QUANTUM ESPRESSO FOUNDATION

density-functional perturbation theory

response functions, phonons, plasmons, magnons, and all that

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the Abdus Salam International Centre for Theoretical Physics, Trieste, June 1-12, 2026

disclaimer

AI for theory and methodological development

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- AI may be an excellent sparring partner to develop your own ideas. Pros: it takes you seriously and it may be easier to admit your ignorance to it than to a colleague/supervisor; Cons: it tends to be sycophantic (by design, I suspect). Beware of its responses, and keep challenging them.

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- It codes better than most and faster than all.

response functions

$$\text{property} = \frac{\partial(\text{variable})}{\partial(\text{strength})}$$

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☛ polarizability, dielectric constant $\quad \dfrac{\partial \mathsf{P}_i}{\partial \mathsf{E}_j}$

☛ elastic constants $\quad \dfrac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}$

☛ piezoelectric constants $\quad \dfrac{\partial \mathsf{P}_i}{\partial \epsilon_{kl}}$

☛ interatomic force constants $\quad \dfrac{\partial f_i^s}{\partial u_j^t}$

☛ Born effective charges $\quad \dfrac{\partial d_i^s}{\partial u_j^s}$

☛ $\cdots$ $\quad \cdots$

MA PER SEGUIR VIRTUTE E CANOSCENZA

the Hellmann-Feynman theorem

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(\hat{\boldsymbol{r}} - \boldsymbol{R}) - e\boldsymbol{E} \cdot \hat{\boldsymbol{r}}$$

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λ: atomic positions ($\boldsymbol{R}$), strength of a field ($\boldsymbol{E}$), electron mass (m) ...

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$$\boxed{\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda}$$

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$$\hat{H}_\lambda = \hat{H}_0 + \underbrace{\lambda \hat{H}_0' + \frac{1}{2}\lambda^2 \hat{H}_0'' + \cdots}_{\Delta \hat{H}_\lambda}$$

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$$E_0' = \frac{d}{d\lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle \Big|_{\lambda=0}$$

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$$E'_0 = \left. \frac{d}{d\lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle \right|_{\lambda=0}$$

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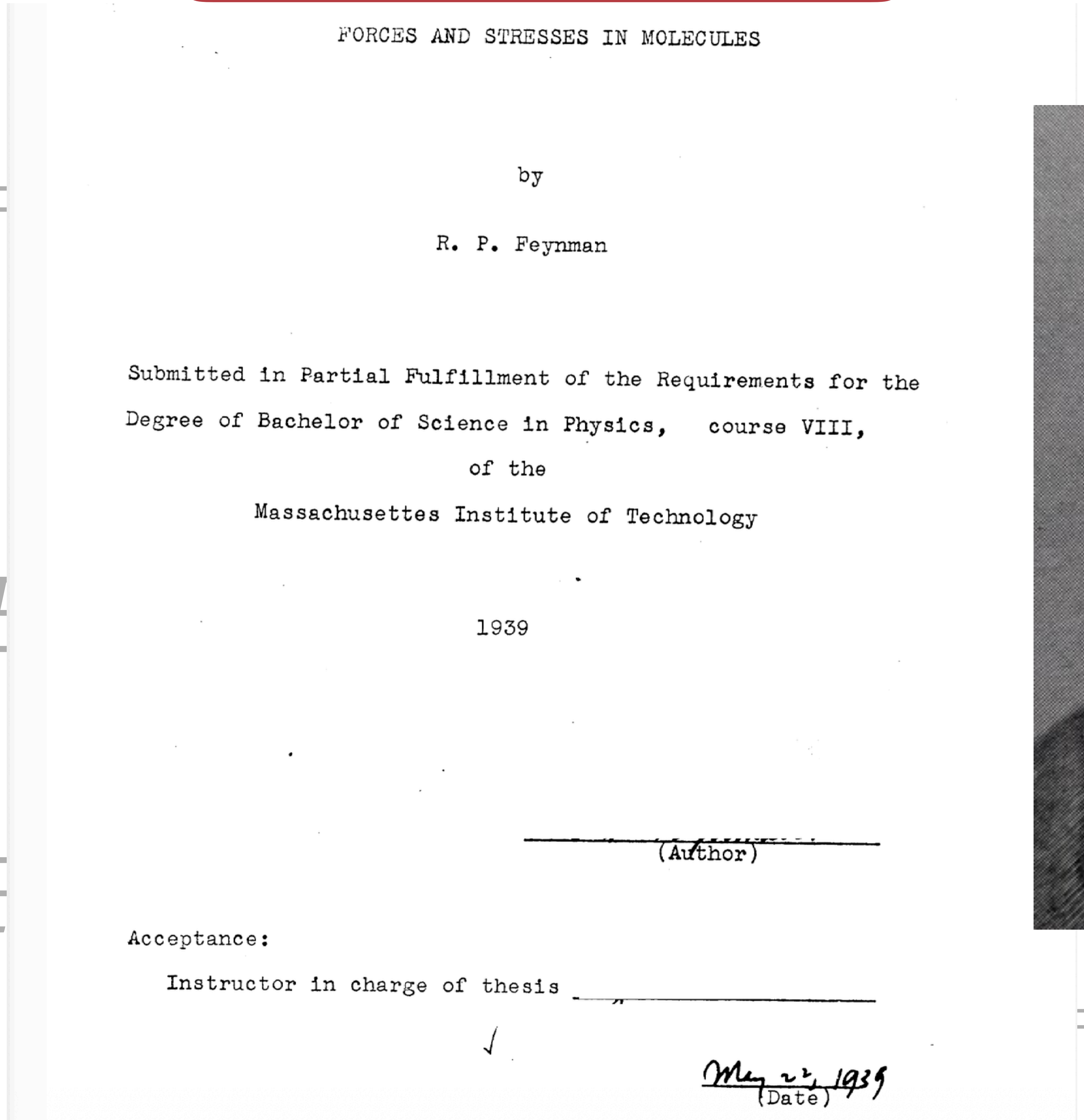


FORCES AND STRESSES IN MOLECULES

by

R. P. Feynman

Submitted in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in Physics, course VIII, of the Massachusettes Institute of Technology

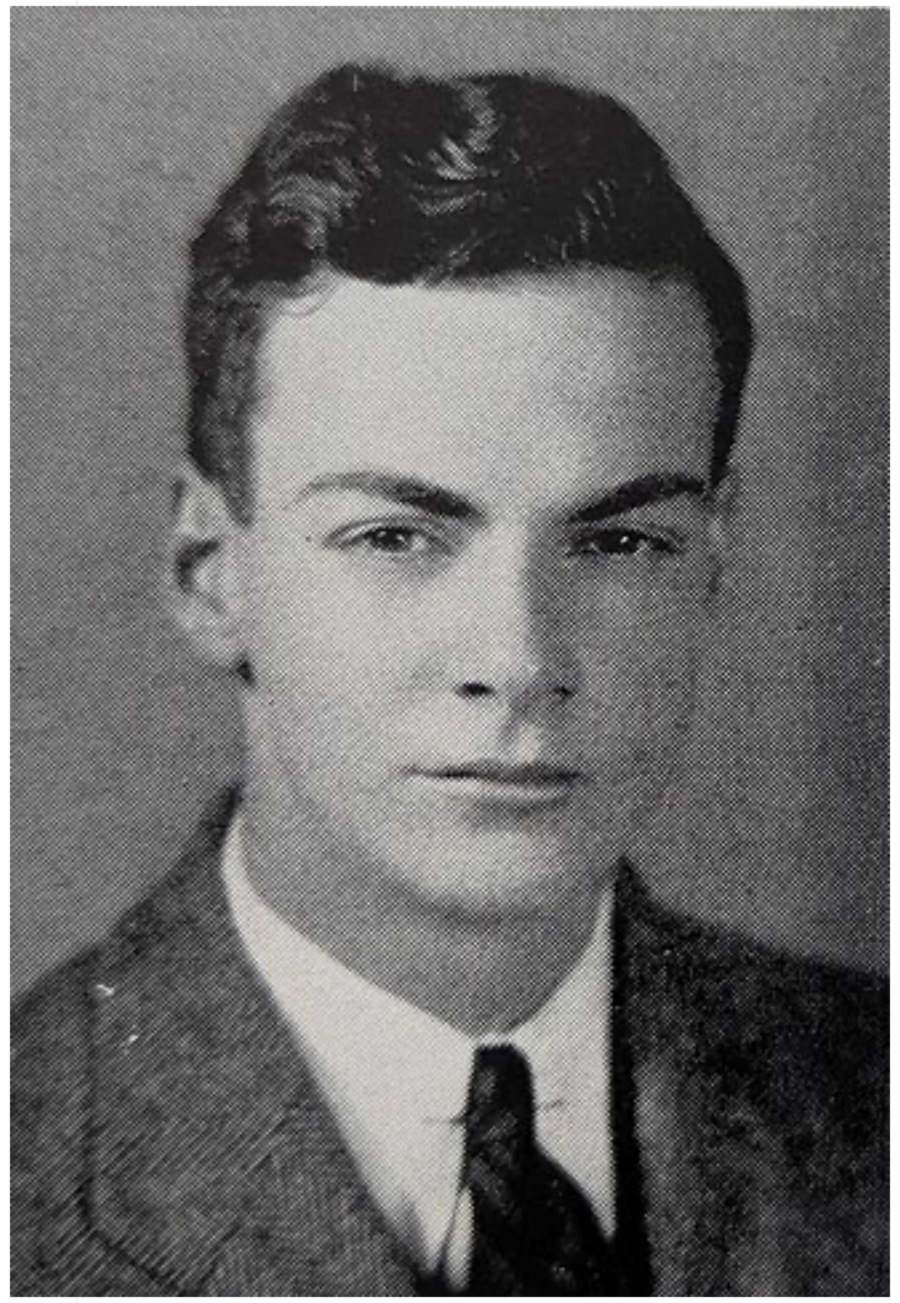
1939

(Author)

