( v_q \) will be replaced by screened Coulomb interaction. The Hartree-Fock corrections to the single particle energies \( \varepsilon_{L_k} \), \( L \in \{v,c\} \) are introduced in the following way:

\[ \varepsilon_{L_k} = \varepsilon_{L_k}^0 + \sum_{k',L'} \left[ \mathcal{V}(L_k L_{k'} L_{q} L_{q'}) \right] f_{L_k}^L. \]  

(3.4)

As already noted (Sec. [11]), Hartree-Fock corrections have been phenomenologically included in the TBA and 

dispersions. Therefore, \( E_{L_k}^F = \varepsilon_{L_k}^0 \). The solution of the equation (3.4), evaluated using the Wick theorem (3.1), can be written down to the first order in Coulomb interaction:

\[ (\omega + E_{L_k}^c - f_{L_k}^c) \hat{\phi}_{k,k+q}^c = \frac{2}{V} \sum_{k'} v_q e^2 G_{k+q,k,k+q}^c G_{k',k'+q}^c \left[ f_{L_k}^c - f_{L_{k'}}^c \right] \hat{\phi}_{k',k'+q}^c \]
\[ + \frac{1}{V} \sum_{k'} v_{k'-k} e^2 G_{k+q,k,k+q}^c G_{k',k}^c G_{k,k'}^c \left[ f_{L_{k'}}^c - f_k^c \right] \hat{\phi}_{k',k+q}^c. \]

(3.5)

Within the self-consistent equation (3.5), the four main contributions to the interband electron-hole propagator can be defined. The Hartree and Fock terms have been absorbed in the single particle energies, leaving RPA and ladder contribution on the right side, respectively. These four contributions are depicted using Feynman diagrams in Fig.2. It should be noted that (off-resonance) band changing scattering processes are omitted in Eq.3.5. This, so called Tamm-Dancoff approximation [35], is valid here, due to the \( q \approx 0 \) form of interband the intraband charge vertices, as shown in Appendix C.

IV. SOLUTIONS OF THE (3.5) IN THE q \( \approx 0 \) LIMIT

The expression (3.5) is a self-consistent integral equation which is usually solved numerically. Various approximations have to be performed in order to obtain a more appealing analytical solution. The first step is to take the \( q \approx 0 \) limit (since the lowest form of bound exciton energy are of interest), thus neglecting the kinetic energy of the electron-hole pair. In this limit the RPA contribution in the equation (3.5) vanishes. This is because the interband charge vertices are proportional to \( q \) (Appendix C). Then even in the case of the bare Coulomb potential \( v_q = 2\pi/|q'| \), the RPA term is proportional to \( q \), thus leaving only the ladder part as the dominant term in (3.5). Next, interband transitions are restricted only to the narrow area around the K point between the

\[ \psi(r) = \frac{1}{V} \sum_k \hat{\phi}_{k,k}^c e^{i k \cdot r}, \]  

(4.4)
which is, by assumption, a smooth and well behaved function \( \psi(\infty) = \nabla \psi(\infty) = 0 \) of the electron-hole distance \( |r| \). The Eq. (4.3) then becomes two-body Schrödinger-like equation

\[
\left[ -\frac{\hbar^2}{2\mu} \nabla^2 - e^2 \frac{1}{|r|} \right] \psi(r) = \Omega \psi(r). \tag{4.5}
\]

After the separation of variables \( \psi(r) = R(r)\Phi(\varphi) \), two equations are obtained, which describe the radial and angular part of the wave function

\[
\frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} + \frac{2 \mu}{\hbar^2} \left( \Omega + \frac{e^2}{r} \right) R(r) - \frac{\ell^2}{r^2} R(r) = 0
\]

\[
\ell^2 = -\frac{1}{\Phi(\varphi)} \frac{\partial^2 \Phi(\varphi)}{\partial \varphi^2}. \tag{4.6}
\]

The eigenvalues are well-known 2D hydrogen-like form

\[
\Omega_n = -\frac{\mu}{m_e} \frac{1}{(n - 1/2)^2}, \tag{4.7}
\]

with each state \( n \) being \((n - 1)\) times degenerated (not including the valley degeneracy which brings an extra factor of 2), since \( \ell = 0, 1, \cdots, n - 1 \). By inserting the reduced mass \( \mu = 0.35 m_e \) \([22,23]\) in the above equation, the ground state exciton energy in hBN-ML \( \Omega_1 = -1.4 \text{ Ry} \) \((-19 \text{ eV})\) is obtained. It is evident that \( \Omega_1 \) is too low, suggesting that Wannier model should be improved by the introduction of the screened Coulomb interaction.

