Electrostatic screening in 2D semiconductors: an efficient atomistic implementation

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POLIMA weekly seminar

Where have I been?

Where have I been?

Outline

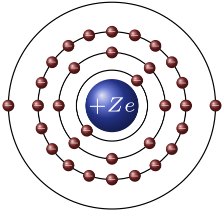
Outline

Outline

Screening...

...in an atom.

(Bare) Coulomb potential $v_c = \frac{Ze^2}{r}$



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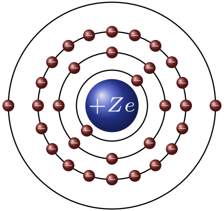

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$$W < v_c$$

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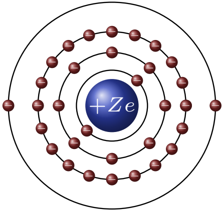

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Phys. Rev. 36, 57, J.C. Slater

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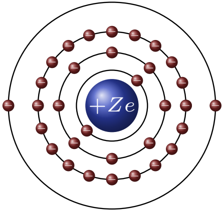

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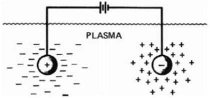
Phys. Rev. 36, 57, J.C. Slater

...in a plasma.

$\phi(r) \propto e^{-\lambda_D r}/r\,,\lambda_D^2 = \varepsilon_r\varepsilon_0 k_B T/nq^2$



"Intro. to Plasma Physics and Controlled Fusion", F.F. Chen

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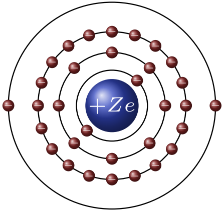

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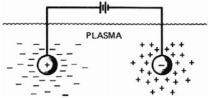

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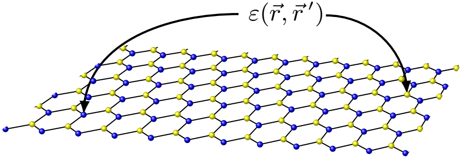
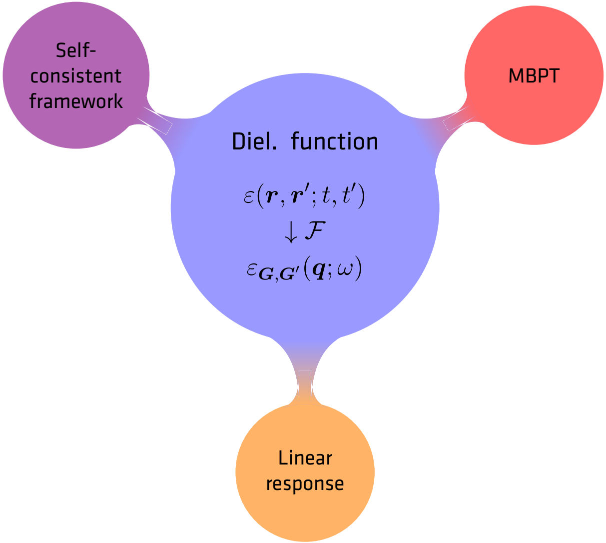
...in a crystal.

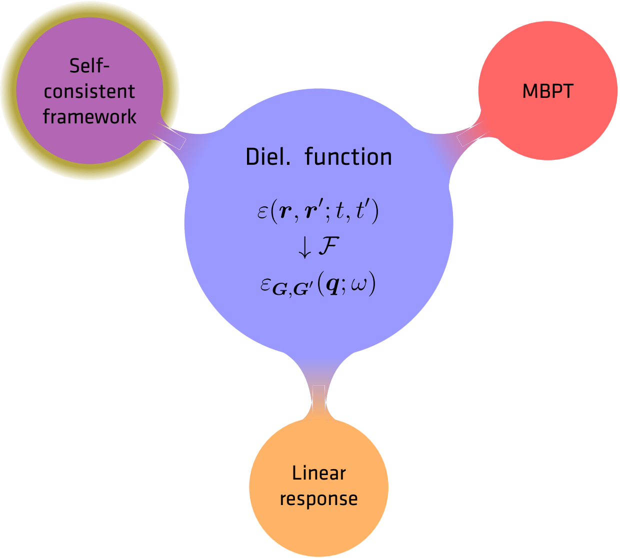


Outline

The dielectric function: technical contexts



The dielectric function: technical contexts



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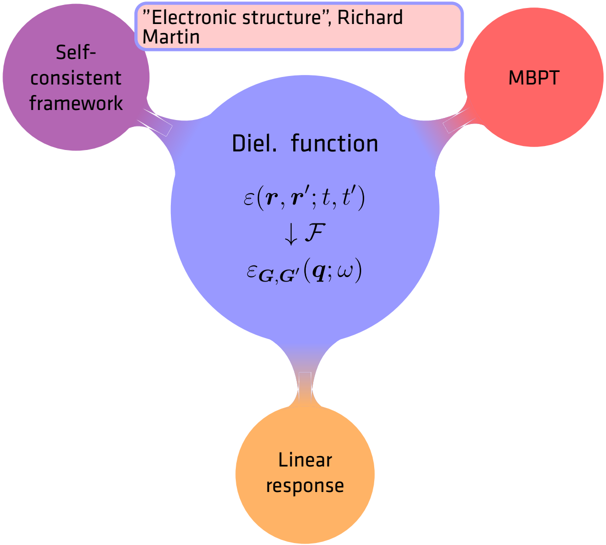

The dielectric function: technical contexts

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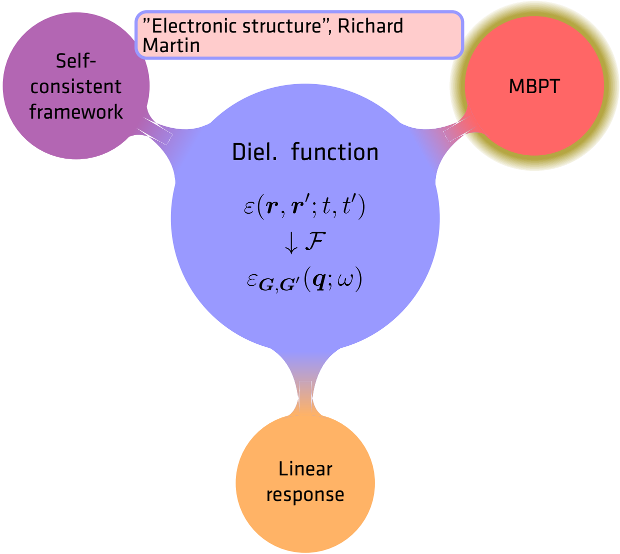