Acceptance:

Instructor in charge of thesis

May 22, 1939
(Date)



aged 21

$$\boxed{E_0' = \langle \Psi_0 | \hat{H}_0' | \psi_0 \rangle}$$

the Hellmann-Feynman theorem: what about DFT?

$$E_\lambda = \min_{\left\{n(\mathbf{r}):\, \int n(\mathbf{r})d\mathbf{r}=N\right\}} \left[F[n] + \int n(\mathbf{r})V_\lambda(\mathbf{r})d\mathbf{r}\right]$$

no quantum mechanics, no (obvious) perturbation theory

what then?

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$$g(\lambda) = \min_x G[x, \lambda]$$

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$$\boxed{\left.\frac{\partial G}{\partial x}\right|_{x=x(\lambda)} = 0}$$

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$$\boxed{E'_\lambda = \int n_\lambda(\mathbf{r}) V'_\lambda(\mathbf{r}) d\mathbf{r}}$$

food for thoughts

$$\boxed{E'_\lambda = \int n_\lambda(\boldsymbol{r}) V'_\lambda(\boldsymbol{r}) d\boldsymbol{r}}$$

- $$\frac{\partial V_\lambda(\boldsymbol{r})}{\partial \lambda} \mapsto \frac{\partial E_\lambda}{\partial \lambda}$$

- $$\frac{\partial V_\lambda^{SCF}(\boldsymbol{r})}{\partial \lambda} \mapsto ???$$

the “2n+1” theorem

$$\Phi = \Phi_0 + \mathcal{O}(\epsilon) \Rightarrow E = E_0 + \mathcal{O}(\epsilon^2)$$

$$\Phi = \Phi_0 + \underbrace{\sum_{l=1}^{n} \lambda^l \Phi^{(l)}}_{\Phi'}$$

the "2n+1" theorem

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$$E = \frac{\langle \Phi_0 + \Phi' | (H_0 + V') | \Phi_0 + \Phi' \rangle}{\langle \Phi_0 + \Phi' | \Phi_0 + \Phi' \rangle} + \mathcal{O}(V'^4)$$

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$$\boxed{E^{(3)} = \langle \Phi' | V' | \Phi' \rangle - \langle \Phi' | \Phi' \rangle \langle \Phi_0 | V' | \Phi_0 \rangle}$$

Dalgarno & Stewart (1956); generalization to DFT: Gonze & Vigneron (1989)

susceptibilities as energy derivatives

$$\hat{H}_\alpha = \hat{H}^\circ + \alpha \hat{A}$$

$$\chi_{BA} = \frac{\partial \langle \hat{B} \rangle_\alpha}{\partial \alpha}$$

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$$\hat{H}_\beta = \hat{H}^\circ + \beta \hat{B}$$

susceptibilities as energy derivatives

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$$\chi_{BA} = \frac{\partial\langle\hat{B}\rangle_\alpha}{\partial\alpha}$$

$$\langle\hat{B}\rangle = \frac{\partial E_\beta}{\partial\beta}$$ (Hellmann & Feynman)

$$\hat{H}_\beta = \hat{H}^\circ + \beta\hat{B}$$

$$\boxed{\chi_{BA} = \frac{\partial^2 E_{\alpha\beta}}{\partial\alpha\partial\beta}}$$

$$\hat{H}_{\alpha\beta} = \hat{H}^\circ + \alpha\hat{A} + \beta\hat{B}$$

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☛ structural optimization & molecular dynamics

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- ☛ structural optimization & molecular dynamics
- ☛ (static) response functions
  - elastic constants
  - dielectric tensor
  - piezoelectric tensor
  - ...
- ☛ vibrational modes in the adiabatic approximation
  - interatomic force constants
  - Born effective charges
  - ...

energy derivatives from perturbation theory

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energy derivatives from perturbation theory

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density-functional perturbation theory

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$$\boxed{\frac{\partial^2 E(\lambda)}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_j} v_i(\mathbf{r}) d\mathbf{r}}$$ DFPT

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$n'(\mathbf{r}) = 2\mathrm{Re} \sum_v \phi_v^{\circ *}(\mathbf{r}) \phi'_v(\mathbf{r})$$

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$$\boxed{\left(H^\circ - \epsilon_v^\circ\right) \bar{\phi}'_v = -P_c V' \phi_v^\circ}$$

calculating the response

$$n'(\mathbf{r}) = 2\mathrm{Re}\sum_v \phi_v^{\circ *}(\mathbf{r})\phi'_v(\mathbf{r})$$

$$\boxed{(H^\circ - \epsilon_v^\circ)\bar{\phi}'_v = -P_c V' \phi_v^\circ}$$

DFPT: the equations

DFT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$\left(-\Delta + V_{SCF}(\mathbf{r})\right)\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})$$

DFPT: the equations

DFT

DFPT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$V'(\mathbf{r}) \leftrightarrows n'(\mathbf{r})$$

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$$V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r})$$

$$n'(\mathbf{r}) = 2\ \mathrm{Re} \sum_{\epsilon_v < E_F} \phi^*_v(\mathbf{r})\phi'_v(\mathbf{r})$$

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SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

DFPT: the batch representation

$$\left(-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v\right)\phi'_v(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r})\phi_v(\mathbf{r})$$

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$n'(\boldsymbol{r})$ is a linear functional of $\{\phi_v'(\boldsymbol{r})\}$ ⇒ $V_{HXC}'(\boldsymbol{r})$ is also a linear functional of $\{\phi_v'(\boldsymbol{r})\}$

DFPT: the batch representation

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$n'(\boldsymbol{r})$ is a linear functional of $\{\phi_v{}'(\boldsymbol{r})\}$ ⇒ $V_{HXC}{}'(\boldsymbol{r})$ is also a linear functional of $\{\phi_v{}'(\boldsymbol{r})\}$

$$(\mathcal{D}+\mathcal{K})\{\phi'_v\} = -\{\hat{P}_c V'_{ext}\phi^\circ_v\}$$

$$\mathcal{D}\{\phi'_v\} = \left\{\left(\hat{H}^\circ - \epsilon_v\right)\phi'_v\right\}$$

$$\mathcal{K}\{\phi'_v\} = \left\{4\phi^\circ_v(\boldsymbol{r})\sum_{v'}\int d\boldsymbol{r}'\left(\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + \kappa_{XC}(\boldsymbol{r},\boldsymbol{r}')\right)\phi^\circ_{v'}(\boldsymbol{r}')\phi'_{v'}(\boldsymbol{r}')\right\}$$

Baroni & Giannozzi (1994); Gonze (1995); Rocca, Gebauer, Saad & Baroni (2008)

variational perturbation theory

$$E = \min_{\langle\Psi|\Psi\rangle=1} \langle\Psi|\hat{H}|\Psi\rangle$$

$$\delta\Big[\langle\Psi|\hat{H}|\Psi\rangle - \Lambda(\langle\Psi|\Psi\rangle - 1)\Big] = 0 \Longrightarrow \left\{ \begin{array}{cl} \hat{H}\Psi & = \Lambda\Psi \\ E & = \Lambda \end{array} \right.$$

