Excitonic properties of hBN from a time-dependent Hartree-Fock mean-field theory

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Introduction

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- Eletronic model for the single-particle states
- Electron-electron interaction

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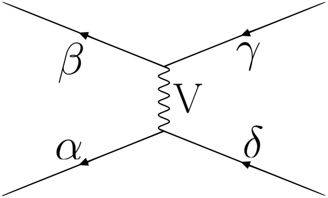
- Numerical implementation of eigenproblem

Theoretical description of excitons

Time-dependent Hartree-Fock mean-field theory

Many-body system of electrons

$$H_{\text{eq}} = \sum_{\alpha\beta} h_{\alpha\beta} c_\alpha^\dagger c_\beta + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} V_{\gamma\delta}^{\alpha\beta} c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta$$



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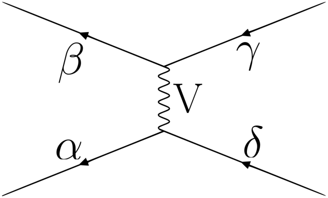

External perturbation

$$H_{\text{ext}} = \sum_{\alpha\beta} B_{\alpha\beta} c^\dagger_\alpha c_\beta F(t)$$

Time-dependent Hartree-Fock mean-field theory

Reduced density matrix

$$\rho_{ba}(t) = \left\langle c_a^\dagger(t) c_b(t) \right\rangle$$

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$$\frac{d}{dt}\rho_{ab}(t) = \frac{i}{\hbar}\left\langle [H, c_b^\dagger(t)] c_a(t) \right\rangle + \frac{i}{\hbar}\left\langle c_b^\dagger(t)[H, c_a(t)] \right\rangle$$

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$$\begin{aligned} -i\hbar\frac{d}{dt}\rho_{ab}(t) = \rho_{a\alpha}(t)\left(h_{\alpha b} + B^i_{\alpha b}F^i(t)\right) - \left(h_{a\beta} + B^i_{a\beta}F^i(t)\right)\rho_{\beta b}(t) \\ + \frac{1}{2}V^{\alpha\beta}_{\gamma b}\left\langle c_\alpha^\dagger c_\beta^\dagger c_\gamma c_a \right\rangle - \frac{1}{2}V^{\alpha\beta}_{b\delta}\left\langle c_\alpha^\dagger c_\beta^\dagger c_\delta c_a \right\rangle \\ + \frac{1}{2}V^{\alpha a}_{\gamma\delta}\left\langle c_b^\dagger c_\alpha^\dagger c_\gamma c_\delta \right\rangle - \frac{1}{2}V^{a\beta}_{\gamma\delta}\left\langle c_b^\dagger c_\beta^\dagger c_\gamma c_\delta \right\rangle \end{aligned}$$

Time-dependent Hartree-Fock mean-field theory

Mean-field decoupling

$$\left\langle c_{\alpha}^{\dagger} c_{\beta}^{\dagger} c_{\gamma} c_{\delta} \right\rangle \approx -\rho_{\gamma\alpha}(t)\rho_{\delta\beta}(t) + \rho_{a\alpha}(t)\rho_{\gamma\beta}(t)$$

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$$i\hbar\frac{d}{dt}\boldsymbol{\rho}(t) = [\boldsymbol{h} + \boldsymbol{B}\cdot\boldsymbol{F}(t) + \boldsymbol{\Sigma}^H[\boldsymbol{\rho}(t)] + \boldsymbol{\Sigma}^F[\boldsymbol{\rho}(t)], \boldsymbol{\rho}(t)]$$

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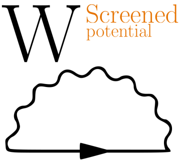
Hartree and Fock self-energy terms

$$\Sigma^H_{a\gamma}[\rho(t) - \rho^{(0)}] = V^{a\alpha}_{\delta\gamma}\rho_{\delta\alpha}(t)$$

$$\Sigma^F_{a\gamma}[\rho(t) - \rho^{(0)}] = -W^{a\alpha}_{\gamma\delta}\rho_{\delta\alpha}(t)$$



Time-dependent Hartree-Fock mean-field theory

Linear response in the single-particle eigenbasis at zero temperature

$$\boldsymbol{\rho}(t) \approx \boldsymbol{\rho}^{(0)} + \boldsymbol{\rho}^{(1)}(t) \quad \Big| \quad \begin{aligned} h_{ac} &= \epsilon_a \delta_{ac} \\ \rho^{(0)}_{ab} &= f_a \delta_{ab} \end{aligned} \quad \Big| \quad \begin{aligned} f_o &= 1 \\ f_e &= 0 \end{aligned}$$

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Effective two-particle Hamiltonian

$$\boldsymbol{H}_{\text{e-h}} = \begin{bmatrix} \boldsymbol{R} & \boldsymbol{C} \\ \boldsymbol{C}^\dagger & \boldsymbol{R}^* \end{bmatrix} \overset{\text{TDA}}{\approx} \boldsymbol{R}$$

Resonant Block

$$\boldsymbol{R} \equiv H^{e_3 o_4}_{e_1 o_2} = \left(\epsilon_{e_1} - \epsilon_{o_2}\right) \delta_{e_1 e_3} \delta_{o_2 o_4} + \left(V^{o_4 e_1}_{o_2 e_3} - W^{e_1 o_4}_{o_2 e_3}\right)$$

Linear response eigenvalue solution

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$$(\hbar\omega \boldsymbol{S} - \boldsymbol{H}_{\text{e-h}}) \cdot \boldsymbol{\Psi}_\lambda = E_\lambda \boldsymbol{\Psi}.$$