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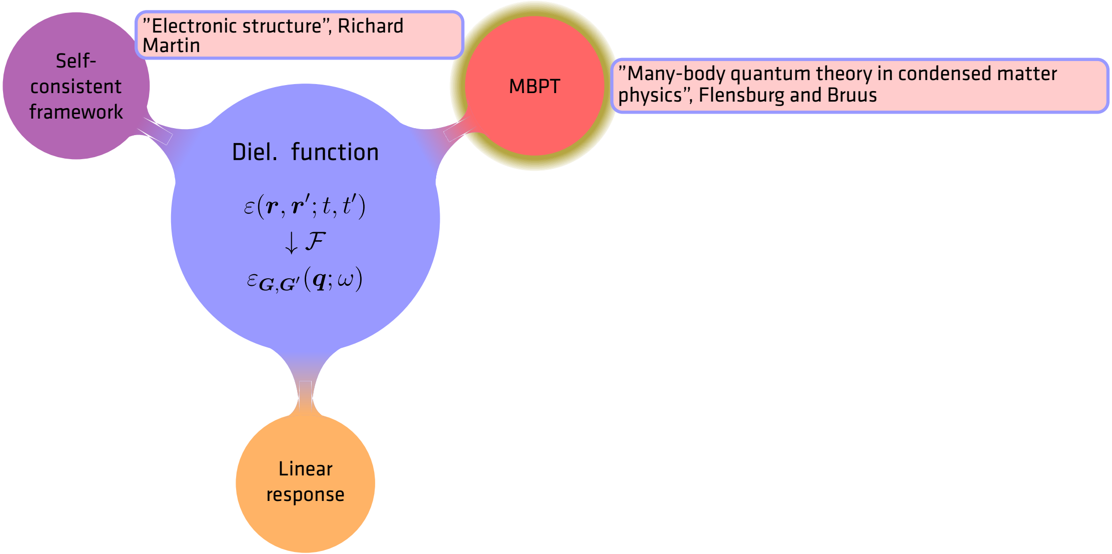

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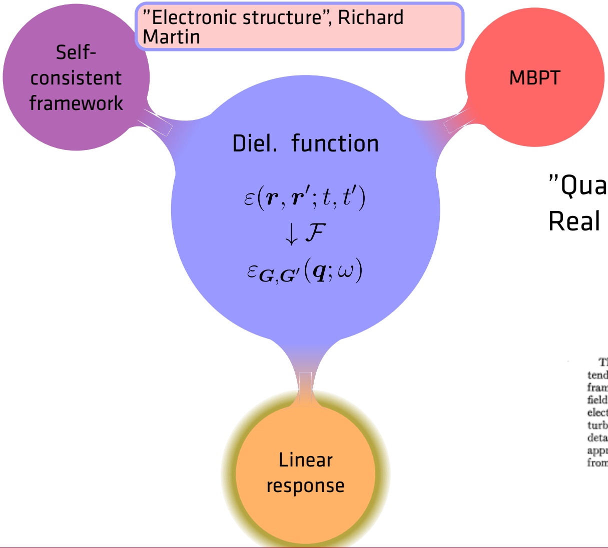

"Many-body quantum theory in condensed matter physics", Flensburg and Bruus

"Quantum Theory of the Dielectric Constant in Real Solids", S.L. Adler, Phys. Rev. 126, 1962

Quantum Theory of the Dielectric Constant in Real Solids

Stephen L. Adler*
General Electric Research Laboratory, Schenectady, New York

(Received October 12, 1961)

The quantum theory of the frequency- and wave-number-dependent dielectric constant in solids is extended in order to study the full dielectric constant tensor and to include local-field effects. Within the framework of the band theory, an explicit expression for the dielectric constant tensor, neglecting local-field effects, is derived. In addition to components which are the ordinary longitudinal and transverse dielectric constants, there are components which couple transverse and longitudinal electromagnetic disturbances. A formalism for calculating the local-field corrections to the dielectric constant is developed in detail for the case of the longitudinal dielectric constant of a cubic insulating solid. In the coarsest (dipole) approximation, the theory gives a Lorenz-Lorentz formula modified by self-polarization corrections arising from the polarization of the charge in a unit cell by its own field.

The dielectric function: technical contexts

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Self-consistent framework

"Electronic structure", Richard Martin

MBPT

"Many-body quantum theory in condensed matter physics", Flensburg and Bruus

Diel. function

$$\varepsilon(\boldsymbol{r},\boldsymbol{r}';t,t')$$
$$\downarrow \mathcal{F}$$
$$\varepsilon_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q};\omega)$$

Linear response

"Many-Particle Physics", Gerald Mahan

"Quantum Theory of the Dielectric Constant in Real Solids", S.L. Adler, Phys. Rev. 126, 1962

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The dielectric function: full and non-interacting

"Interacting Electrons: Theory and Computational Approaches", Richard Martin et. al, 2016

$$\varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}';t,t') = \delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t') + \int \mathrm{d}\boldsymbol{r}'' \int_{-\infty}^{t} \mathrm{d}t'' \chi(\boldsymbol{r},\boldsymbol{r}';t-t'')v_c(\boldsymbol{r}-\boldsymbol{r}')$$

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Hedin's equations: ($(1,2) \equiv (\boldsymbol{r}_1, t_1; \boldsymbol{r}_2, t_2)$, f.egs.)

$$W(1,2) = v_c(1,2) + \int \mathrm{d}3\mathrm{d}4 v_c(1,3)P(3,4)W(4,2) \text{ (Dyson's eq.)}$$

$$P(1,2) = -i\int \mathrm{d}3\mathrm{d}4\, G(1,3)G(4,1^+)\Gamma(3,4;2)$$

$$\Sigma(1,2) = \int \mathrm{d}3\mathrm{d}4\, G(1,3)\Gamma(3,2;4)W(4,1^+)$$

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int \mathrm{d}4\mathrm{d}5\mathrm{d}6\mathrm{d}7\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\Gamma(6,7;3)\,,$$

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The dielectric function: GW and RPA

"Interacting Electrons: Theory and Computational Approaches", Richard Martin et. al, 2016

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$$P^0(1,2) = -i \int \mathrm{d}3\, G(1,3)G(3,2),$$ Random Phase Approximation

$$\Sigma(1,2) = \int \mathrm{d}3\, G(1,3)W(3,2),$$ GW approximation

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \cancel{\int \mathrm{d}4\mathrm{d}5\mathrm{d}6\mathrm{d}7 \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7;3)},$$

Outline

Outline

1. Screening
   - Screening (what is it?)
   - The dielectric function
2. The screened potential
   - RPA polarizability: useful expressions
   - RPA dielectric function and screened potential
3. Dielectric function in the Tight-Binding approximation
   - Tight-Binding approximation
   - Dielectric function within TB
4. Numerical results
5. What is in order? Real space approach

RPA polarizability: general expression

$$\chi_0(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \sum_{i,j} (f_i - f_j) \frac{\phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r})\phi_j^*(\boldsymbol{r}')\phi_i(\boldsymbol{r}')}{\epsilon_i - \epsilon_j + \hbar\omega + \mathrm{i}\hbar\alpha}$$