variational perturbation theory

$$E = \min_{\langle\Psi|\Psi\rangle=1} \langle\Psi|\hat{H}|\Psi\rangle$$

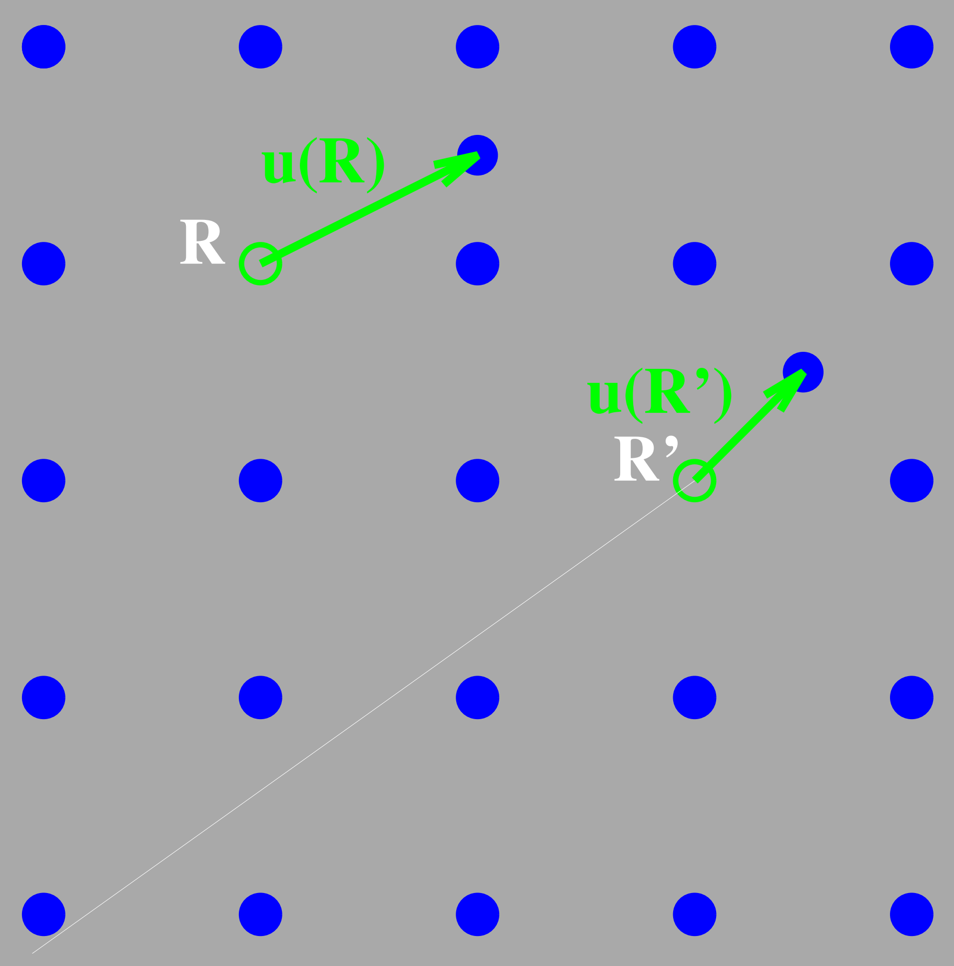
$$\delta\left[\langle\Psi|\hat{H}|\Psi\rangle - \Lambda(\langle\Psi|\Psi\rangle - 1)\right] = 0 \implies \left\{ \begin{array}{ll} \hat{H}\Psi & = \Lambda\Psi \\ E & = \Lambda \end{array} \right.$$

Set $\left\{ \begin{array}{ll} \hat{H} & = \hat{H}^\circ + \hat{H}' \\ \Psi & = \Psi^\circ + \Psi' \\ \Lambda & = \Lambda^\circ + \Lambda' \end{array} \right.$ and neglect terms $o\left(\hat{H}'^2\right)$. Variation with respect to Ψ' and Λ' gives

$$\left(\hat{H}^\circ - E^\circ\right)\Psi' = -\left(\hat{H}' - \Lambda'\right)\Psi^\circ \implies \left\{ \begin{array}{rl} E' = \Lambda' & = \langle\Psi^\circ|\hat{H}'|\Psi^\circ\rangle \\ \left(\hat{H}^\circ - E^\circ\right)\Psi' & = -\left(\hat{H}' - E'\right)\Psi^\circ \\ & = -\hat{Q}^\circ\hat{H}'\Psi^\circ \\ E'' & = \langle\Psi^\circ|\hat{H}'|\Psi'\rangle \end{array} \right.$$

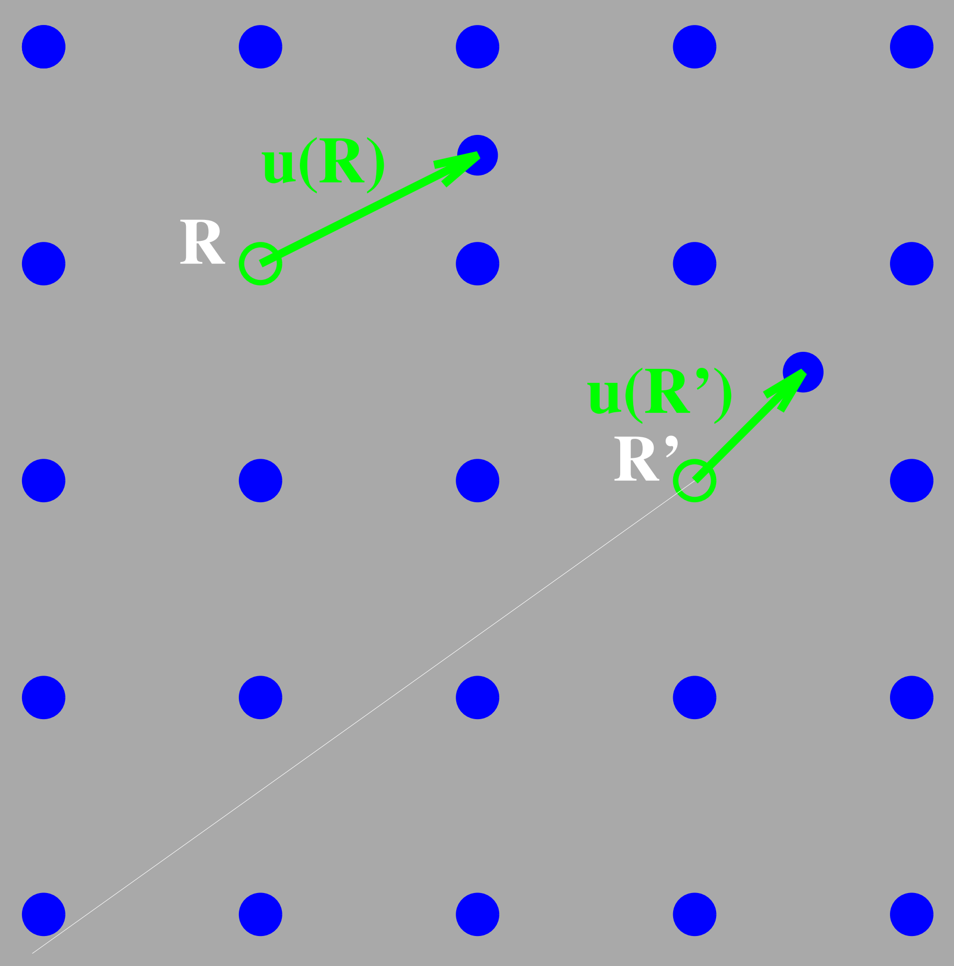
Dalgarno & Lewis (1956); extension to DFT, Gonze (1995) simulating atomic vibrations …

lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

lattice dynamics



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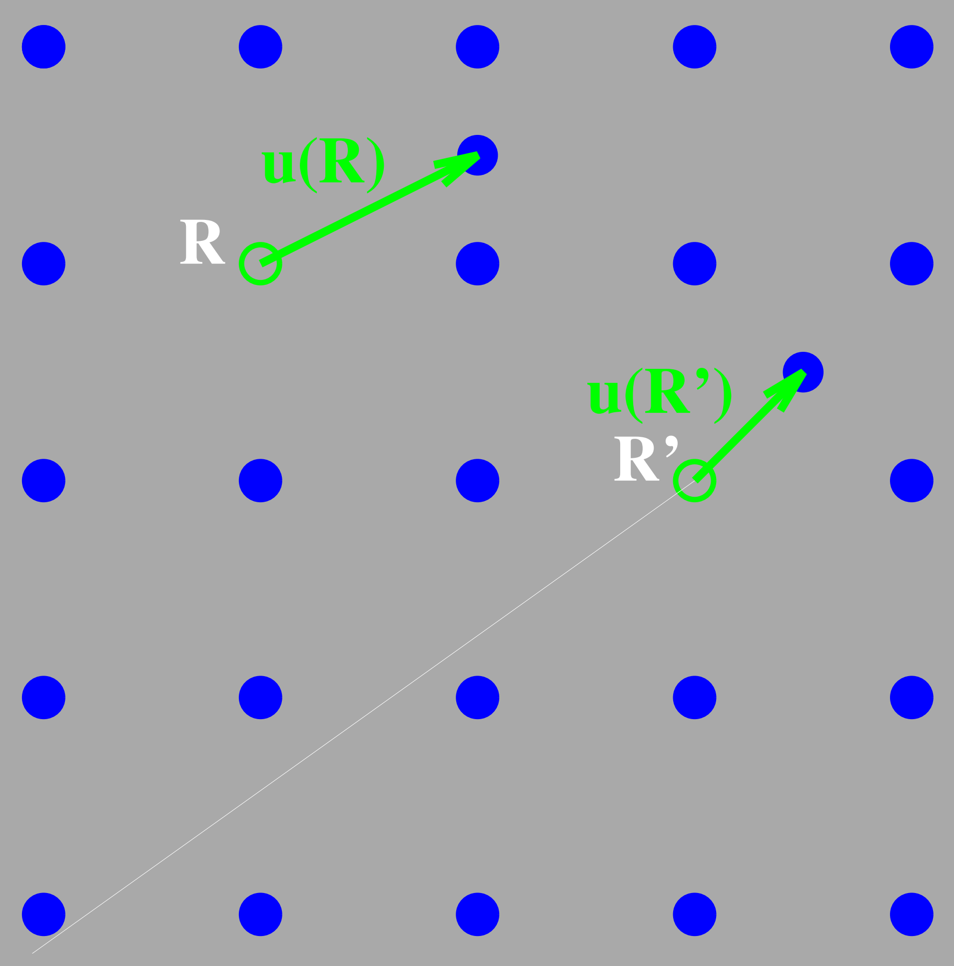
$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

$$+ \cdots$$

lattice dynamics



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$$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$$