Excitonic generalized eigen-problem

$$\boldsymbol{H}_{\text{e-h}} \cdot \boldsymbol{\Psi}_X = E_X \boldsymbol{S} \cdot \boldsymbol{\Psi}_X$$

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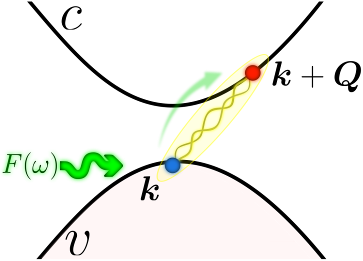
$$\boldsymbol{\rho}^{(1)}(\omega) = \sum_X a_X(\omega) \boldsymbol{\Psi}_X$$

Reduced density matrix solution

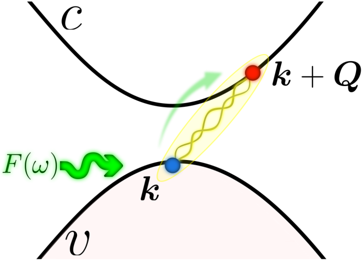
$$\boldsymbol{\rho}^{(1)}(\omega) = \sum_X \boldsymbol{\Psi}_X \frac{\text{sign}(E_X)}{(\hbar\omega - E_X)} \boldsymbol{\Psi}_X \cdot \boldsymbol{S} \cdot \boldsymbol{B} F(\omega)$$

Excitonic generalized eigen-problem in a crystal



Structure in the Bloch momentum degree of freedom

$$\mathcal{J}_{\{\boldsymbol{k}+\boldsymbol{Q}\}c_1,\boldsymbol{k}v_2}(\omega,\boldsymbol{Q}+\boldsymbol{G})$$



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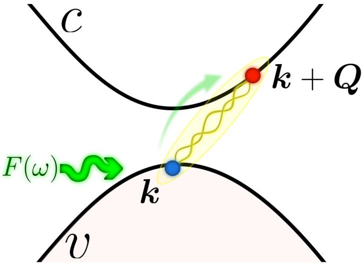

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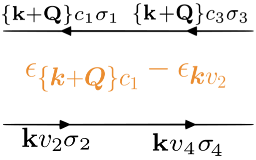
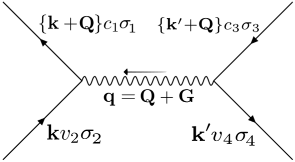
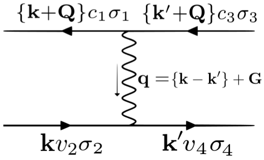
Free (ϵ) + Hartree (V) − Fock (W)







Structure in the spin degree of freedom

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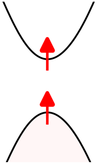
Spin-singlet set of solutions

$$|s\rangle = (1/\sqrt{2})\,(|c\uparrow, v\uparrow\rangle + |c\downarrow, v\downarrow\rangle)$$

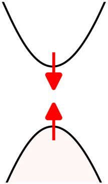
$$R_{\mathrm{s}} = \epsilon - W + 2V$$



Spin-triplet set of solutions

$$|t\rangle = |c\uparrow, v\downarrow\rangle\,,\ |c\downarrow, v\uparrow\rangle\,,\ (1/\sqrt{2})\,(|c\uparrow, v\uparrow\rangle - |c\downarrow, v\downarrow\rangle)$$

$$R_{\mathrm{t}} = \epsilon - W$$



$$\epsilon := \left(\epsilon_{\{\boldsymbol{k}+\boldsymbol{Q}\}c_1} - \epsilon_{\boldsymbol{k}v_2}\right), \quad W := W^{\{\boldsymbol{k}+\boldsymbol{Q}\}c_1, \boldsymbol{k}'v_4}_{\boldsymbol{k}v_2, \{\boldsymbol{k}'+\boldsymbol{Q}\}c_3}, \quad V := V^{\boldsymbol{k}'v_4, \{\boldsymbol{k}+\boldsymbol{Q}\}c_1}_{\boldsymbol{k}v_2, \{\boldsymbol{k}'+\boldsymbol{Q}\}c_3}$$

Excitons on hBN structures

Eletronic single-particle states - NN tight-binding model

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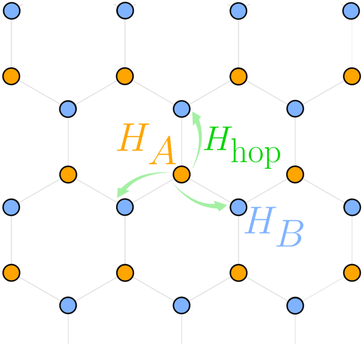
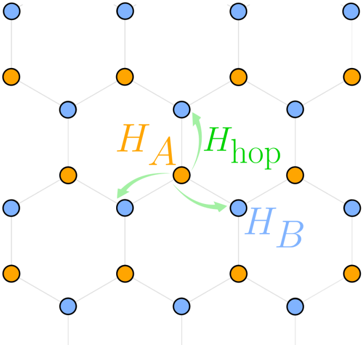


$$H_{\text{TB}} = \sum_i \epsilon_A a^\dagger_{\mathbf{R}_i} a_{\mathbf{R}_i} + \sum_i \epsilon_B b^\dagger_{\mathbf{R}_i} b_{\mathbf{R}_i}$$

$$-t \sum_{\langle i,j \rangle} \left(a^\dagger_{\mathbf{R}_i} b_{\mathbf{R}_i+\delta_j} + b^\dagger_{\mathbf{R}_j} a_{\mathbf{R}_i-\delta_j} \right)$$