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$$\chi_0(\boldsymbol{r},\boldsymbol{r}';\omega) = \sum_{v\boldsymbol{k},c\boldsymbol{k}'}\left[\frac{\psi_{c\boldsymbol{k}'}(\boldsymbol{r})\psi_{v\boldsymbol{k}}^*(\boldsymbol{r})\psi_{v\boldsymbol{k}}(\boldsymbol{r}')\psi_{c\boldsymbol{k}'}^*(\boldsymbol{r}')}{\hbar\omega - (\epsilon_{c\boldsymbol{k}'} - \epsilon_{v\boldsymbol{k}}) + \mathrm{i}\hbar\alpha} - \frac{\psi_{v\boldsymbol{k}}(\boldsymbol{r})\psi_{c\boldsymbol{k}'}^*(\boldsymbol{r})\psi_{c\boldsymbol{k}'}(\boldsymbol{r}')\psi_{v\boldsymbol{k}}^*(\boldsymbol{r}')}{\hbar\omega + (\epsilon_{c\boldsymbol{k}'} - \epsilon_{v\boldsymbol{k}}) + \mathrm{i}\hbar\alpha}\right].$$

$$\langle\boldsymbol{r}|n,\boldsymbol{k}\rangle = \psi_{n\boldsymbol{k}}(\boldsymbol{r})\,,\alpha\to 0^+$$

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\sum_{i\alpha}C_{i\alpha}^{n\boldsymbol{k}}\phi_\alpha(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{t}_i)\text{ , in the TB approx.}$$

RPA polarizability: momentum space

$$\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega)=\frac{1}{N}\sum_{\boldsymbol{q},\boldsymbol{q}'}\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}}\chi^0(\boldsymbol{q},\boldsymbol{q}';\omega)\mathrm{e}^{-\mathrm{i}\boldsymbol{q}'\cdot\boldsymbol{r}'}$$

RPA polarizability: momentum space

$$\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega) = \frac{1}{N}\sum_{\boldsymbol{q},\boldsymbol{q}'} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}}\chi^0(\boldsymbol{q},\boldsymbol{q}';\omega)\mathrm{e}^{-\mathrm{i}\boldsymbol{q}'\cdot\boldsymbol{r}'} =$$

$$= \frac{1}{N}\sum_{\boldsymbol{q}}\sum_{\boldsymbol{G}'} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}\mathrm{e}^{-\mathrm{i}\boldsymbol{G}'\cdot\boldsymbol{r}'}\chi^0(\boldsymbol{q},\boldsymbol{q}+\boldsymbol{G}';\omega)$$

RPA polarizability: momentum space

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$$= \frac{1}{N}\sum_{\boldsymbol{q}\in\mathrm{BZ}}\sum_{\boldsymbol{G},\boldsymbol{G}'} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}\mathrm{e}^{\mathrm{i}\boldsymbol{G}\cdot\boldsymbol{r}}\mathrm{e}^{-\mathrm{i}(\boldsymbol{G}'+\boldsymbol{G})\cdot\boldsymbol{r}'}\chi^0(\boldsymbol{q}+\boldsymbol{G},\boldsymbol{q}+\boldsymbol{G}+\boldsymbol{G}';\omega) =$$

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RPA polarizability: momentum space

$$\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega) = \frac{1}{N}\sum_{\boldsymbol{q},\boldsymbol{q}'} e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\chi^0(\boldsymbol{q},\boldsymbol{q}';\omega)e^{-i\boldsymbol{q}'\cdot\boldsymbol{r}'} =$$

$$= \frac{1}{N}\sum_{\boldsymbol{q}}\sum_{\boldsymbol{G}'} e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}e^{-i\boldsymbol{G}'\cdot\boldsymbol{r}'}\chi^0(\boldsymbol{q},\boldsymbol{q}+\boldsymbol{G}';\omega) =$$

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$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q};\omega) = \int d\boldsymbol{r}\int d\boldsymbol{r}' e^{-i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\chi_0(\boldsymbol{r},\boldsymbol{r}';\omega)e^{i(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}}$$

Static RPA polarizability: r and q spaces

$$\chi_0(\boldsymbol{r},\boldsymbol{r}';\omega)=\sum_{v\boldsymbol{k},c\boldsymbol{k}'}\left[\frac{\psi_{c\boldsymbol{k}'}(\boldsymbol{r})\psi^*_{v\boldsymbol{k}}(\boldsymbol{r})\psi_{v\boldsymbol{k}}(\boldsymbol{r}')\psi^*_{c\boldsymbol{k}'}(\boldsymbol{r}')}{\hbar\omega-(\epsilon_{c\boldsymbol{k}'}-\epsilon_{v\boldsymbol{k}})+\mathrm{i}\hbar\alpha}-\frac{\psi_{v\boldsymbol{k}}(\boldsymbol{r})\psi^*_{c\boldsymbol{k}'}(\boldsymbol{r})\psi_{c\boldsymbol{k}'}(\boldsymbol{r}')\psi^*_{v\boldsymbol{k}}(\boldsymbol{r}')}{\hbar\omega+(\epsilon_{c\boldsymbol{k}'}-\epsilon_{v\boldsymbol{k}})+\mathrm{i}\hbar\alpha}\right].$$

$$\chi_0(\boldsymbol{r},\boldsymbol{r}')=-\sum_{v\boldsymbol{k},c\boldsymbol{k}'}\frac{2\,\mathrm{Re}\{\psi_{c\boldsymbol{k}'}(\boldsymbol{r})\psi^*_{v\boldsymbol{k}}(\boldsymbol{r})\psi_{v\boldsymbol{k}}(\boldsymbol{r}')\psi^*_{c\boldsymbol{k}'}(\boldsymbol{r}')\}}{\epsilon_{c\boldsymbol{k}'}-\epsilon_{v\boldsymbol{k}}}$$

$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q};\omega)=\frac{1}{\Omega}\sum_{n,n'}\sum_{\boldsymbol{k}}(f_{n,\boldsymbol{k}+\boldsymbol{q}}-f_{n',\boldsymbol{k}})\frac{\langle n,\boldsymbol{k}+\boldsymbol{q}|\,\mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\,|n',\boldsymbol{k}\rangle\,\langle n',\boldsymbol{k}|\,\mathrm{e}^{-\mathrm{i}(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}}\,|n,\boldsymbol{k}+\boldsymbol{q}\rangle}{\epsilon_{n,\boldsymbol{k}+\boldsymbol{q}}-\epsilon_{n',\boldsymbol{k}}+\hbar\omega+\mathrm{i}\hbar\alpha}$$

$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q})=\frac{1}{\Omega}\sum_{n}^{\text{occ}}\sum_{n'}^{\text{emp}}\sum_{\boldsymbol{k}}\frac{\langle n,\boldsymbol{k}+\boldsymbol{q}|\,\mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\,|n',\boldsymbol{k}\rangle\,\langle n',\boldsymbol{k}|\,\mathrm{e}^{-\mathrm{i}(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}}\,|n,\boldsymbol{k}+\boldsymbol{q}\rangle}{\epsilon_{n,\boldsymbol{k}+\boldsymbol{q}}-\epsilon_{n',\boldsymbol{k}}}$$

Outline

RPA dielectric function

$$\varepsilon^{\mathsf{RPA}}(\boldsymbol{r},\boldsymbol{r}';t,t') = \delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t') - \int \mathrm{d}\boldsymbol{r}'' \int_{-\infty}^{t} \mathrm{d}t'' \chi^0(\boldsymbol{r},\boldsymbol{r}';t-t'')v_c(\boldsymbol{r}-\boldsymbol{r}')$$

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$$\varepsilon_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) = \delta_{\boldsymbol{G}\boldsymbol{G}'} - v_c(\boldsymbol{q}+\boldsymbol{G})\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q})\,,\, v_c(\boldsymbol{q}) = \frac{e^2}{2\varepsilon_0|\boldsymbol{q}|}$$