$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

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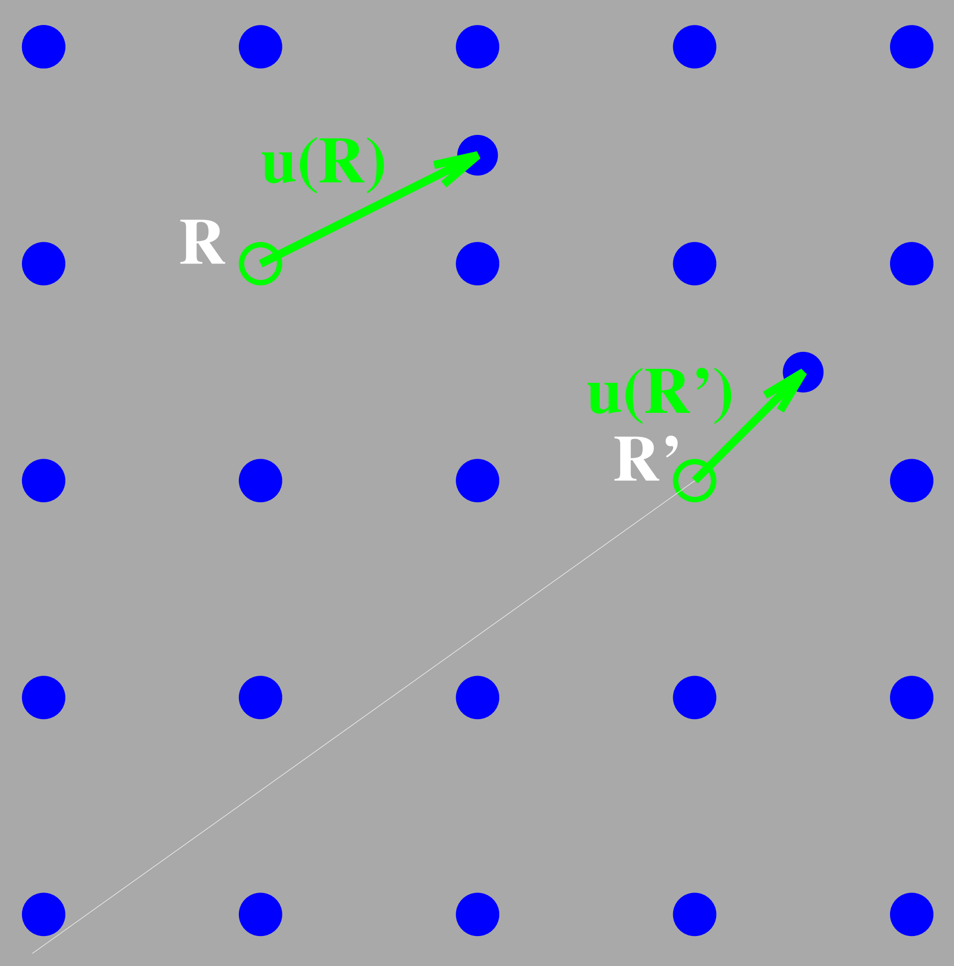

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DFT

DPFT

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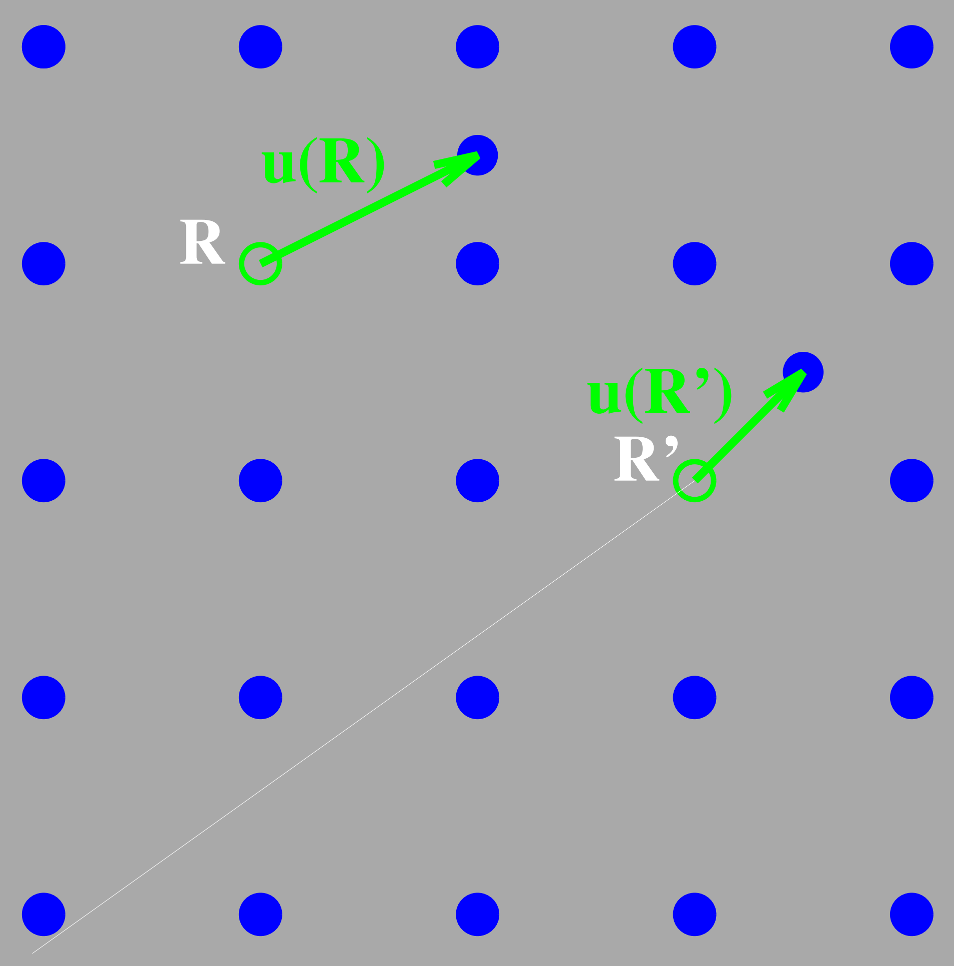
$$+ \cdots$$

lattice dynamics



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DFT

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$$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$$

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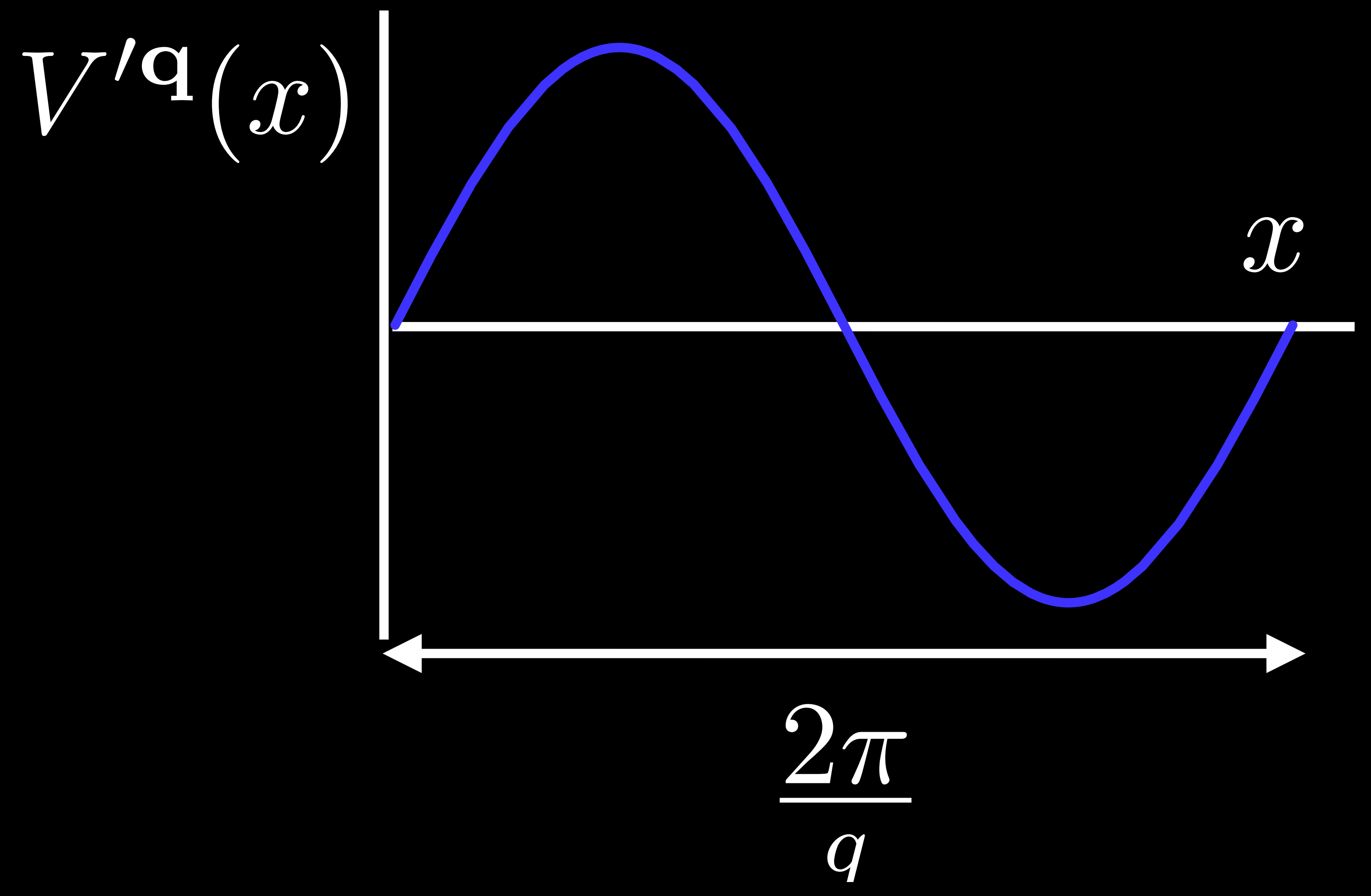
$$+ \cdots$$