Eletronic single-particle states - NN tight-binding model



$$\gamma_{\mathbf{k}} = \sum_{\langle j \rangle} e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_j}$$

$$H_{\text{TB}}(\boldsymbol{k}) = \begin{bmatrix} \epsilon_A & -t\gamma_{\boldsymbol{k}} \\ -t\gamma_{\boldsymbol{k}}^\dagger & \epsilon_B \end{bmatrix}$$

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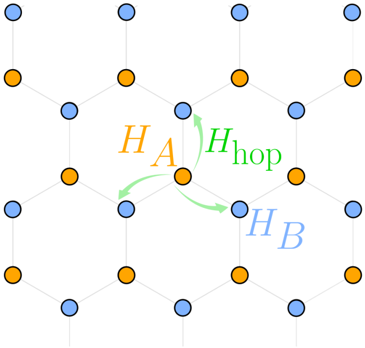

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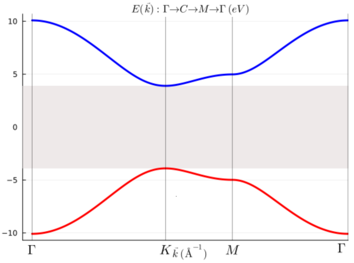

Electron-electron interaction - Atomistic model

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$$H_{\text{e-e}} = \sum_{\substack{\mathbf{R}_1\mathbf{R}_2 \\ \varsigma_1\varsigma_2}} \mathrm{V}\left((\mathbf{R}_1 + \mathbf{s}_{\varsigma_1}) - (\mathbf{R}_2 + \mathbf{s}_{\varsigma_2})\right) c^{\dagger}_{\mathbf{R}_1\varsigma_1} c^{\dagger}_{\mathbf{R}_2\varsigma_2} c_{\mathbf{R}_2\varsigma_2} c_{\mathbf{R}_1\varsigma_1}$$

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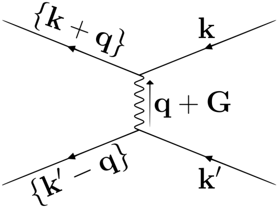

$$\propto \mathrm{V}(\mathbf{q}+\mathbf{G})\,\varrho_{\substack{\{\mathbf{k}+\mathbf{q}\}\\ \mathbf{k}}}\,\varrho_{\substack{\mathbf{k}'\\ \{\mathbf{k}'+\mathbf{q}\}}}$$

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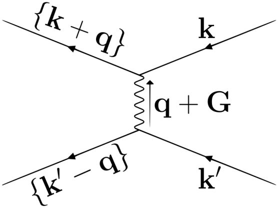

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Coulomb Potential

$$\mathrm{V}_{2D}(\mathbf{k}) = \frac{e^2}{2\varepsilon_0} \frac{1}{|\mathbf{k}|}$$

Rytova-Keldysh Potential

$$\mathrm{W}(\mathbf{k}) = \frac{e^2}{2\varepsilon_0} \frac{1}{|\mathbf{k}|} \frac{1}{1 + r_0 |\mathbf{k}|}$$

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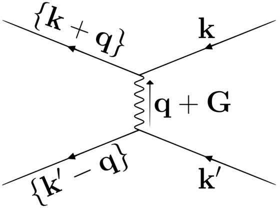

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Static limit

$$\mathrm{W}(\omega = 0)$$

Quick recap

&

Numerical implementation

Implementing the electron-hole Hamiltonian

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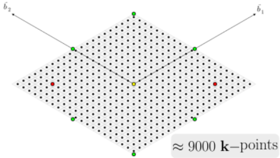
$$H_{\text{e-h}}(\mathbf{Q}) = \begin{bmatrix} R^{\{\mathbf{k}_1'+\mathbf{Q}\}c_3,\mathbf{k}_1'v_4}_{\{\mathbf{k}_1+\mathbf{Q}\}c_1,\mathbf{k}_1v_2} & \xrightarrow{\mathbf{k}'} \\ \downarrow\mathbf{k} & \ddots \end{bmatrix}$$

Discretization of the hBN 1BZ



Implementing the electron-hole Hamiltonian

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Fixed excitonic center of mass momentum

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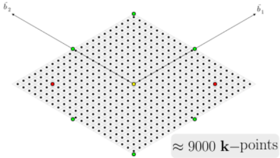

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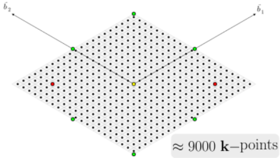
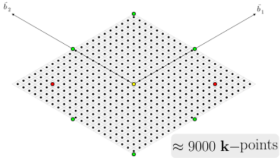
Discretization of the hBN 1BZ



$$\left(\epsilon_{\{\mathbf{k}+\mathbf{Q}\}c_1} - \epsilon_{\mathbf{k}v_2}\right)\delta_{\{\mathbf{k}+\mathbf{Q}\}c_1,\{\mathbf{k}'+\mathbf{Q}\}c_3}\delta_{\mathbf{k}v_2,\mathbf{k}'v_4} + \left(V^{\mathbf{k}'v_4,\{\mathbf{k}+\mathbf{Q}\}c_1}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3} - W^{\{\mathbf{k}+\mathbf{Q}\}c_1,\mathbf{k}'v_4}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3}\right)$$

Implementing the electron-hole Hamiltonian

Discretization of the hBN 1BZ



$$H_{\text{e-h}}(\mathbf{Q}) = \begin{bmatrix} R^{\{\mathbf{k}_1'+\mathbf{Q}\}c_3,\mathbf{k}_1'v_4}_{\{\mathbf{k}_1+\mathbf{Q}\}c_1,\mathbf{k}_1v_2} & \xrightarrow{\mathbf{k}'} \\ \downarrow\mathbf{k} & \ddots \end{bmatrix}$$