### B. Screening of Coulomb interaction

It is shown (Eq.3.5) that to the first order in \( \mathcal{O}(v_{q'}) \), the ladder term is the one describing the dynamics of the electron-hole pair in the \( q \approx 0 \) limit. The inclusion of the higher order contributions \( \mathcal{O}(v_{q''}) \) is usually performed by summing infinite number of RPA contributions to the ladder diagram of the electron-hole propagator, shown by Feynman diagrams in Fig.3. This procedure is equivalent to changing the bare Coulomb interaction to a screened one in the expression (4.3)

\[
v_{q'} \rightarrow w_{q'}(\omega) = v_{q'} / \epsilon(q', \omega). \tag{4.8}
\]

The RPA longitudinal dielectric function is

\[
\epsilon(q', \omega) = 1 - v_{q'} \chi^0(q', \omega), \tag{4.9}
\]

where the density-density response function, known as the generalized Lindhard function \([31]\) can be written as

\[
\chi^0(q', \omega) = \frac{\epsilon^2}{V} \sum_{LL', \kappa \sigma} \left| G_{L', L + q'}^{\kappa} \right|^2 \frac{f_L^{\kappa} - f_{L + q'}^{\kappa}}{\hbar \omega + E_L^{\kappa} - E_{L + q'}^{\kappa} + i \eta}. \tag{4.10}
\]

Here, Eq. (4.3) is evaluated within the two-band TBA model presented in section II B for the \( q' \approx 0 \). The Hartree-Fock energies are given by the TBA energies \( E_L^{\kappa} = \epsilon_L^{\kappa} \) (considering that many particle correlations are already implemented in the simple single particle TBA model) and the charge vertices \( G_{LL', \kappa}^{\kappa} \) are derived in Appendix C. Finally, to the first order in \( \mathcal{O}(q') \), the dielectric function is given by

\[
\epsilon(q', \omega) = 1 + 2 \pi \alpha(\omega)|q'| + \mathcal{O}(q'^2). \tag{4.11}
\]

The function \( \alpha(\omega) \) is called the electronic polarizability of the insulator. It is usually calculated \textit{ab initio}\([27]\); however, here it is evaluated within the two-band model presented earlier using the relaxation constant approximation. In this case the adiabatic term \( \eta \) in (4.10) is replaced by an interband relaxation constant \( \Gamma \). The results for \( \alpha(\omega) \) for various relaxation constants \( \Gamma \) are presented in the Fig.4a.

In the case of \( \eta \rightarrow 0 \), the polarizability function \( \alpha(\omega) \) can be analytically estimated by considering the direct transitions around the K point. The expression (4.10) is integrated to the cut-off wave vector \( k_0 \) which determines the extent around the K point to which the bands are described by a parabolic dispersion with the effective masses \([22,23]\). By inspecting the band structure in Fig.1(b) the value of \( k_0 \approx K/3 \) can be chosen. The result is

\[
\Re \alpha(\omega) = \frac{\epsilon^2}{2 \pi} \frac{1}{2 \Delta} \ln \left( \frac{(\hbar \omega)^2 - (2 \Delta + \epsilon_0)^2}{(\hbar \omega)^2 - (2 \Delta)^2} \right),
\]

\[
\Im \alpha(\omega) = 0. \tag{4.12}
\]

Here, the cut-off energy is \( \epsilon_0 = \hbar^2 k_0^2 / (2m^*) \approx 3 \text{ eV} \). The \( \alpha(\omega) \) given by (4.12) is in excellent agreement with the exact two-band TBA model result for vanishing \( \Gamma = 1 \text{ meV} \), as shown by the brown circles in the Fig.4a. Inserting 4.11 into 4.8 the dynamically screened Coulomb potential

\[
w_{q'}(\omega) = \frac{2 \pi}{|q'| (1 + 2 \pi \alpha(\omega)|q'|)} \tag{4.13}
\]

is obtained.
After Fourier transformation to the direct space it becomes a $\omega$-dependent Keldysh potential \[ W(r, \omega) = \frac{e^2}{2\lambda(\omega)} \left[ Y_0(\frac{r}{\lambda(\omega)}) - N_0(\frac{r}{\lambda(\omega)}) \right] , \quad (4.14) \]
where $Y_0(x)$ and $N_0(x)$ represents Struve and Neumann function respectively. The dynamical screening length is \( \lambda(\omega) = 2\pi\omega(\omega) \), where $\omega_0(\omega)$ is given by \( \frac{\omega}{\omega_0} \). Next, the bare Coulomb potential $e^2/r$ is replaced in equation \( \ref{eq:4.6} \) by $W(r, \omega)$ and solved self-consistently.