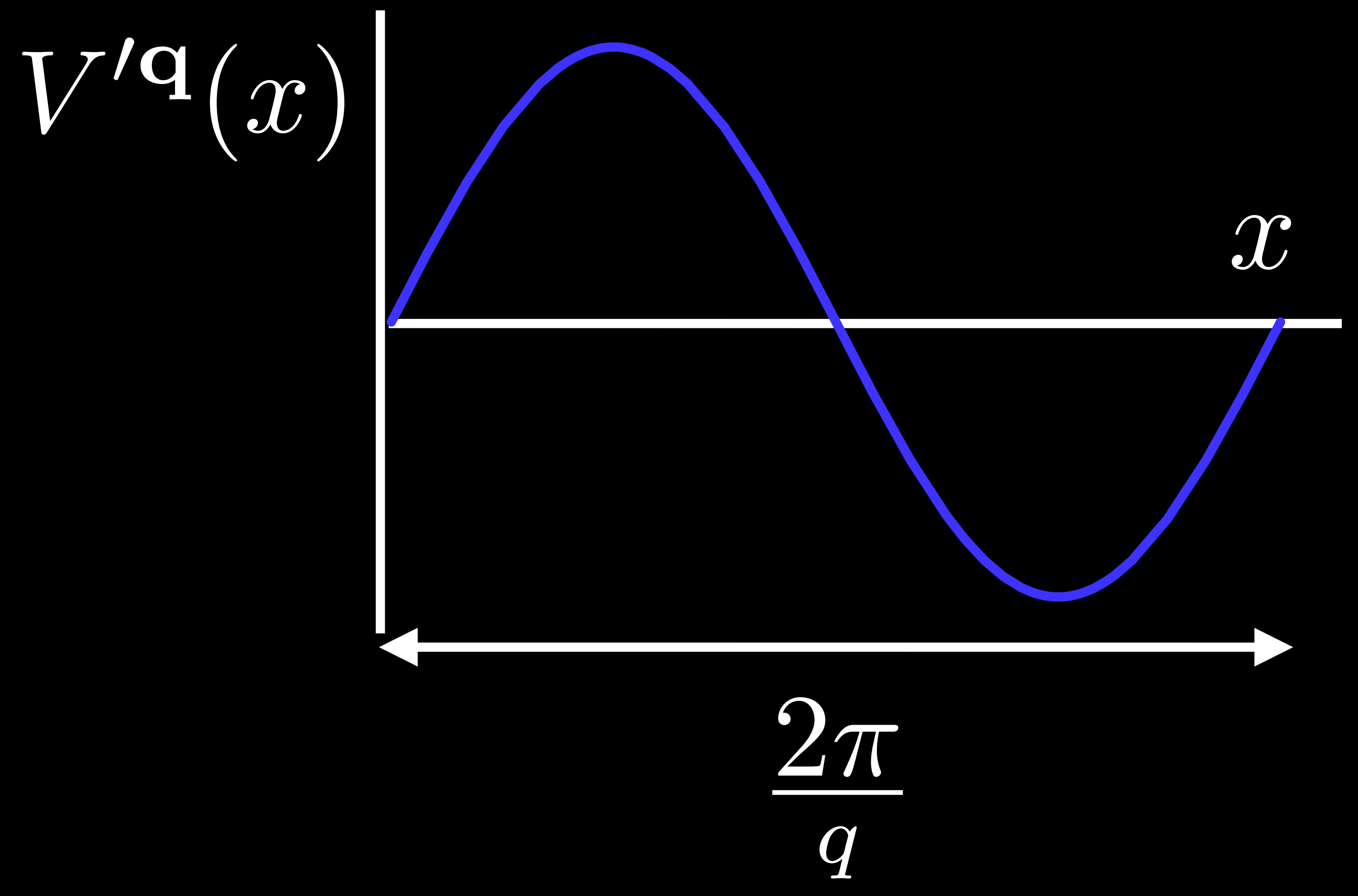
$$\det \left[\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} - \omega^2 M(\mathbf{R}) \delta_{\mathbf{R},\mathbf{R}'} \right] = 0$$

monochromatic perturbations



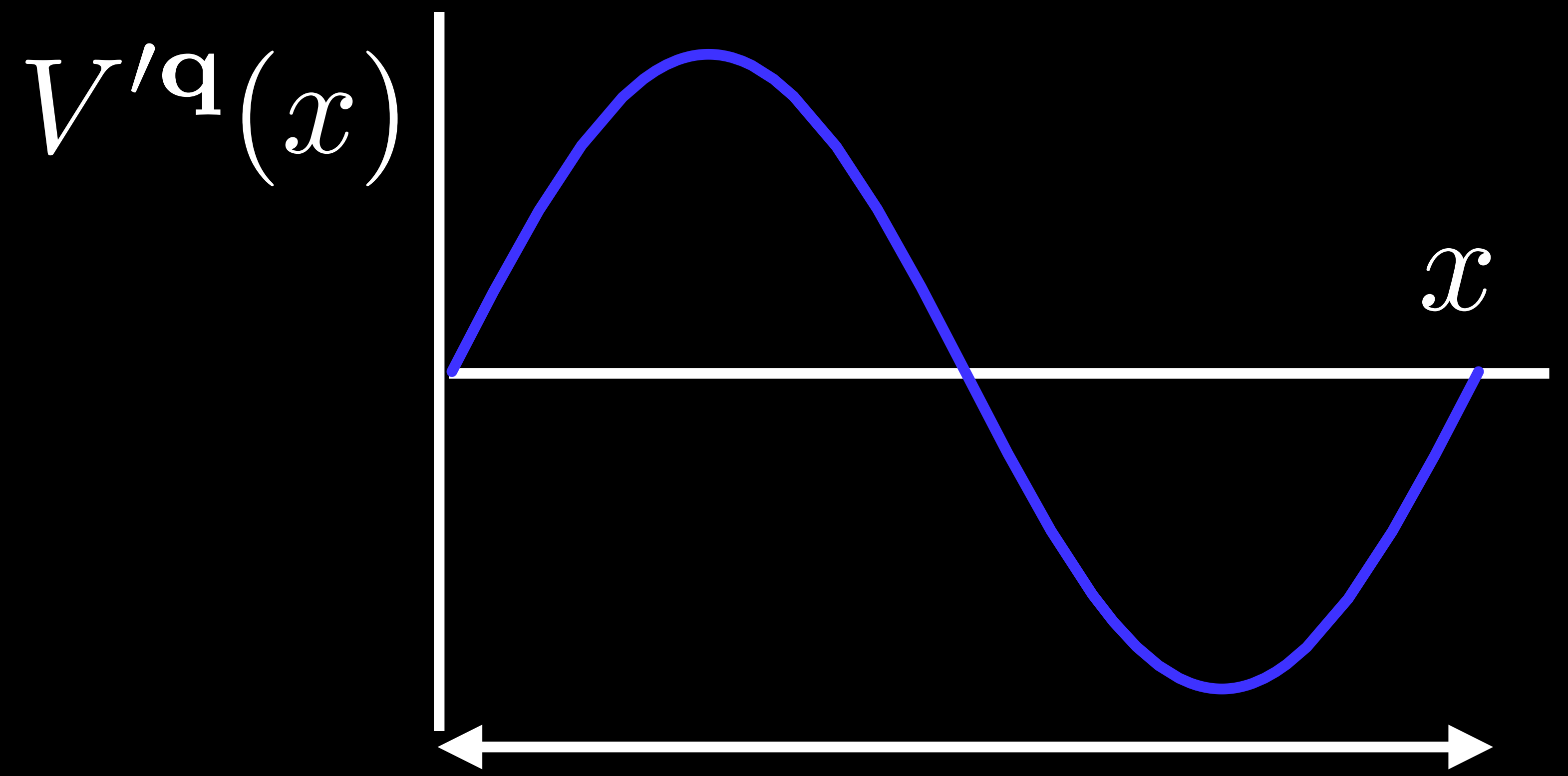
DFPT rhs: $-P_c V'^{\mathbf{q}}_{SCF} \phi^{\mathbf{k}}_v(\mathbf{r})$