Fixed excitonic center of mass momentum

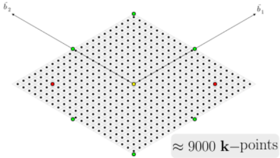
$$\left(\epsilon_{\{\mathbf{k}+\mathbf{Q}\}c_1} - \epsilon_{\mathbf{k}v_2}\right)\delta_{\{\mathbf{k}+\mathbf{Q}\}c_1,\{\mathbf{k}'+\mathbf{Q}\}c_3}\delta_{\mathbf{k}v_2,\mathbf{k}'v_4}$$
$$+\left(V^{\mathbf{k}'v_4,\{\mathbf{k}+\mathbf{Q}\}c_1}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3} - W^{\{\mathbf{k}+\mathbf{Q}\}c_1,\mathbf{k}'v_4}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3}\right)$$

$\epsilon_{\mathbf{k}\lambda}$ $\phi^{\varsigma}_{\mathbf{k}\lambda}$

$$\mathbf{H}_{\text{TB}}(\mathbf{k})$$

Eletronic single-particle properties

Discretization of the hBN 1BZ



$$H_{\text{e-h}}(\mathbf{Q}) = \begin{bmatrix} R^{\{\mathbf{k}'_1+\mathbf{Q}\}c_3,\mathbf{k}'_1 v_4}_{\{\mathbf{k}_1+\mathbf{Q}\}c_1,\mathbf{k}_1 v_2} & \overset{\mathbf{k}'}{\longrightarrow} \\ \downarrow\mathbf{k} & \ddots \end{bmatrix}$$

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$$\left(\epsilon_{\{\mathbf{k}+\mathbf{Q}\}c_1} - \epsilon_{\mathbf{k}v_2}\right)\delta_{\{\mathbf{k}+\mathbf{Q}\}c_1,\{\mathbf{k}'+\mathbf{Q}\}c_3}\delta_{\mathbf{k}v_2,\mathbf{k}'v_4}$$

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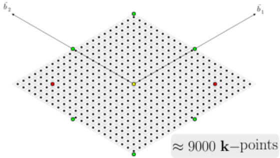


$$\left(\epsilon_{\{\mathbf{k}+\mathbf{Q}\}c_1} - \epsilon_{\mathbf{k}v_2}\right)\delta_{\{\mathbf{k}+\mathbf{Q}\}c_1,\{\mathbf{k}'+\mathbf{Q}\}c_3}\delta_{\mathbf{k}v_2,\mathbf{k}'v_4}$$
$$+\left(V^{\mathbf{k}'v_4,\{\mathbf{k}+\mathbf{Q}\}c_1}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3} - W^{\{\mathbf{k}+\mathbf{Q}\}c_1,\mathbf{k}'v_4}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3}\right)$$

$\epsilon_{\mathbf{k}\lambda}$ $\phi^{\varsigma}_{\mathbf{k}\lambda}$

$$\mathbf{H}_{\text{TB}}(\mathbf{k})$$

Eletronic single-particle properties

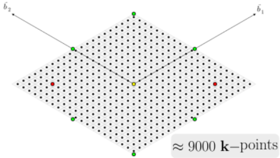
$$\varrho_{\substack{\mathbf{k}\lambda\\ \mathbf{k}'\lambda'}}(\mathbf{p}) = \sum_{\varsigma} e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{p})\cdot\mathbf{s}_{\varsigma}}\left(\phi^{\varsigma}_{\mathbf{k}\lambda}\right)^{*}\phi^{\varsigma}_{\mathbf{k}'\lambda'}$$

Atomistic electron-electron interaction form factors

$$H_{\text{e-h}}(\mathbf{Q}) = \begin{bmatrix} R^{\{\mathbf{k}'_1+\mathbf{Q}\}c_3,\mathbf{k}'_1 v_4}_{\{\mathbf{k}_1+\mathbf{Q}\}c_1,\mathbf{k}_1 v_2} & \overset{\mathbf{k}'}{\rightarrow} \\ \downarrow \mathbf{k} & \ddots \end{bmatrix}$$

Fixed excitonic center of mass momentum

Discretization of the hBN 1BZ



$$\left(\epsilon_{\{\mathbf{k}+\mathbf{Q}\}c_1} - \epsilon_{\mathbf{k}v_2}\right)\delta_{\{\mathbf{k}+\mathbf{Q}\}c_1,\{\mathbf{k}'+\mathbf{Q}\}c_3}\delta_{\mathbf{k}v_2,\mathbf{k}'v_4}$$

$$+\left(V^{\mathbf{k}'v_4,\{\mathbf{k}+\mathbf{Q}\}c_1}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3} - W^{\{\mathbf{k}+\mathbf{Q}\}c_1,\mathbf{k}'v_4}_{\mathbf{k}v_2,\{\mathbf{k}'+\mathbf{Q}\}c_3}\right)$$

$\epsilon_{\mathbf{k}\lambda}$ $\phi^{\varsigma}_{\mathbf{k}\lambda}$

$$\mathrm{V}(\mathbf{k}) = \frac{e^2}{2\varepsilon_0}\frac{1}{|\mathbf{k}|}$$

Bare Coulomb

$$\mathrm{W}(\mathbf{k}) = \frac{e^2}{2\varepsilon_0}\frac{1}{|\mathbf{k}|}\frac{1}{1+r_0|\mathbf{k}|}$$