V. RESULTS AND DISCUSSION

A. Exciton energies and spatial extent

Here the solutions of the Schrödinger equation \( \ref{eq:4.6} \) with the potential \( \ref{eq:4.14} \) are presented. The exciton energies are given in Table I and are presented in terms of two quantum numbers \((n_r, \ell)\). The radial quantum number $n_r$ gives the number of nodes in the radial part of the wave function $R(r)$ and $\ell$ is the orbital quantum number. The states denoted by the $\ell = 0, 1, 2, ...$ are labeled as $s, p, d, ...$. This is an adequate choice since the absolute square of the angular part of the wave function behaves like \( |\Phi(\varphi)|^2 \sim \cos^2(\ell \varphi) \), thus resembling to the 2D projections of the 3D atomic hydrogen orbitals. Moreover, the principal quantum number $n = 1 + n_r + \ell$ can be introduced. Then the energy states labeled as $\Omega(n_r, \ell)$ can be equally labeled $\Omega_{n_\ell}$. For example, a state $\Omega(n_r = 1, \ell = 1)$ is equivalent to the $\Omega_{3p}$ state, etc. All energy states having the same $n$ are given in the same color in Table I. The first entry in Table I is the

| $\Omega(n_r, \ell)$ | $\ell = 0$ | $\ell = 1$ | $\ell = 2$ | $\ell = 3$ |
|-------------------|-----------|-----------|-----------|-----------|
| $n_r = 0$         | 0.64 (4.73) | 1.30 (1.57) | 0.60 (0.70) | 0.34 (0.38) |
| $n_r = 1$         | 0.95 (1.20) | 0.92 (0.64) | 0.31 (0.37) |
| $n_r = 2$         | 0.42 (0.54) | 0.28 (0.34) |
| $n_r = 3$         | 0.24 (0.30) |

**TABLE I.** (color online) The first ten exciton energy levels in eV. The states within the same shell are given in the same color: $n = 1, 2, 3, 4$ in maroon, red, orange and olive green, respectively.

The exciton energy obtained by solving the self-consistently equation \( \ref{eq:4.10} \) with the frequency depended potential $W(r, \omega)$. The second entry (in the brackets) is the solution of the \( \ref{eq:4.14} \) in the case of the static potential $W(r, 0)$ where expression \( \ref{eq:4.12} \) was used to calculate $\lambda(0) = \lambda_{TBA} = 3.5 \alpha_0$. By examining the $\Omega_{3s}$ state from the Table I it can be seen that even small (two-band TBA model) values of $\lambda(\omega)$ produce a strong reduction of the exciton ground state energy in comparison with the energy of $-19$ eV obtained using the bare Coulomb potential, i.e. from Eq. \( \ref{eq:4.7} \).

The states with higher $\ell$ have lower energy for the same $n$. This can be seen from the Fig. I in the case of $n = 3$ series. The energy ordering of the states $\Omega_{3d} < \Omega_{3p} < \Omega_{3s}$ is the same, regardless whether they are calculated with dynamical or statical Keldysh potential. This energy ordering is experimentally observed in the two-photon absorption experiments on tungsten disulphide \( \text{WSe}_2 \). The relative difference between $\Omega_{1s}$ obtained by the $W(r, \omega)$ and those obtained by the $W(r, 0)$ increases as the band gap edge is approached. For $\hbar \omega \ll 2\Delta$ the Keldysh potential can be approximated by its statical limit since $\lambda(\omega) \ll 2\Delta \approx \lambda(0)$ Fig. I(a). As the conduction band is approached the logarithmic divergence in the dynamical screening length $\lambda(\omega)$ becomes more apparent and $\Omega_{n\ell}$ increase compared with those calculated with $\lambda(0)$. The mean exciton radius, defined as the average electron-hole separation in the state $\psi_{n\ell}(r)$, is calculated as $r_{n\ell} = \langle r | \psi_{n\ell} \rangle$. In the ground state $\Omega_{1s} \approx 4 \alpha_0$, which is comparable with the unit cell dimension. However, it should be noted that the two-band TBA polarizabilities are low in comparison with $\lambda_{DFT} = 10.5 \alpha_0$ giving $r_{1s} \approx 10 \alpha_0$, which is in accordance with the Wannier scheme. The mean exciton radius decreases with $\Omega_{n\ell}$. For example, $r_{2s} \approx 20 \alpha_0$ and $r_{2p} \approx 13 \alpha_0$, while for the highest calculated energy level $\Omega_{4s} \approx 83 \alpha_0$.