monochromatic perturbations



$$\left(H_0 - \epsilon_v^{\mathbf{k}}\right)\phi_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r}) = -P_c V_{SCF}'^{\mathbf{q}} \phi_v^{\mathbf{k}}(\mathbf{r})$$

monochromatic perturbations

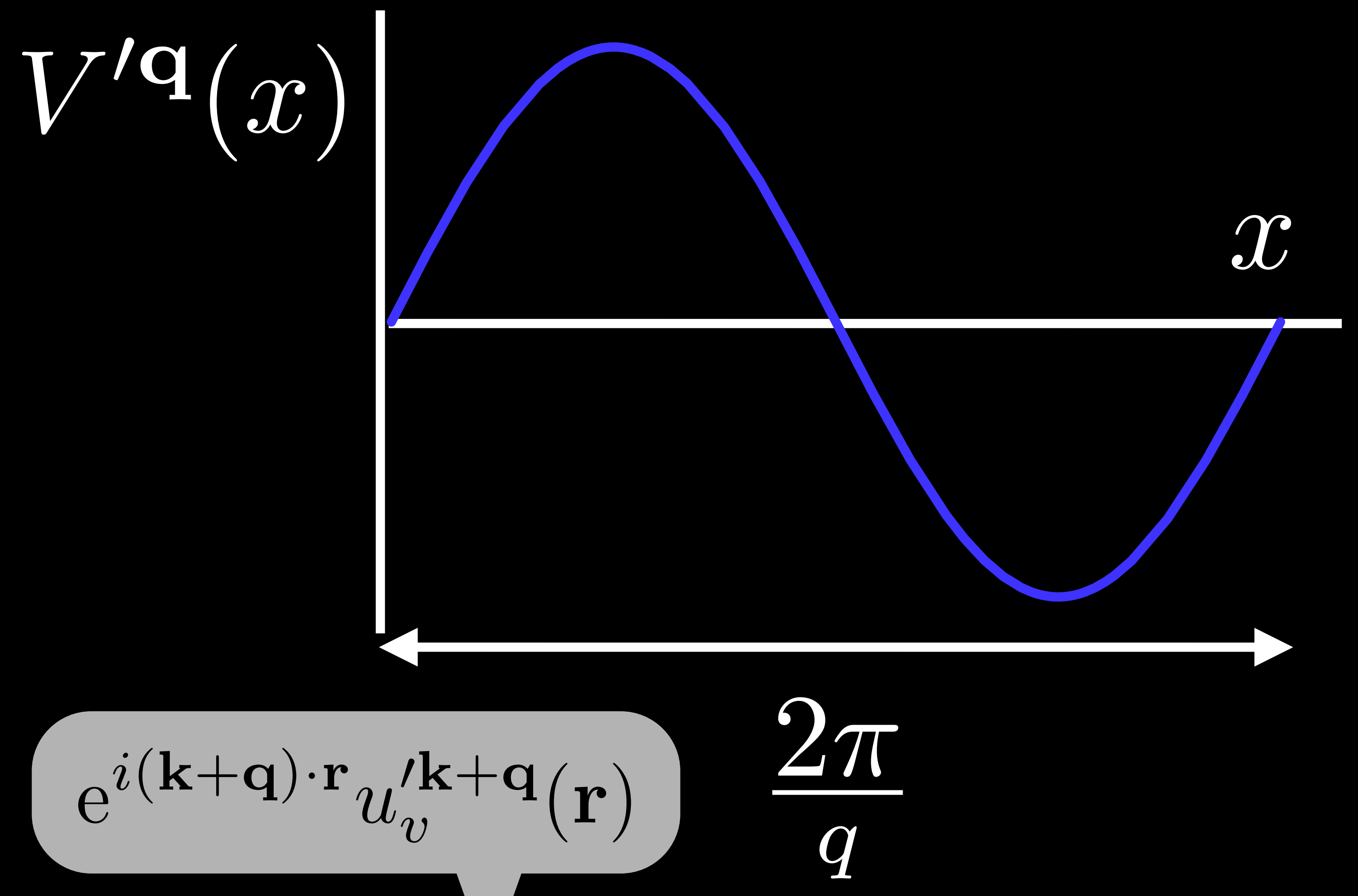


$$\frac{2\pi}{q}$$

$e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}u'^{\mathbf{k}+\mathbf{q}}_v(\mathbf{r})$ $\qquad$ $e^{i\mathbf{k}\cdot\mathbf{r}}u^{\circ\mathbf{k}}_v(\mathbf{r})$

$$\left(H_0-\epsilon^{\mathbf{k}}_v\right)\phi'^{\mathbf{k}+\mathbf{q}}_v(\mathbf{r}) = -P_c V'^{\mathbf{q}}_{SCF}\phi^{\mathbf{k}}_v(\mathbf{r})$$

monochromatic perturbations



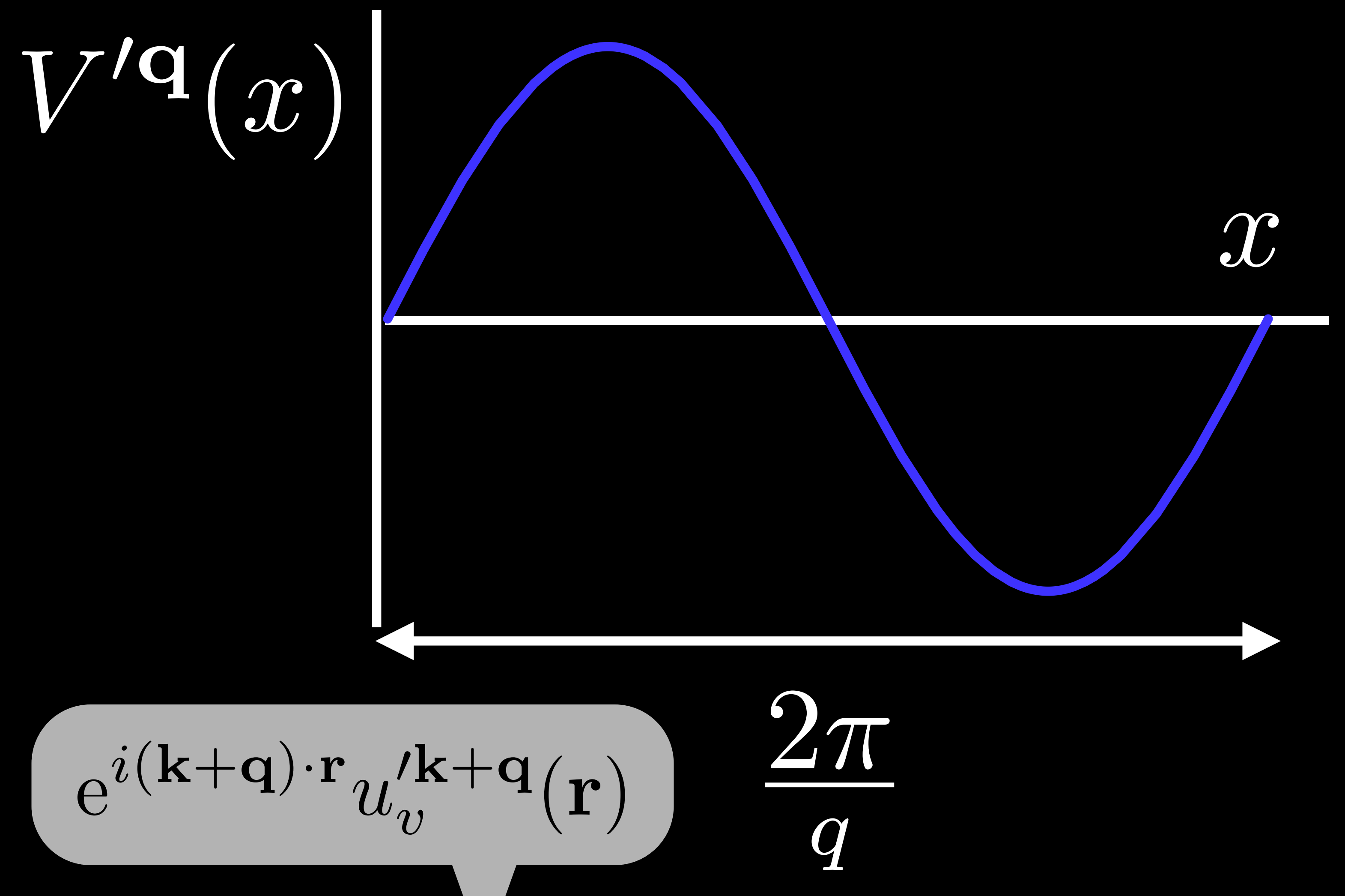
$e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} u_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r})$