Rytova-Keldysh

$$\mathbf{H}_{\mathrm{TB}}(\mathbf{k})$$

Eletronic single-particle properties

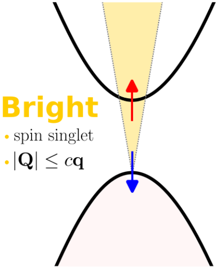
$$\varrho_{\substack{\mathbf{k}\lambda \\ \mathbf{k}'\lambda'}}(\mathbf{p}) = \sum_{\varsigma} e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{p})\cdot\mathbf{s}_{\varsigma}}\left(\phi^{\varsigma}_{\mathbf{k}\lambda}\right)^{*}\phi^{\varsigma}_{\mathbf{k}'\lambda'}$$

Atomistic electron-electron interaction form factors

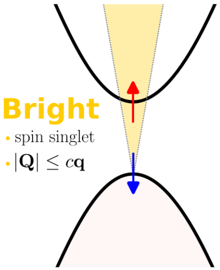
Results for the excitonic energy band-structure and wave-functions

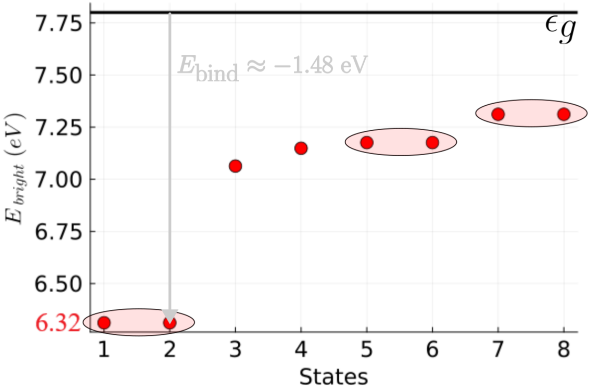
Isolated hBN monolayer: Spin-singlet with $\mathbf{Q} = 0$

Isolated hBN monolayer: Spin-singlet with $\mathbf{Q} = 0$



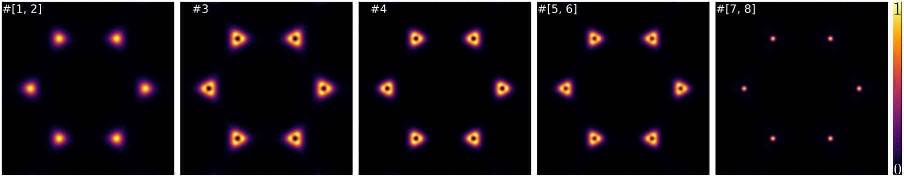
Isolated hBN monolayer: Spin-singlet with $\mathbf{Q} = 0$



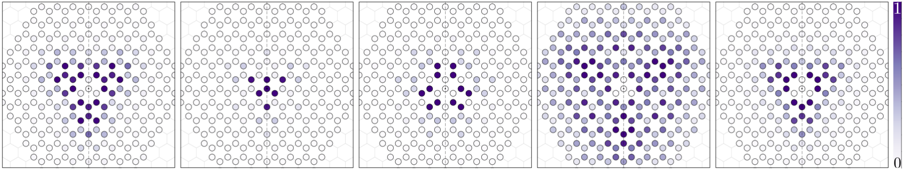


T. Galvani, Phys. Rev. B 94 (2016): $E_{\text{bind}} = -1.93$ eV
Quintela, Phys. Status Solidi. B 259(7) (2022): $E_{\text{bind}} = -1.31$ eV

In recriprocal space:

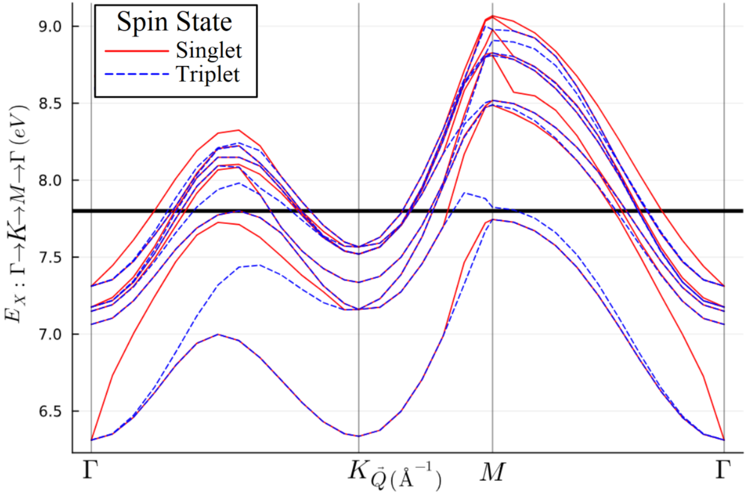


In real space:



Isolated hBN monolayer: band structure

Isolated hBN monolayer: band structure



hBN-metal hetero-structure

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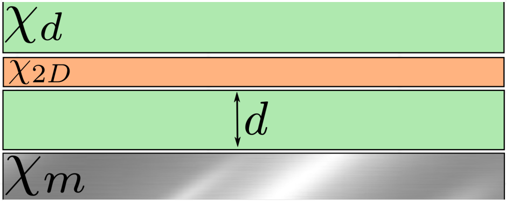
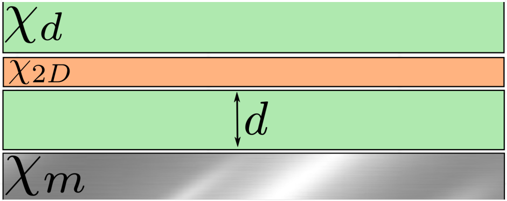