RPA dielectric function

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$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) = \frac{1}{\Omega}\sum_{v,c}\sum_{\boldsymbol{k}} \frac{\langle v,\boldsymbol{k}+\boldsymbol{q}|\,\mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\,|c,\boldsymbol{k}\rangle\,\langle c,\boldsymbol{k}|\,\mathrm{e}^{-\mathrm{i}(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}}\,|v,\boldsymbol{k}+\boldsymbol{q}\rangle}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}}-\epsilon_{c,\boldsymbol{k}}}$$ see [1]

[1] Jack Deslippe et al., “BerkeleyGW: A massively parallel computer package for the calculation of the quasiparticle and optical properties of materials and nanostructures”, Computer Physics Communications 183.6 (2012)

The (RPA) screened electrostatic potential

$$W(\boldsymbol{r}, \boldsymbol{r}') = \int \mathrm{d}\boldsymbol{r}'' \varepsilon^{-1}(\boldsymbol{r}, \boldsymbol{r}'') v_c(\boldsymbol{r}'', \boldsymbol{r}')$$

$$W_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q}) = \varepsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) v_c(\boldsymbol{q} + \boldsymbol{G}') \, ,$$

The (RPA) screened electrostatic potential

$$W(\boldsymbol{r},\boldsymbol{r}') = \int \mathrm{d}\boldsymbol{r}'' \varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'') v_c(\boldsymbol{r}'',\boldsymbol{r}')$$

$$W_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q}) = \varepsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) v_c(\boldsymbol{q}+\boldsymbol{G}')\,,$$

Ignoring local field effects ($\boldsymbol{G} = \boldsymbol{G}' = 0$) and defining $\varepsilon_{\text{mac}}(\boldsymbol{q}) = 1/\varepsilon^{-1}_{\boldsymbol{00}}(\boldsymbol{q})$

$$W(\boldsymbol{q}) = \frac{v_c(\boldsymbol{q})}{\varepsilon_{\text{mac}}(\boldsymbol{q})}\,,$$

The (RPA) screened electrostatic potential

$$W(\boldsymbol{r},\boldsymbol{r}') = \int \mathrm{d}\boldsymbol{r}'' \varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'') v_c(\boldsymbol{r}'',\boldsymbol{r}')$$

$$W_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q}) = \varepsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) v_c(\boldsymbol{q}+\boldsymbol{G}')\,,$$

Ignoring local field effects ($\boldsymbol{G}=\boldsymbol{G}'=0$) and defining $\varepsilon_{\mathsf{mac}}(\boldsymbol{q}) = 1/\varepsilon^{-1}_{\mathbf{00}}(\boldsymbol{q})$

$$W(\boldsymbol{q}) = \frac{v_c(\boldsymbol{q})}{\varepsilon_{\mathsf{mac}}(\boldsymbol{q})}\,,$$

For a 2D semiconductor/insulator $\varepsilon_{\mathsf{mac}}(\boldsymbol{q}) = \varepsilon_{\mathsf{2D}}(\boldsymbol{q}) \approx 1 + r_0 q \equiv \varepsilon_{\mathsf{RK}}(\boldsymbol{q})$

$$V_{\mathsf{RK}}(q) = \frac{v_c(q)}{\varepsilon_{\mathsf{RK}}(q)} = \frac{e^2}{2\varepsilon_0(1+r_0 q)q}\,,$$

Outline

Outline

Bloch states in the TB approx.

In the linear combination of atomic orbitals (LCAO) method

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

Bloch states in the TB approx.

In the linear combination of atomic orbitals (LCAO) method

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

Frequently, we work under the tight-binding approximation: retain nearest neighbors and neglect overlap between orbitals.

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}_j} \psi_j(\boldsymbol{k}) \Phi_j(\boldsymbol{k},\boldsymbol{r}) \,, \Phi_j(\boldsymbol{k},\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \phi(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_j)$$

Bloch states in the TB approx.

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$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

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$$H\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = E\psi_{n\boldsymbol{k}}(\boldsymbol{r}) \Leftrightarrow \sum_j \psi_j(\boldsymbol{k}) H\Phi_j(\boldsymbol{k}, \boldsymbol{r}) = E \sum_j \psi_j(\boldsymbol{k}) \Phi_j(\boldsymbol{k}, \boldsymbol{r}) \, .$$

Bloch states in the TB approx.

In the linear combination of atomic orbitals (LCAO) method

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

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$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}_j} \psi_j(\boldsymbol{k}) \Phi_j(\boldsymbol{k}, \boldsymbol{r})\,, \Phi_j(\boldsymbol{k}, \boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \phi(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_j)$$

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$$\sum_j \psi_j(\boldsymbol{k}) \underbrace{\int \mathrm{d}\boldsymbol{r}\, \Phi_i^*(\boldsymbol{k}, \boldsymbol{r}) H \Phi_j(\boldsymbol{k}, \boldsymbol{r})}_{H_{ij}(\boldsymbol{k})} = E \sum_j \psi_j(\boldsymbol{k}) \underbrace{\int \mathrm{d}\boldsymbol{r}\, \Phi_i^*(\boldsymbol{k}, \boldsymbol{r}) \Phi_j(\boldsymbol{k}, \boldsymbol{r})}_{S_{ij}(\boldsymbol{k})}$$

Bloch Hamiltonian in the TB approx.

Defining $H_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r}) | H | \Phi_j(\boldsymbol{k},\boldsymbol{r}) \rangle$ and $S_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r}) | \Phi_j(\boldsymbol{k},\boldsymbol{r}) \rangle$

$$\sum_j \psi_j(\boldsymbol{k}) H_{ij}(\boldsymbol{k}) = E \sum_j \psi_j(\boldsymbol{k}) S_{ij}(\boldsymbol{k})$$

Bloch Hamiltonian in the TB approx.

Defining $H_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r})|H|\Phi_j(\boldsymbol{k},\boldsymbol{r})\rangle$ and $S_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r})|\Phi_j(\boldsymbol{k},\boldsymbol{r})\rangle$

$$\sum_j \psi_j(\boldsymbol{k}) H_{ij}(\boldsymbol{k}) = E \sum_j \psi_j(\boldsymbol{k}) S_{ij}(\boldsymbol{k})$$

The transfer integral matrix elements read

$$H_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r})|H|\Phi_j(\boldsymbol{k},\boldsymbol{r})\rangle = \sum_{ij} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_j-\boldsymbol{R}_i)} \langle \phi(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{t}_i)|H|\phi(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{t}_j)\rangle =$$

$$= \sum_{\boldsymbol{R}_j} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j} \langle \phi_i(\boldsymbol{r})|H|\phi_j(\boldsymbol{r}-\boldsymbol{R}_j)\rangle = \underbrace{\sum_{\boldsymbol{R}_j} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j} H_{ij}(\boldsymbol{R}_j)}_{\text{Bloch Ham.}}, H(\boldsymbol{R}_j) \rightarrow \text{Fock matrix at } \boldsymbol{R}_j$$

Bloch Hamiltonian in the TB approx.