$e^{i\mathbf{k}\cdot\mathbf{r}} u_v^{\circ\mathbf{k}}(\mathbf{r})$

$$\left(H_0 - \epsilon_v^{\mathbf{k}}\right)\phi_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r}) = -P_c V'^{\mathbf{q}}_{SCF}\phi_v^{\mathbf{k}}(\mathbf{r})$$

$$n'^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{v,\mathbf{k}} u_v^{\circ\mathbf{k}*}(\mathbf{r}) u_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

monochromatic perturbations



$\mathrm{e}^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} u_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r})$

$\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_v^{\circ\mathbf{k}}(\mathbf{r})$

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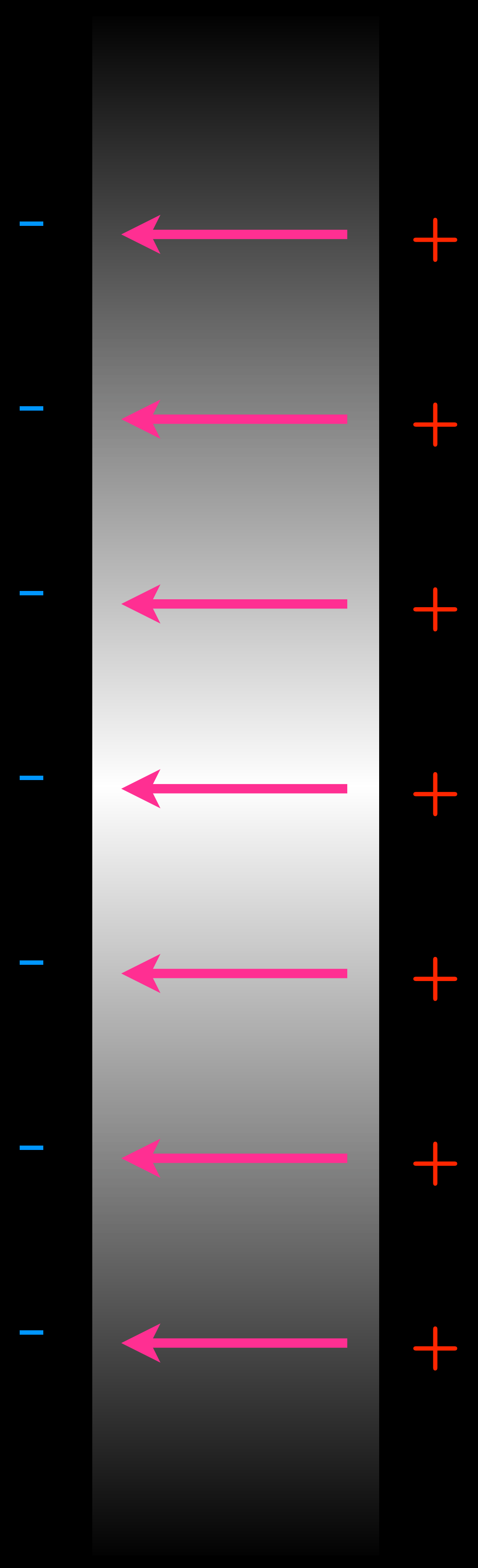
$$V'^{\mathbf{q}}(\mathbf{r}) = V_{ext}'^{\mathbf{q}}(\mathbf{r}) + \int \left(\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \kappa_{xc}(\mathbf{r},\mathbf{r}') \right) n'^{\mathbf{q}}(\mathbf{r}')d\mathbf{r}'$$

macroscopic electric fields

$$\mathbf{E} = \text{const}$$



$$V'(\mathbf{r}) = \mathbf{E} \cdot \mathbf{r}$$

macroscopic electric fields

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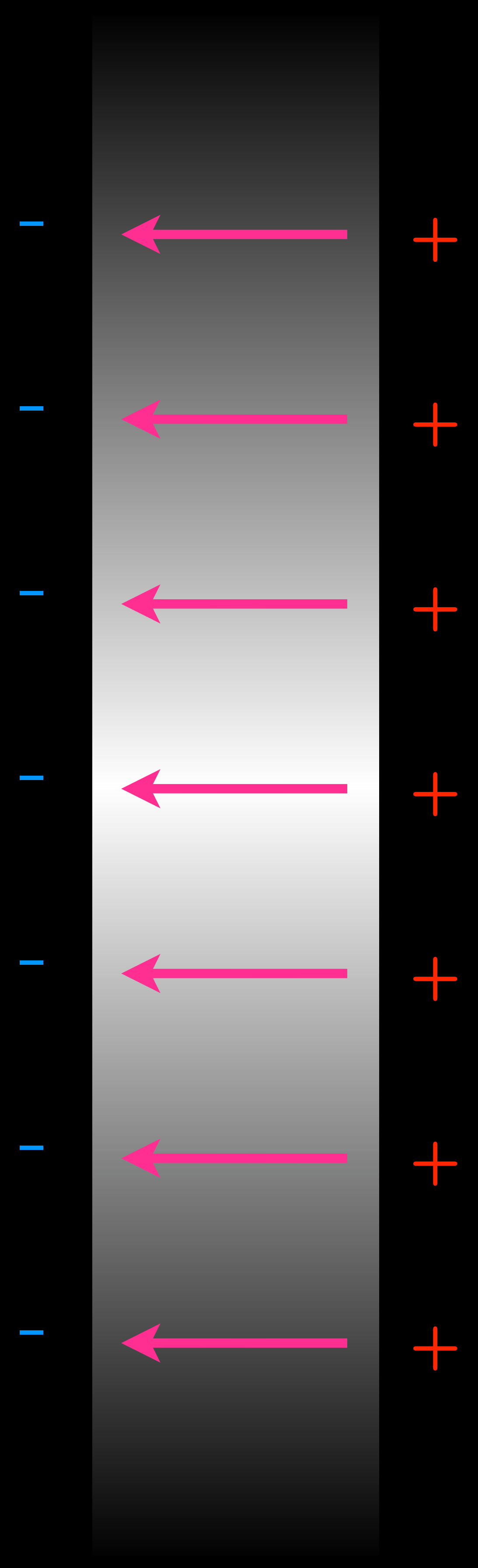

$V'(\mathbf{r}) = \mathbf{E} \cdot \mathbf{r}$

$$\phi_v^0(\mathbf{r}) \quad = \quad \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r})$$

macroscopic electric fields

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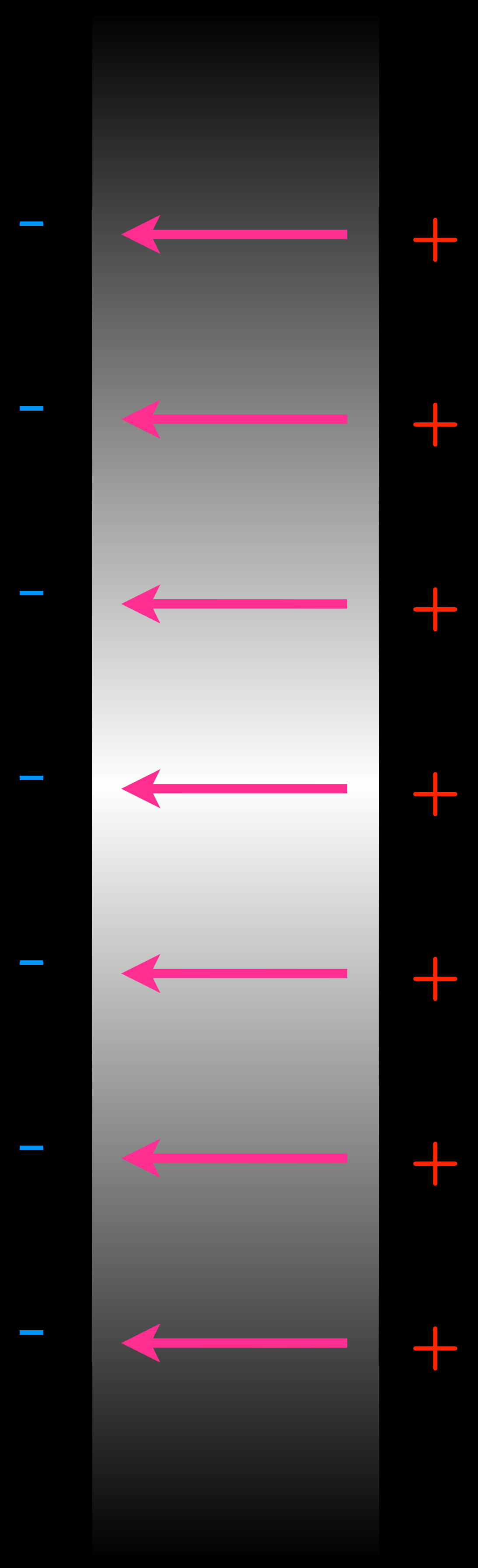

$$V'(\mathbf{r}) = \mathbf{E}\cdot\mathbf{r}$$

$$\begin{aligned}
\phi_v^0(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r}) \\
V'(\mathbf{r})\phi_v^0(\mathbf{r}) &= ??
\end{aligned}$$