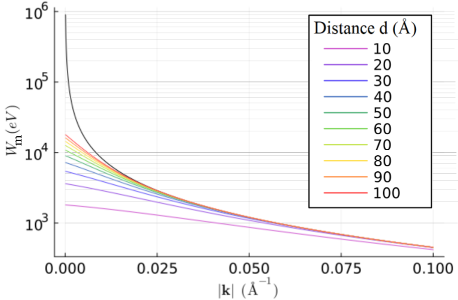
hBN-metal hetero-structure



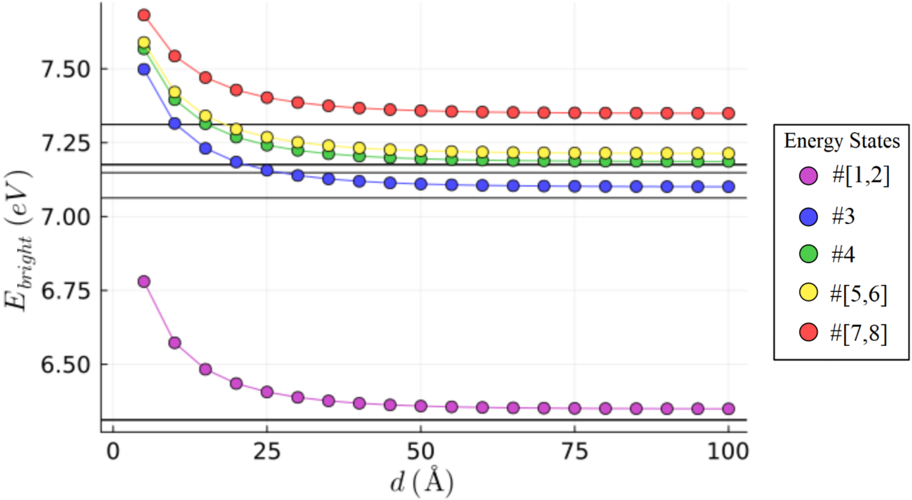
Metal-screened Rytova-Keldysh

$$W_m(\mathbf{k}) = \frac{e}{2\varepsilon_0}\frac{1}{k}\frac{1}{r_0 k + \frac{1}{2}\frac{e^{kd}}{\sinh(kd)}}$$

For metal-screened Coulomb set $r_0 = 0$



hBN-metal hetero-structure: Spin-singlet with $\mathbf{Q} = 0$



Conclusions

&

Future works

Formulated a method to calculate excitonic energies and wave-function

- Simple yet effective:
  - Easy to compute
  - Relatively small computational time
  - Precision up to 2 decimal places (scaling with **k**-point sampling)
  - Results within reason when comparing to more challenging techniques
- Versatile in the:
  - System's degrees of freedom (could account for spin-orbit effects or three-band models with some additional tweaks)
  - Eletronic model to the single particle eletronic states
  - Eletron-eletron interaction
  - Choice of eletrostatic potential (different types of screenings)

Future work...

Future work...

Generalized susceptibility

$$\chi_{AB}(\omega) = \frac{\langle A \rangle (\omega)}{F(\omega)} = \frac{\sum_{ab} A_{ab} \rho_{ba}^{(1)}(\omega)}{F(\omega)}$$

Optical conductivity

Exciton life-times

Future work...

Generalized susceptibility

$$\chi_{AB}(\omega) = \frac{\langle A \rangle (\omega)}{F(\omega)} = \frac{\sum_{ab} A_{ab} \rho_{ba}^{(1)}(\omega)}{F(\omega)}$$

Optical conductivity

Exciton life-times

Dependence on the screening effective radius

Dependence on the dieletric of the hetero-structure

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Optical conductivity

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Dependence on the screening effective radius

Dependence on the dieletric of the hetero-structure

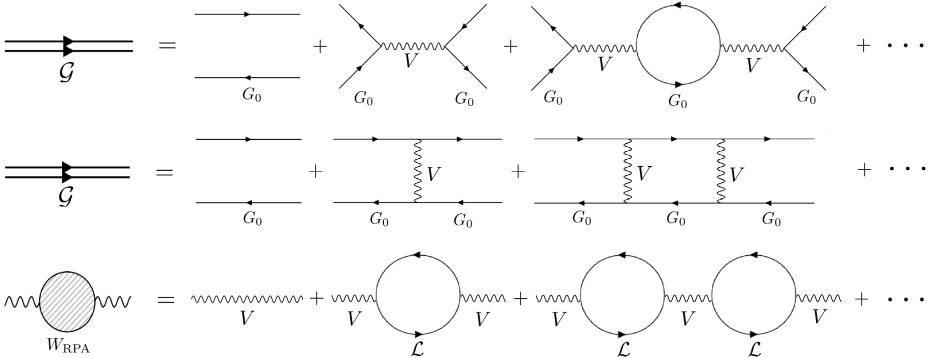
Three-band model TMDs

Thank you for listening!
Any questions?

The author acknowledges funding from Fundação para a Ciência e a Tecnologia (FCT-Portugal) through grant No. EXPL/FIS-MAC/0953/2021.

Fundação
para a Ciência
e a Tecnologia

More on the screening of the Hartree and the Fock terms...