Defining $H_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r}) | H | \Phi_j(\boldsymbol{k},\boldsymbol{r}) \rangle$ and $S_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r}) | \Phi_j(\boldsymbol{k},\boldsymbol{r}) \rangle$

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$$H_{ij}(\boldsymbol{k}) = \langle \Phi_i(\boldsymbol{k},\boldsymbol{r}) | H | \Phi_j(\boldsymbol{k},\boldsymbol{r}) \rangle = \sum_{ij} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_j - \boldsymbol{R}_i)} \langle \phi(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i) | H | \phi(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_j) \rangle =$$

$$= \sum_{\boldsymbol{R}_j} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j} \langle \phi_i(\boldsymbol{r}) | H | \phi_j(\boldsymbol{r} - \boldsymbol{R}_j) \rangle = \underbrace{\sum_{\boldsymbol{R}_j} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j} H_{ij}(\boldsymbol{R}_j)}_{\text{Bloch Ham.}}, \; H(\boldsymbol{R}_j) \rightarrow \text{Fock matrix at } \boldsymbol{R}_j$$

TB approx. $\Rightarrow S_{ij}(\boldsymbol{k}) \approx \delta_{ij}$ and eigenvalue/eigenvector problem:

$$H(\boldsymbol{k})\psi(\boldsymbol{k}) = E\psi(\boldsymbol{k})$$

Tight-Binding coefficients

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

$$H(\boldsymbol{k})\underline{C}^{n\boldsymbol{k}} = \epsilon_{n\boldsymbol{k}}\underline{C}^{n\boldsymbol{k}}$$

$$H(\boldsymbol{k}) \begin{bmatrix} C_{1,1}^{n\boldsymbol{k}} \\ C_{1,2}^{n\boldsymbol{k}} \\ \vdots \\ C_{1,N_o^1}^{n\boldsymbol{k}} \\ C_{2,1}^{n\boldsymbol{k}} \\ \vdots \\ C_{2,N_o^2}^{n\boldsymbol{k}} \\ \vdots \\ C_{N_a,N_o^{N_a}-1}^{n\boldsymbol{k}} \\ C_{N_a,N_o^{N_a}}^{n\boldsymbol{k}} \end{bmatrix} = \epsilon_{n\boldsymbol{k}} \begin{bmatrix} C_{1,1}^{n\boldsymbol{k}} \\ C_{1,2}^{n\boldsymbol{k}} \\ \vdots \\ C_{1,N_o^1}^{n\boldsymbol{k}} \\ C_{2,1}^{n\boldsymbol{k}} \\ \vdots \\ C_{2,N_o^2}^{n\boldsymbol{k}} \\ \vdots \\ C_{N_a,N_o^{N_a}-1}^{n\boldsymbol{k}} \\ C_{N_a,N_o^{N_a}}^{n\boldsymbol{k}} \end{bmatrix}$$

Outline

Polarizability in the TB approximation

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) = \frac{1}{\Omega} \sum_{v,c} \sum_{\boldsymbol{k}} \frac{\langle v, \boldsymbol{k}+\boldsymbol{q}|\, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\, |c, \boldsymbol{k}\rangle \langle c, \boldsymbol{k}+\boldsymbol{q}|\, \mathrm{e}^{-\mathrm{i}(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}}\, |v, \boldsymbol{k}\rangle}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{c,\boldsymbol{k}}} =$$

$$= \frac{1}{\Omega} \sum_{v,c} \sum_{\boldsymbol{k}} \frac{M_{vc}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}) M^*_{vc}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}')}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{c,\boldsymbol{k}}}$$

Polarizability in the TB approximation

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) = \frac{1}{\Omega} \sum_{v,c} \sum_{\boldsymbol{k}} \frac{\langle v, \boldsymbol{k}+\boldsymbol{q}|\, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\, |c, \boldsymbol{k}\rangle \langle c, \boldsymbol{k}+\boldsymbol{q}|\, \mathrm{e}^{-\mathrm{i}(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}}\, |v, \boldsymbol{k}\rangle}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{c,\boldsymbol{k}}} =$$

$$= \frac{1}{\Omega} \sum_{v,c} \sum_{\boldsymbol{k}} \frac{M_{vc}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}) M^*_{vc}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}')}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{c,\boldsymbol{k}}}$$

Point-like orbitals approximation $\phi^*_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)\phi_\beta(\boldsymbol{r} - \boldsymbol{R}' - \boldsymbol{t}_j) \approx \delta_{ij}\delta_{\alpha\beta}\delta_{\boldsymbol{R}\boldsymbol{R}'}\delta(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$:

$$M_{nn'}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}) \equiv \langle n, \boldsymbol{k}+\boldsymbol{q}|\, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\, |n', \boldsymbol{k}\rangle = \int \mathrm{d}\boldsymbol{r}\, \psi^*_{n,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \psi_{n'\boldsymbol{k}}(\boldsymbol{r}) =$$

$$= \sum_{i\alpha} (C_{i\alpha}^{n\boldsymbol{k}+\boldsymbol{q}})^* C_{i\alpha}^{n'\boldsymbol{k}} \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{t}_i} \equiv I^{\boldsymbol{G}}_{n\boldsymbol{k}+\boldsymbol{q},n'\boldsymbol{k}}$$

Polarizability in the TB approximation

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$$

$$\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) = \frac{1}{\Omega} \sum_{v,c} \sum_{\boldsymbol{k}} \frac{\langle v, \boldsymbol{k}+\boldsymbol{q}| \, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \, |c, \boldsymbol{k}\rangle \langle c, \boldsymbol{k}+\boldsymbol{q}| \, \mathrm{e}^{-\mathrm{i}(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}} \, |v, \boldsymbol{k}\rangle}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{c,\boldsymbol{k}}} =$$

$$= \frac{1}{\Omega} \sum_{v,c} \sum_{\boldsymbol{k}} \frac{M_{vc}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}) M^*_{vc}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}')}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{c,\boldsymbol{k}}} = \frac{1}{A_{\mathsf{UC}} N_k} \sum_{vc} \sum_{\boldsymbol{k}} \frac{I^{\boldsymbol{G}}_{v\boldsymbol{k}+\boldsymbol{q},c\boldsymbol{k}} (I^{\boldsymbol{G}'}_{v\boldsymbol{k}+\boldsymbol{q},c\boldsymbol{k}})^*}{\epsilon_{v,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{c,\boldsymbol{k}}}$$

Point-like orbitals approximation $\phi^*_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)\phi_\beta(\boldsymbol{r} - \boldsymbol{R}' - \boldsymbol{t}_j) \approx \delta_{ij}\delta_{\alpha\beta}\delta_{\boldsymbol{R}\boldsymbol{R}'}\delta(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i)$:

$$M_{nn'}(\boldsymbol{k}, \boldsymbol{q}, \boldsymbol{G}) \equiv \langle n, \boldsymbol{k}+\boldsymbol{q}| \, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \, |n', \boldsymbol{k}\rangle = \int \mathrm{d}\boldsymbol{r} \, \psi^*_{n,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \psi_{n'\boldsymbol{k}}(\boldsymbol{r}) =$$

$$= \sum_{i\alpha} (C^{n\boldsymbol{k}+\boldsymbol{q}}_{i\alpha})^* C^{n'\boldsymbol{k}}_{i\alpha} \mathrm{e}^{\mathrm{i}(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{t}_i} \equiv I^{\boldsymbol{G}}_{n\boldsymbol{k}+\boldsymbol{q},n'\boldsymbol{k}}$$