In the Fig. (b) the screened potential $W(r, 0)$ is plotted as a function of the screening length $\lambda$. As $\lambda$ increases, the logarithmic nature of the potential becomes more apparent for small electron-hole separations. This can be seen by taking the two opposite limits of the expression \( \ref{eq:4.14} \)

\[ W(r \to \infty, 0) \to -e^2/r \]
\[ W(r \to 0, 0) \to (e^2/2\gamma)\ln(\gamma^2/2\lambda), \]
where $\gamma$ is Euler-Mascheron constant.

The shape of the above potential suggests the reason why the states within the same shell $n$ differ in energy. The radial wave function $R(r)$ of the states with lower $\ell$ is located closer to the origin where it is governed by a weaker logarithmic potential \( \ref{eq:5.2} \). Therefore, the binding energy is smaller and the mean radius is larger compared to the states with larger values of $\ell$ which are under the influence of stronger bare Coulomb potential \( \ref{eq:5.1} \) and thus have larger binding energy and smaller spatial extension. It is useful to determine the dependence of the exciton ground state energy $\Omega_{1s}$ as a function of the screening length $\lambda$. This dependence is shown in the insert of Fig. (b). In the limit $\lambda \to 0$, $\Omega_{1s}(\lambda)$ is given by the expression \( \ref{eq:4.7} \), while in the opposite limit ($\lambda \to \infty$) a saturation of the $\Omega_{1s}(\lambda)$ can be seen. The analytical approximation of $\Omega_{1s}(\lambda \to \infty)$ will be considered in the last section.

B. The single particle gap problem

In optical absorption experiments on quasi hBN-ML \( \text{WSe}_2 \) the exciton ground state signal appears at energy $\hbar \omega_{\text{exc}} \approx 6$ eV. The theoretical result for the exciton ground state energy, calculated using the screened model, with \textit{ab initio} screening length $\lambda_{DFT} = 10.5 \alpha_0$, yields
As presented in Sec. II A, the lower limit of the quasiparticle band gap is estimated as 2∆ ≥ 8.5 eV. This simple estimation agrees well with the statical COH-SEX correction of band gap, 2∆_{GW} = 9 eV, as presented in Sec. II A.

Observing Fig. 5, some conclusions can be made regarding the interaction of excitons with phonons, impurities, and electrons, changing their appearance in the absorption spectrum. Due to these interactions, the exciton signals will be broader and slightly shifted in energy. This causes overlapping between the individual exciton signals that are close in energy, to the point that they can even be joined with the single particle threshold. This would imply the indistinguishability of partial contributions originating from the single particle excitations and the excitons in the optical absorption spectra.

### C. The limit of high polarizability - EBK procedure

The analytical form of the ground state exciton energy Ω_{1s} is presented in the limit of high screening length (λ → ∞). As the ab initio results predict, hBN-ML can not be considered a material where the above condition applies, since λ_{DFT} = 10.5 a_0. However, other two-dimensional materials, such as transition-metal dichalcogenides, have much larger λ. DFT calculations for molybdenum disulfide (MoS_2-ML) and molybdenum ditelluride (MoTe_2-ML) were also performed, giving λ_{DFT} = 70 a_0 and 120 a_0 and μ = 0.25 \mu_e and 0.32 \mu_e, respectively. This is a direct consequence of their spatial structure where a transition metal plane lies between the planes of two chalcogenide atoms. This geometrical coordination reduces the electronic hopping elements between the atomic orbitals of the neighboring atoms and hence causes flattening of electron bands. Smaller dispersivity of the electron bands combined with the smaller band

\[ \hbar \omega_{1s} = 2\Delta' + \Omega_{1s}(\lambda_{DFT}), \]
The similar expression has been found as the limiting solution of the Schrödinger equation for the logarithmic potential, unlike the results of [10] which predict \( \Omega_{1s}(\lambda) \approx - (3/4 \pi) e^2 / \lambda \) in this limit and thus neglecting the logarithmic term. The expression (5.6) gives a fairly accurate description of \( \Omega_{1s}(\lambda) \) in \( \lambda \to \infty \) limit, but it can be improved by setting \( z = 3.5 \). Fig. 6 shows the comparison between the ground state energy \( \Omega_{1s}(\lambda) \) obtained using the static screened potential (solid lines) and the analytical form (5.6) with \( z = 3.5 \) (dashed lines), for two different reduced masses \( \mu \). It is evident that the agreement between the curves becomes noticeable for large values of \( \lambda \).