More on the structure in the spin degree of freedom...

$$\left(\hbar\omega\mathbb{1} - \begin{bmatrix} R^{\uparrow_3\uparrow_4}_{\uparrow_1\uparrow_2} & R^{\uparrow_3\downarrow_4}_{\uparrow_1\uparrow_2} & R^{\downarrow_3\uparrow_4}_{\uparrow_1\uparrow_2} & R^{\downarrow_3\downarrow_4}_{\uparrow_1\uparrow_2} \\ R^{\uparrow_3\uparrow_4}_{\uparrow_1\downarrow_2} & R^{\uparrow_3\downarrow_4}_{\uparrow_1\downarrow_2} & R^{\downarrow_3\uparrow_4}_{\uparrow_1\downarrow_2} & R^{\downarrow_3\downarrow_4}_{\uparrow_1\downarrow_2} \\ R^{\uparrow_3\uparrow_4}_{\downarrow_1\uparrow_2} & R^{\uparrow_3\downarrow_4}_{\downarrow_1\uparrow_2} & R^{\downarrow_3\uparrow_4}_{\downarrow_1\uparrow_2} & R^{\downarrow_3\downarrow_4}_{\downarrow_1\uparrow_2} \\ R^{\uparrow_3\uparrow_4}_{\downarrow_1\downarrow_2} & R^{\uparrow_3\downarrow_4}_{\downarrow_1\downarrow_2} & R^{\downarrow_3\uparrow_4}_{\downarrow_1\downarrow_2} & R^{\downarrow_3\downarrow_4}_{\downarrow_1\downarrow_2} \end{bmatrix}\right) \begin{bmatrix} \rho^{(1)}_{c_3\uparrow_3, v_4\uparrow_4} \\ \rho^{(1)}_{c_3\uparrow_3, v_4\downarrow_4} \\ \rho^{(1)}_{c_3\downarrow_3, v_4\uparrow_4} \\ \rho^{(1)}_{c_3\downarrow_3, v_4\downarrow_4} \end{bmatrix} = \begin{bmatrix} \mathcal{J}_{c_1\uparrow_1, v_2\uparrow_2} \\ \mathcal{J}_{c_1\uparrow_1, v_2\downarrow_2} \\ \mathcal{J}_{c_1\downarrow_1, v_2\uparrow_2} \\ \mathcal{J}_{c_1\downarrow_1, v_2\downarrow_2} \end{bmatrix}$$

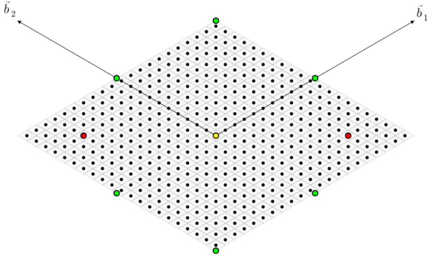
More on the structure in the spin degree of freedom...

$$\mathbf{R} = \begin{bmatrix} \epsilon + V - W & 0 & 0 & V \\ 0 & \epsilon - W & 0 & 0 \\ 0 & 0 & \epsilon - W & 0 \\ V & 0 & 0 & \epsilon + V - W \end{bmatrix} \begin{matrix} \uparrow\uparrow \\ \uparrow\downarrow \\ \downarrow\uparrow \\ \downarrow\downarrow \end{matrix}$$

$$\epsilon := \left(\epsilon_{\{\boldsymbol{k}+\boldsymbol{Q}\}c_1} - \epsilon_{\boldsymbol{k}v_2}\right), \quad W := W^{\{\boldsymbol{k}+\boldsymbol{Q}\}c_1, \boldsymbol{k}'v_4}_{\boldsymbol{k}v_2, \left\{\boldsymbol{k}'+\boldsymbol{Q}\right\}c_3}, \quad V := V^{\boldsymbol{k}'v_4, \{\boldsymbol{k}+\boldsymbol{Q}\}c_1}_{\boldsymbol{k}v_2, \left\{\boldsymbol{k}'+\boldsymbol{Q}\right\}c_3}$$

$$U = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 & 0 \end{bmatrix}$$

More on the discretization of the linear response problem...



$$\left(\hbar\omega \mathbb{1}_{N_{\mathbf{k}}\times N_{\mathbf{k}}} - \begin{bmatrix} R^{\{\mathbf{k}'_1+\mathbf{Q}\}c_3,\mathbf{k}'_1 v_4}_{\{\mathbf{k}_1+\mathbf{Q}\}c_1,\mathbf{k}_1 v_2} & R^{\{\mathbf{k}'_2+\mathbf{Q}\}c_3,\mathbf{k}'_2 v_4}_{\{\mathbf{k}_1+\mathbf{Q}\}c_1,\mathbf{k}_1 v_2} & \overset{\mathbf{k}'}{\rightarrow} \\ R^{\{\mathbf{k}'_1+\mathbf{Q}\}c_3,\mathbf{k}'_1 v_4}_{\{\mathbf{k}_2+\mathbf{Q}\}c_1,\mathbf{k}_2 v_2} & R^{\{\mathbf{k}'_2+\mathbf{Q}\}c_3,\mathbf{k}'_2 v_4}_{\{\mathbf{k}_2+\mathbf{Q}\}c_1,\mathbf{k}_2 v_2} & \overset{\mathbf{k}'}{\rightarrow} \\ \downarrow\mathbf{k} & \downarrow\mathbf{k} & \ddots \end{bmatrix} \right) \times$$

$$\times \begin{bmatrix} \boldsymbol{\rho}^{(1)}_{\{\mathbf{k}'_1+\mathbf{Q}\}c_3\mathbf{k}'_1 v_4} \\ \boldsymbol{\rho}^{(1)}_{\{\mathbf{k}'_2+\mathbf{Q}\}c_3\mathbf{k}'_2 v_4} \\ \downarrow\mathbf{k}' \end{bmatrix} = \begin{bmatrix} \mathcal{J}_{\{\mathbf{k}_1+\mathbf{Q}\}c_1,\mathbf{k}_1 v_2} \\ \mathcal{J}_{\{\mathbf{k}_2+\mathbf{Q}\}c_1,\mathbf{k}_2 v_2} \\ \downarrow\mathbf{k} \end{bmatrix}$$

Parameters used

Eletronic parameters:

- $e^2/\varepsilon_0 = 10^4/55.3$ eVÅ
- $\epsilon_g = 7.8$ eV
- $t = 3.1$ eV
- $a_0 = 1.42\sqrt{3}$ Å
- $r_0 = 10$ Å

Numerical parameters:

- $N_{\boldsymbol{k}} = 8649$ $\boldsymbol{k}$-points
- $|\boldsymbol{k}_{\text{cutoff}}| = 1.5$ Å

Tamm-Dancoff Approx.