Dielectric function computation scheme

POLIMA

1. Diagonalize $H(\boldsymbol{k})$ and store all $\{\epsilon_{n\boldsymbol{k}}\}$,$\{\underline{C}^{n\boldsymbol{k}}\}$ in a BZ mesh
2. Compute dielectric matrix $\varepsilon_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) = \delta_{\boldsymbol{G}\boldsymbol{G}'} - v_c(\boldsymbol{q}+\boldsymbol{G})\chi^0_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}),\ \forall \boldsymbol{q} \in \mathrm{BZ}$
3. Invert $\varepsilon_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q})\, \forall \boldsymbol{q} \in \mathrm{BZ}$
4. Compute $W_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q}) = \varepsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}) v_c(\boldsymbol{q}+\boldsymbol{G}')\, \forall \boldsymbol{q} \in \mathrm{BZ}$
5. Compute the exciton (details for another time)

Outline

Polarizability convergence

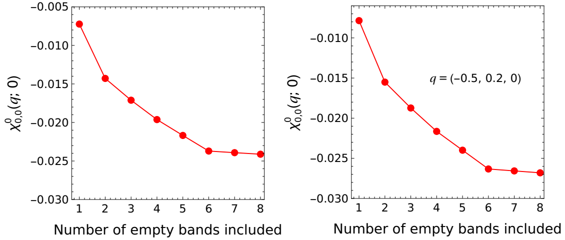


Figure: *MoS_2 tight-binding model by Ridolfi [1].*

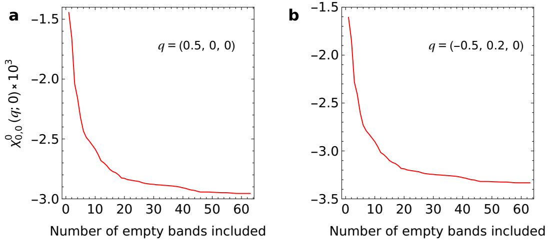


Figure: *hBN, DFT (HSE06 functional) using CRYSTAL [2].*

- [1] E. Ridolfi et al., Journal of Physics: Condensed Matter 27.36 (2015)
- [2] A. Erba et al., Journal of Chemical Theory and Computation 19.20 (2023)

Polarizability convergence: comparing models

POLIMA

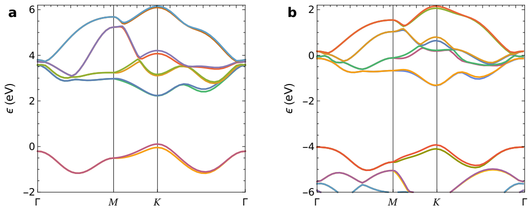


Figure: *MoS_2 bands, **a**-Ridolfi's TB model, **b**-Wannier90 [1].*

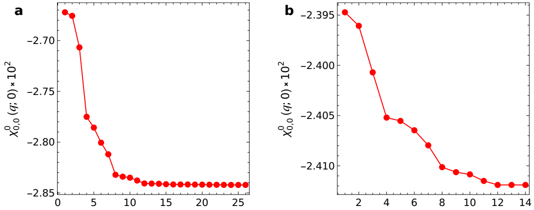


Figure: $\chi_{00}(\boldsymbol{q})$, $\boldsymbol{q} = (0.5, 0)$. *(a->b, b->a)*

Convergence of the polarizability with the number of included valence bands, including all the conduction bands. Different values justified by a different band structure.

- [1] G. Pizzi et al., Journal of Physics: Condensed Matter 32.16 (2020)

Polarizability in the Brillouin Zone

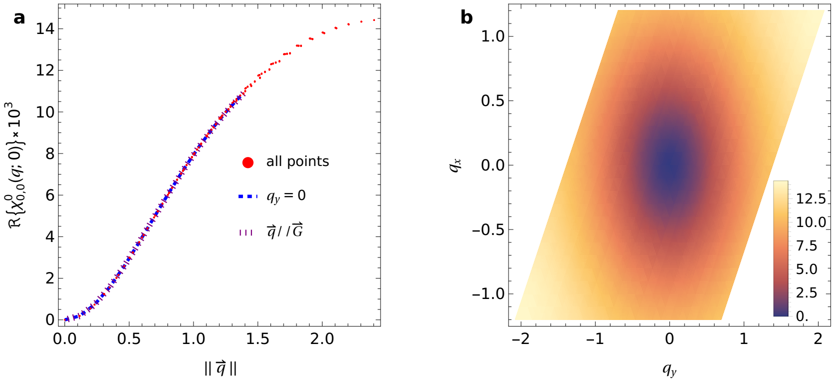


Figure: *Panel* ***a***: $\chi^0_{\mathbf{00}}(\boldsymbol{q})$ *vs.* $|\boldsymbol{q}|$; *Panel* ***b***: $\chi^0_{\mathbf{00}}(\boldsymbol{q})$ *vs.* $\boldsymbol{q} \in$ *BZ. Calculation for hBN, whose bands were obtained within DFT with the HSE06 functional.*

Convergence of the inverse dielectric function

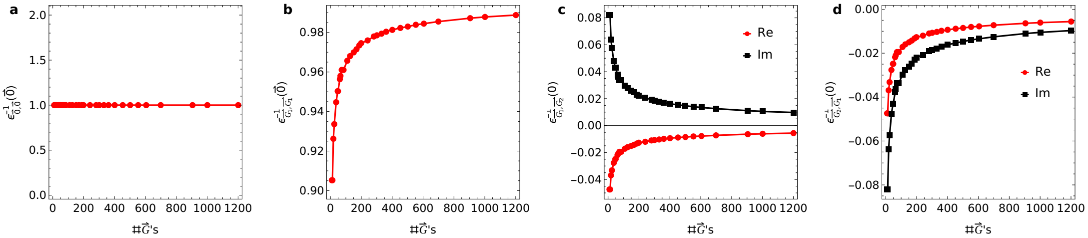


Figure: *Selection of matrix elements $\varepsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{0})$ for MoS_2 using Ridolfi's tight-binding model. All bands included, and with a BZ mesh with 20 momentum points in each direction.* ***a*** $(\boldsymbol{G},\boldsymbol{G}')=(\boldsymbol{0},\boldsymbol{0})$, ***b*** $(\boldsymbol{G},\boldsymbol{G}')=(\boldsymbol{G}_1,\boldsymbol{G}_1)$, ***c*** $(\boldsymbol{G},\boldsymbol{G}')=(\boldsymbol{G}_1,\boldsymbol{G}_2)$, ***d*** $(\boldsymbol{G},\boldsymbol{G}')=(\boldsymbol{G}_2,\boldsymbol{G}_1)$. $\boldsymbol{G}_1=(-1.98835, 1.14797)$*($Å^{-1}$) and* $\boldsymbol{G}_2=-\boldsymbol{G}_1$.