Using the same arguments outlined in Sec. VI B together with Eq. (5.6), the single particle band gap of MoS\(_2\) and MoTe\(_2\) monolayers can be estimated, in which the experimentally determined exciton energies are \( \hbar \omega_{1s}^{exp}(\text{MoS}_2) \approx 1.9 \text{ eV} \) and \( \hbar \omega_{1s}^{exp}(\text{MoTe}_2) \approx 1.2 \text{ eV} \) [47–49]. Inserting the calculated polarizabilities and reduced masses into (5.6) and using (5.3) gives \( 2\Delta_{\text{MoS}_2} \approx 2.5 \text{ eV} \) and \( 2\Delta_{\text{MoTe}_2} \approx 1.6 \text{ eV} \). The DFT polarizabilities, the experimental exciton energies and estimated quasiparticle band-gaps for three studied 2D crystals are summarised in Table II. The calculated values of the single-particle band

| 2D Cryst | hBN | MoS\(_2\) | MoTe\(_2\) |
|---------|-----|---------|---------|
| \( \lambda_{\text{DFT}}/a_0 \) | 10.5 | 76 | 120 |
| \( \mu/m_e \) | 0.35 | 0.25 | 0.3 |
| \( \hbar \omega_{1s}^{exp}/eV \) | 6.0 | 1.9 | 1.2 |
| \( 2\Delta/\text{eV} \) | 8.5 | 2.3 | 1.6 |

TABLE II. The quasi-particle band-gap \( 2\Delta' \) estimated from DFT polarizabilities \( \lambda_{\text{DFT}} \), reduced masses \( \mu \), the experimental exciton energies \( \hbar \omega_{1s}^{exp} \) and from Eqs. (5.3) and (5.6).

Gaps are in accordance with the results of the BSE-GW approach [18, 20].

VI. CONCLUSION

By examining the equation of motion for the electron-hole propagator, in the leading order of Coulomb interaction, it was possible to reduce it to the two-body Schrödinger equation. The inclusion of the higher order contributions to the electron-hole propagator leads to the Schrödinger equation with the dynamically screened Coulomb potential. The parameters like the dynamical screening length and the electron and hole effective masses are obtained from the TBA approximation and supported by \textit{ab initio} calculations. Using this parameters the exciton binding energies and wave functions are calculated. The exciton binding energies obtained using the bare Coulomb potential are compared to the ones obtained using the staticaly screened Coulomb potential, demonstrating how the bare Coulomb interaction leads to the unrealistically large exciton binding energy. Comparing the calculated and experimental exciton ground
state energies, a realistic value of the single particle band gap is estimated, which in the case of hBN-ML is 8.5 eV. Using the EBK procedure an analytical expression for the exciton ground state energy is obtained in the high polarizability limit. This is shown to be valid for the family of transition metal dichalcogenides where the single particle band gap is calculated for MoS$_2$ and MoTe$_2$ monolayers.

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Appendix A: matrices $U$ and $V$

Bloch operators $c_{L \nu \sigma}^\dagger$ are a solution to the Heisenberg equation

$$[\hat{H}_0, c_{L \nu \sigma}^\dagger] = \varepsilon_{L \nu \sigma}^\dagger c_{L \nu \sigma}^\dagger.$$  \hfill (1.1)

Inserting (2.15) in (1.1) one obtains the eigenvalue problem

$$\sum_{n'} U_k(L, n') \left( H_k^{n n'} - \varepsilon_{k \nu \sigma}^{n n'} \delta_{n n'} \right) = 0, \hfill (1.2)$$

where the orthogonalization condition for Bloch functions implies the unitarity of matrix $U$

$$\{c_{L \nu \sigma}, c_{L' \nu' \sigma'}^\dagger\} = \delta_{L L'} \delta_{\nu \nu'} \sum_n |U_k(L, n)|^2 = 1. \hfill (1.3)$$