More on the TD Hartree-Fock mean-field theory...

Linear regime

$$\boldsymbol{\rho}(t) \approx \boldsymbol{\rho}^{(0)} + \boldsymbol{\rho}^{(1)}(t)$$

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$$h_{ac} = \epsilon_a \delta_{ac}$$
$$\rho^{(0)}_{ab} = f_a \delta_{ab}$$

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$$\left(\hbar\omega\delta^{\gamma\delta}_{ab} - H^{\gamma\delta}_{ab}\right)\rho^{(1)}_{ab}(\omega) = J_{ab}(\omega)$$

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Source term

$$J_{ab}(\omega) = (f_b - f_a)\,B^i_{ab}F^i(\omega)$$

More on the TD Hartree-Fock mean-field theory...

Zero temperature regime

At $T = 0K$, the occupational degree of freedom can only be classified as either occupied $|o\rangle$ or empty $|e\rangle$ meaning that $f_o = 1$ or $f_e = 0$.

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$$\left(\hbar\omega\mathbb{1} - \begin{bmatrix} H^{e_3e_4}_{e_1e_2} & H^{e_3o_4}_{e_1e_2} & H^{o_3e_4}_{e_1e_2} & H^{o_3o_4}_{e_1e_2} \\ H^{e_3e_4}_{e_1o_2} & H^{e_3o_4}_{e_1o_2} & H^{o_3e_4}_{e_1o_2} & H^{o_3o_4}_{e_1o_2} \\ H^{e_3e_4}_{o_1e_2} & H^{e_3o_4}_{o_1e_2} & H^{o_3e_4}_{o_1e_2} & H^{o_3o_4}_{o_1e_2} \\ H^{e_3e_4}_{o_1o_2} & H^{e_3o_4}_{o_1o_2} & H^{o_3e_4}_{o_1o_2} & H^{o_3o_4}_{o_1o_2} \end{bmatrix}\right) \begin{bmatrix} \rho^{(1)}_{e_3e_4}(\omega) \\ \rho^{(1)}_{e_3o_4}(\omega) \\ \rho^{(1)}_{o_3e_4}(\omega) \\ \rho^{(1)}_{o_3o_4}(\omega) \end{bmatrix} = \begin{bmatrix} \mathcal{J}_{e_1e_2}(\omega) \\ \mathcal{J}_{e_1o_2}(\omega) \\ \mathcal{J}_{o_1e_2}(\omega) \\ \mathcal{J}_{o_1o_2}(\omega) \end{bmatrix}$$

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$$\left(\hbar\omega\mathbb{1} - \begin{bmatrix} H^{e_3 e_4}_{e_1 e_2} & 0 & 0 & 0 \\ H^{e_3 e_4}_{e_1 o_2} & H^{e_3 o_4}_{e_1 o_2} & H^{o_3 e_4}_{e_1 o_2} & H^{o_3 o_4}_{e_1 o_2} \\ H^{e_3 e_4}_{o_1 e_2} & H^{e_3 o_4}_{o_1 e_2} & H^{o_3 e_4}_{o_1 e_2} & H^{o_3 o_4}_{o_1 e_2} \\ 0 & 0 & 0 & H^{o_3 o_4}_{o_1 o_2} \end{bmatrix}\right) \begin{bmatrix} \rho^{(1)}_{e_3 e_4}(\omega) \\ \rho^{(1)}_{e_3 o_4}(\omega) \\ \rho^{(1)}_{o_3 e_4}(\omega) \\ \rho^{(1)}_{o_3 o_4}(\omega) \end{bmatrix} = \begin{bmatrix} 0 \\ \mathcal{J}_{e_1 o_2}(\omega) \\ \mathcal{J}_{o_1 e_2}(\omega) \\ 0 \end{bmatrix}$$

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Zero temperature regime

At $T = 0K$, the occupational degree of freedom can only be classified as either occupied $|o\rangle$ or empty $|e\rangle$ meaning that $f_o = 1$ or $f_e = 0$.

$$\left(\hbar\omega\mathbb{1} - \begin{bmatrix} H^{e_3 o_4}_{e_1 o_2} & H^{o_4 e_3}_{e_1 o_2} \\ H^{e_3 o_4}_{o_2 e_1} & H^{o_4 e_3}_{o_2 e_1} \end{bmatrix}\right) \begin{bmatrix} \rho^{(1)}_{e_3 o_4}(\omega) \\ \rho^{(1)}_{o_4 e_3}(\omega) \end{bmatrix} = \begin{bmatrix} \mathcal{J}_{e_1 o_2}(\omega) \\ \mathcal{J}_{o_2 e_1}(\omega) \end{bmatrix}$$

$$H^{o_4 e_4}_{o_1 e_2} = -\left(H^{e_3 o_4}_{e_1 o_2}\right)^* \quad \text{and} \quad H^{e_4 o_3}_{o_2 e_1} = -\left(H^{o_3 e_4}_{e_1 o_2}\right)^\dagger$$