Macroscopic dielectric function

POLIMA

$$\varepsilon_{\mathsf{2D}}(\boldsymbol{q}) \equiv \frac{1}{\varepsilon_{\mathbf{00}}^{-1}(\boldsymbol{q})}$$

$$\varepsilon_{\mathsf{RK}}(\boldsymbol{q}) = 1 + r_0 q$$

Macroscopic dielectric function

$$\varepsilon_{\text{2D}}(\boldsymbol{q}) \equiv \frac{1}{\varepsilon_{\mathbf{00}}^{-1}(\boldsymbol{q})}$$

$$\varepsilon_{\text{RK}}(\boldsymbol{q}) = 1 + r_0 q$$

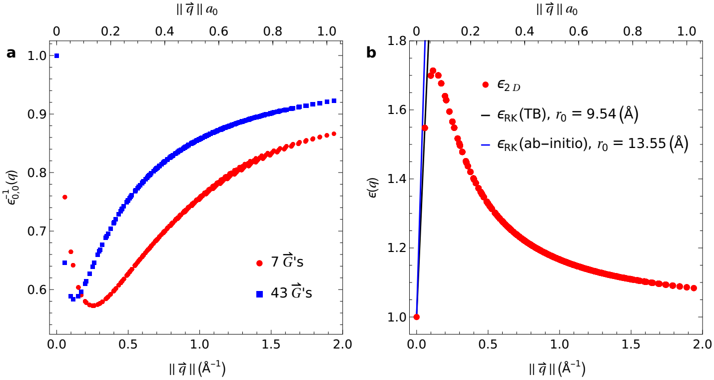


Figure: ***a*** $\varepsilon_{\mathbf{00}}^{-1}(|\boldsymbol{q}|)$ *and* ***b*** $\varepsilon_{2D}(|\boldsymbol{q}|)$. *For MoS_2 using Ridolfi's tight-binding model. In* ***b*** *we display the numerical ε_{2D}, the Rytova-Keldysh dielectric function with an estimated $r_0 \approx 9.54$ Å and with the ab-initio one $r_0 = 13.55$ Å.*

Screened potential

$$v_c(\boldsymbol{q}) = \frac{e^2}{2\varepsilon_0 q}$$

$$V_{\mathsf{RK}}(\boldsymbol{q}) = \frac{e^2}{2\varepsilon_0(1 + r_0 q)q}$$

$$W_{\mathbf{00}}(\boldsymbol{q}) = \varepsilon^{-1}_{\mathbf{00}}(\boldsymbol{q}) v_c(\boldsymbol{q})$$

Screened potential

$$v_c(\boldsymbol{q}) = \frac{e^2}{2\varepsilon_0 q} \text{ (black dots)}$$

$$V_{\mathsf{RK}}(\boldsymbol{q}) = \frac{e^2}{2\varepsilon_0(1 + r_0 q)q} \text{ (blue dots)}$$

$$W_{\mathbf{00}}(\boldsymbol{q}) = \varepsilon^{-1}_{\mathbf{00}}(\boldsymbol{q})v_c(\boldsymbol{q}) \text{ (red dots)}$$

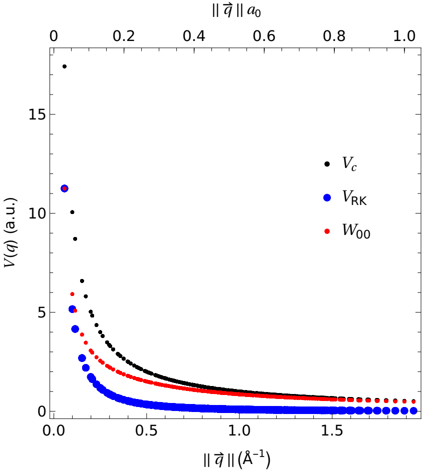


Figure: *Bare and screened potentials for MoS_2 using Ridolfi's TB model. 43 $\boldsymbol{G}$s included.*

Screened potential

$$v_c(\boldsymbol{q}) = \frac{e^2}{2\varepsilon_0 q} \text{ (black dots)}$$

$$V_{\mathsf{RK}}(\boldsymbol{q}) = \frac{e^2}{2\varepsilon_0(1+r_0 q)q} \text{ (blue dots)}$$

$$W_{\mathbf{00}}(\boldsymbol{q}) = \varepsilon^{-1}_{\mathbf{00}}(\boldsymbol{q}) v_c(\boldsymbol{q}) \text{ (red dots)}$$

- $W_{\mathbf{00}}(\boldsymbol{q}) \xrightarrow{q \nearrow} v_c(\boldsymbol{q})$
- RK approx. overestimates screening

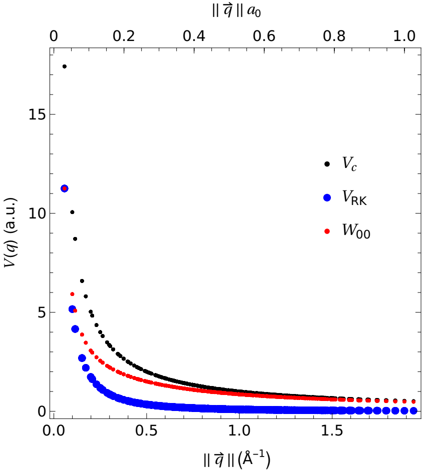


Figure: *Bare and screened potentials for MoS_2 using Ridolfi's TB model. 43 $\mathbf{G}$s included.*

A use case: excitons in MoS_2

Please consult: Alejandro José Uría-Álvarez et al. "Efficient computation of optical excitations in 2D materials with the Xatu code", Computer Physics Communications 295 (2024)

State	Energy (RK) (eV)	B. energy (RK) (eV)	Energy ($\varepsilon_{G,G'}$) (eV)	B. energy ($\varepsilon_{G,G'}$) (eV)
1a	1.15051	-0.96949	0.858549	-1.261451
1b			0.858551	-1.261449
2a	1.187938	-0.932062	0.900934	-1.219066
2b			0.900936	-1.219064
3a	1.266467	-0.853533	0.971518	-1.148482
3b			0.971520	-1.14848
4a	1.305554	-0.814446	1.015683	-1.104317
4b			1.015685	-1.104315

Table: *Exciton spectrum of MoS_2 described by Ridolfi's tight-binding model, using the Rytova-Keldysh potential and the computed inverse dielectric matrix to compute the interaction matrix elements, at the left and right, respectively.* $N_k = 40^2$, $N_c = N_v = 2$ *for the exciton,* $N_G = 43$. *Excludes the exchange interaction term in both approaches to screening.*