Introducing the amplitude and the phase of the parameter $t_k$ (2.14) and the auxiliary phase $\varphi_k$

$$t_k = |t_k| e^{i \varphi_k}, \quad \tan \varphi_k = \frac{\Im t_k}{\Re t_k} \quad \tan \varphi_k = \frac{|t_k|}{\Delta}, \hfill (1.4)$$

the matrix $U$ can now be written

$$U_k(L, n) = \begin{pmatrix} e^{-i \varphi_k} \cos(\varphi_k/2) & -\sin(\varphi_k/2) \\ e^{i \varphi_k} \sin(\varphi_k/2) & \cos(\varphi_k/2) \end{pmatrix}. \hfill (1.5)$$

The inverse matrix $V$ is then

$$V_k(n, L) = \begin{pmatrix} e^{i \varphi_k} \cos(\varphi_k/2) & e^{i \varphi_k} \sin(\varphi_k/2) \\ -\sin(\varphi_k/2) & \cos(\varphi_k/2) \end{pmatrix}. \hfill (1.6)$$

Appendix B: useful derivatives

For explicit determination of the charge vertices the following derivatives have to be determined

$$\frac{\partial |t_k|}{\partial k_\alpha}, \frac{\partial \varphi_k}{\partial k_\alpha}, \frac{\partial \varphi_k}{\partial k_\alpha}, \frac{\partial \varphi_k}{\partial k_\alpha}, \frac{\partial \varphi_k}{\partial k_\alpha}, \text{ where } \alpha \in \{x, y\} \text{ is an }$$

Cartesian coordinate. From the definition (1.4) one has

$$\frac{\partial |t_k|}{\partial k_\alpha} = \frac{t_0^2 a \sqrt{3}}{|t_k|} \left( \sin a k_x + \frac{a k_x}{2} \cos \frac{a k_y \sqrt{3}}{2} \right), \hfill (2.1)$$

and the explicit derivatives of $|t_k|$ are

$$\frac{\partial |t_k|}{\partial k_x} = \frac{t_0^2 a \sqrt{3}}{|t_k|} \left( -\cos a k_x + \frac{a k_x}{2} \cos \frac{a k_y \sqrt{3}}{2} \right), \hfill (2.2)$$

$$\frac{\partial |t_k|}{\partial k_y} = \frac{t_0^2 a \sqrt{3}}{|t_k|} \left( \frac{a k_y}{2} \cos \right), \hfill (2.3)$$

Explicit derivatives of $\varphi_k$ are

$$\frac{\partial \varphi_k}{\partial k_x} = \frac{t_0^2 a \sqrt{3}}{|t_k|} \left( -\cos a k_x + \frac{a k_x}{2} \cos \frac{a k_y \sqrt{3}}{2} \right), \hfill (2.3)$$

In the Dirac regime, i.e. for the states $k_\approx K$, the derivatives of the amplitude and the phase of the hopping parameter simplify substantially. Introducing $k = K - k$

gives

$$\frac{\partial |t_k|}{\partial k_\alpha} = \frac{t_0^2 a \sqrt{3}}{|t_k|} \frac{1}{2} \left( k_x \delta_{\alpha x} + k_y \delta_{\alpha y} \right), \hfill (3.1)$$

$$\frac{\partial \varphi_k}{\partial k_\alpha} = \frac{\tilde{k}_x \delta_{\alpha x} - \tilde{k}_y \delta_{\alpha y}}{k_x^2 + k_y^2}. \hfill (3.2)$$

Appendix C: charge vertices

Explicit values of the interband and intraband charge vertices in the long wave limit are obtained by inserting the matrix elements (1.6) in (2.28) and expand them in the leading order in $q$. The result is

$$G_{k,k+q}^{cc} = \left(G_{k,k+q}^{\alpha\alpha}\right)^*, \hfill (3.1)$$

$$G_{k,k+q}^{cc} \approx \frac{1}{2} \sum_{\alpha} \frac{q_\alpha}{2} \frac{\partial \varphi_k}{\partial k_\alpha} - \frac{i}{2} \sin \varphi_k \sum_{\alpha} \frac{q_\alpha}{2} \frac{\partial \varphi_k}{\partial k_\alpha}, \hfill (3.1)$$

Around the $K$ point this result simplifies. Inserting (2.1) and (2.28) in (3.1), leaves

$$|G_{k,k+q}^{cc}| \approx 1, \hfill (3.2)$$

$$|G_{k,k+q}^{cc}| \approx \frac{t_0 a \sqrt{3}}{2 \Delta} |q|. \hfill (3.2)$$