Outline

Revisiting Dyson's equation

$$\chi_0(\boldsymbol{r},\boldsymbol{r}';\omega) = \sum_{v\boldsymbol{k},c\boldsymbol{k}'} \left[\frac{\psi_{c\boldsymbol{k}'}(\boldsymbol{r})\psi^*_{v\boldsymbol{k}}(\boldsymbol{r})\psi_{v\boldsymbol{k}}(\boldsymbol{r}')\psi^*_{c\boldsymbol{k}'}(\boldsymbol{r}')}{\hbar\omega - (\epsilon_{c\boldsymbol{k}'} - \epsilon_{v\boldsymbol{k}}) + \mathrm{i}\hbar\alpha} - \frac{\psi_{v\boldsymbol{k}}(\boldsymbol{r})\psi^*_{c\boldsymbol{k}'}(\boldsymbol{r})\psi_{c\boldsymbol{k}'}(\boldsymbol{r}')\psi^*_{v\boldsymbol{k}}(\boldsymbol{r}')}{\hbar\omega + (\epsilon_{c\boldsymbol{k}'} - \epsilon_{v\boldsymbol{k}}) + \mathrm{i}\hbar\alpha} \right].$$

$$W(\boldsymbol{r},\boldsymbol{r}') = \int \mathrm{d}\boldsymbol{r}'' \varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'')v_c(\boldsymbol{r}'',\boldsymbol{r}') = v_c(\boldsymbol{r},\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{y}\, v_c(\boldsymbol{r},\boldsymbol{x})\chi_0(\boldsymbol{x},\boldsymbol{y})W(\boldsymbol{y},\boldsymbol{r}')$$

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{i\alpha} C^{n\boldsymbol{k}}_{i\alpha} \phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{t}_i),$$

Revisiting Dyson's equation

In the continuum

$$W(\boldsymbol{r},\boldsymbol{r}') = \int \mathrm{d}\boldsymbol{r}''\varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'')v_c(\boldsymbol{r}'',\boldsymbol{r}') = v_c(\boldsymbol{r},\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{x}\int \mathrm{d}\boldsymbol{y}\, v_c(\boldsymbol{r},\boldsymbol{x})\chi_0(\boldsymbol{x},\boldsymbol{y})W(\boldsymbol{y},\boldsymbol{r}')$$

Discretized version, in the point-like orbital approximation

$$W(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) = v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) + \sum_{i',\boldsymbol{R}_1}^{\boldsymbol{R}_1+\boldsymbol{t}_{i'}\neq\boldsymbol{R}+\boldsymbol{t}_i} v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{R}_1+\boldsymbol{t}_{i'}) \sum_{j',\boldsymbol{R}''}^{\boldsymbol{R}''+\boldsymbol{t}_{j'}\neq\boldsymbol{t}_j} \mathcal{T}^{i',j'}_{\boldsymbol{R}_1,\boldsymbol{R}''} W(\boldsymbol{R}''+\boldsymbol{t}_{j'},\boldsymbol{t}_j)$$

$$\mathcal{T}^{i,j}_{\boldsymbol{R},\boldsymbol{R}'} \equiv \frac{1}{N^2}\sum_{v\boldsymbol{k},c\boldsymbol{k}'}\sum_{\alpha\beta}\frac{-2\,\mathrm{Re}\left\{(C^{c\boldsymbol{k}'}_{i\alpha})^* C^{v\boldsymbol{k}}_{i\alpha}(C^{v\boldsymbol{k}}_{j\beta})^* C^{c\boldsymbol{k}'}_{j\beta}\,\mathrm{e}^{-\mathrm{i}(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{R}-\boldsymbol{R}')}\right\}}{\epsilon_{c\boldsymbol{k}'}-\epsilon_{v\boldsymbol{k}}}$$

Screened potential in real space

$$W(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) = v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) + \sum_{i',\boldsymbol{R}_1}^{\boldsymbol{R}_1+\boldsymbol{t}_{i'}\neq\boldsymbol{R}+\boldsymbol{t}_i} v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{R}_1+\boldsymbol{t}_{i'}) \sum_{j',\boldsymbol{R}''}^{\boldsymbol{R}''+\boldsymbol{t}_{j'}\neq\boldsymbol{t}_j} \mathcal{T}^{i',j'}_{\boldsymbol{R}_1,\boldsymbol{R}''} W(\boldsymbol{R}''+\boldsymbol{t}_{j'},\boldsymbol{t}_j)$$

is equivalent to

$$W(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) - \sum_{j',\boldsymbol{R}''}^{\boldsymbol{R}''+\boldsymbol{t}_{j'}\neq\boldsymbol{t}_j} \left[\sum_{i',\boldsymbol{R}_1}^{\boldsymbol{R}_1+\boldsymbol{t}_{i'}\neq\boldsymbol{R}+\boldsymbol{t}_i} v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{R}_1+\boldsymbol{t}_{i'})\mathcal{T}^{i',j'}_{\boldsymbol{R}_1,\boldsymbol{R}''}\right] W(\boldsymbol{R}''+\boldsymbol{t}_{j'},\boldsymbol{t}_j) = v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j)$$

System of linear equations, however....

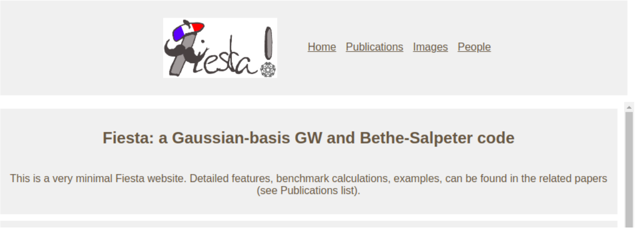
- $W(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) > 0$ sometimes, $W(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) < 0$ other times;
- Situation improves including the term $\boldsymbol{R}_1+\boldsymbol{t}_{i'} = \boldsymbol{R}+\boldsymbol{t}_i$, but result is regularization dependent.

Screened potential in real space: what to do?

POLIMA

- Look at what chemists do.
- Self-consistent approach?

$$W(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j) =$$
$$v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{t}_j)+\sum_{i',\boldsymbol{R}_1}^{\boldsymbol{R}_1+\boldsymbol{t}_{i'}\neq\boldsymbol{R}+\boldsymbol{t}_i} v_c(\boldsymbol{R}+\boldsymbol{t}_i,\boldsymbol{R}_1+\boldsymbol{t}_{i'})\sum_{j',\boldsymbol{R}''}^{\boldsymbol{R}''+\boldsymbol{t}_{j'}\neq\boldsymbol{t}_j}\mathcal{T}^{i',j'}_{\boldsymbol{R}_1,\boldsymbol{R}''}v_c(\boldsymbol{R}''+\boldsymbol{t}_{j'},\boldsymbol{t}_j)+\ldots.$$



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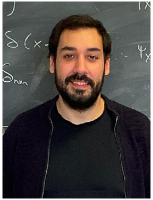
Juan José Palácios

Alex



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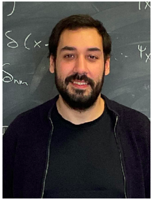
Alex Juanjo Manuel António



Simran David

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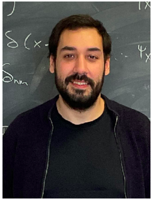

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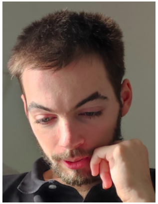

Acknowledgments

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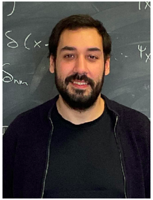

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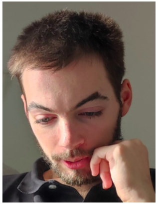

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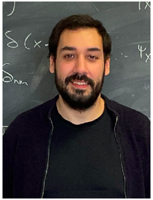

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