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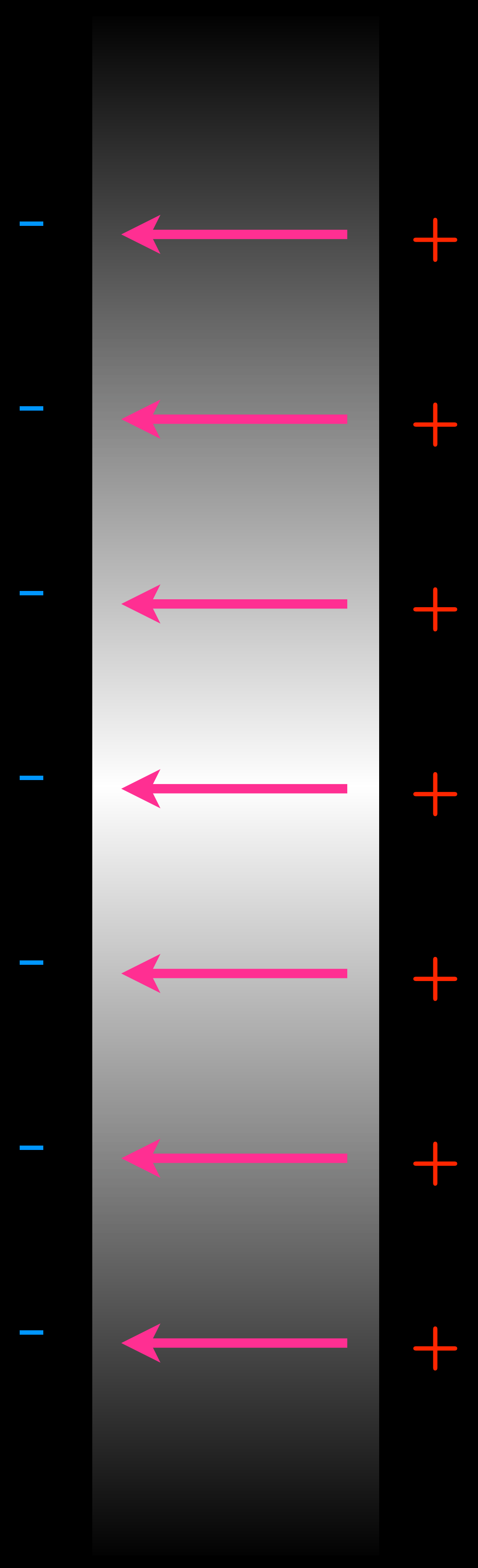

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$$-P_c V' \phi_v^0 = -\mathsf{E} \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle$$

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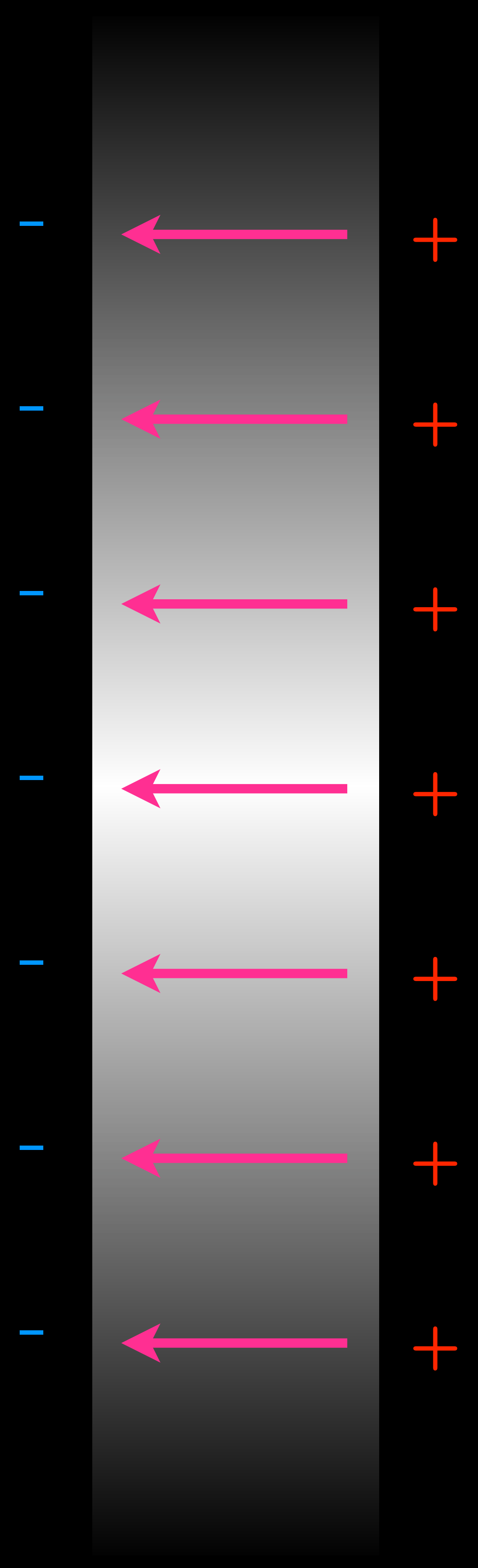

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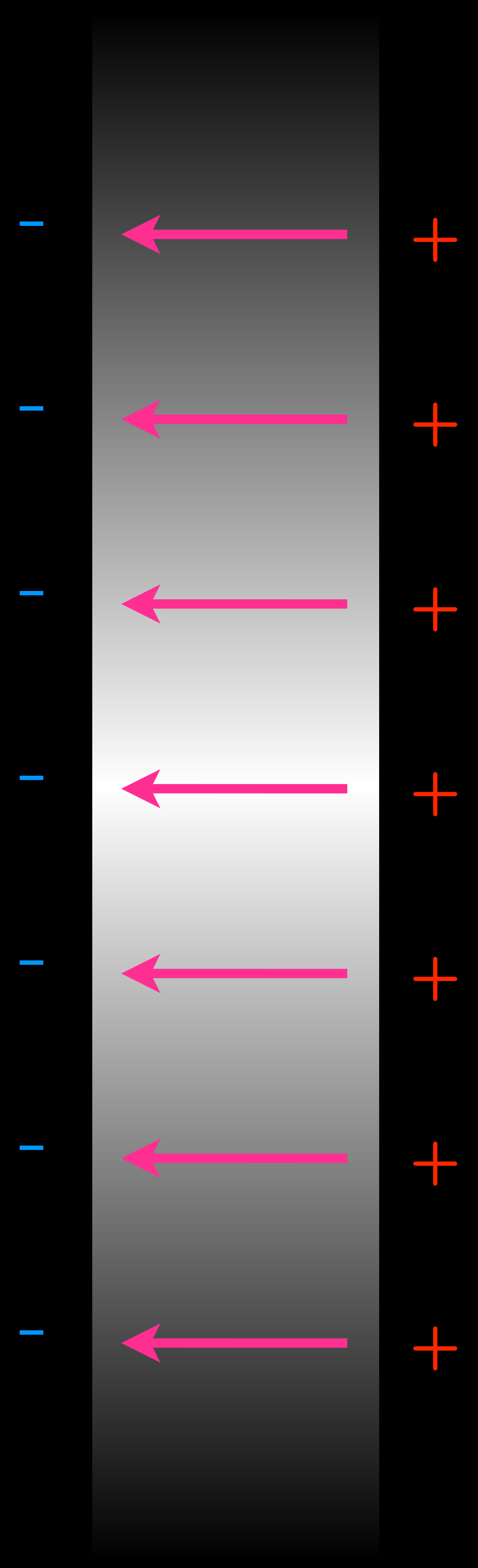
\end{aligned}
$$

$$
\langle \phi_v^0 | x | \phi_u^0 \rangle = \frac{\langle \phi_v^0 | [H, x] | \phi_u^0 \rangle}{\epsilon_v^0 - \epsilon_u^0} \qquad [H, x] = -\frac{\hbar^2}{m}\frac{\partial}{\partial x} + [H, V_{nl}]
$$

$$
-P_c V' \phi_v^0 = -\mathsf{E} \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle
$$

macroscopic electric fields

$$\mathsf{E} = \text{const}$$



$$V'(\mathbf{r}) = \mathsf{E} \cdot \mathbf{r}$$

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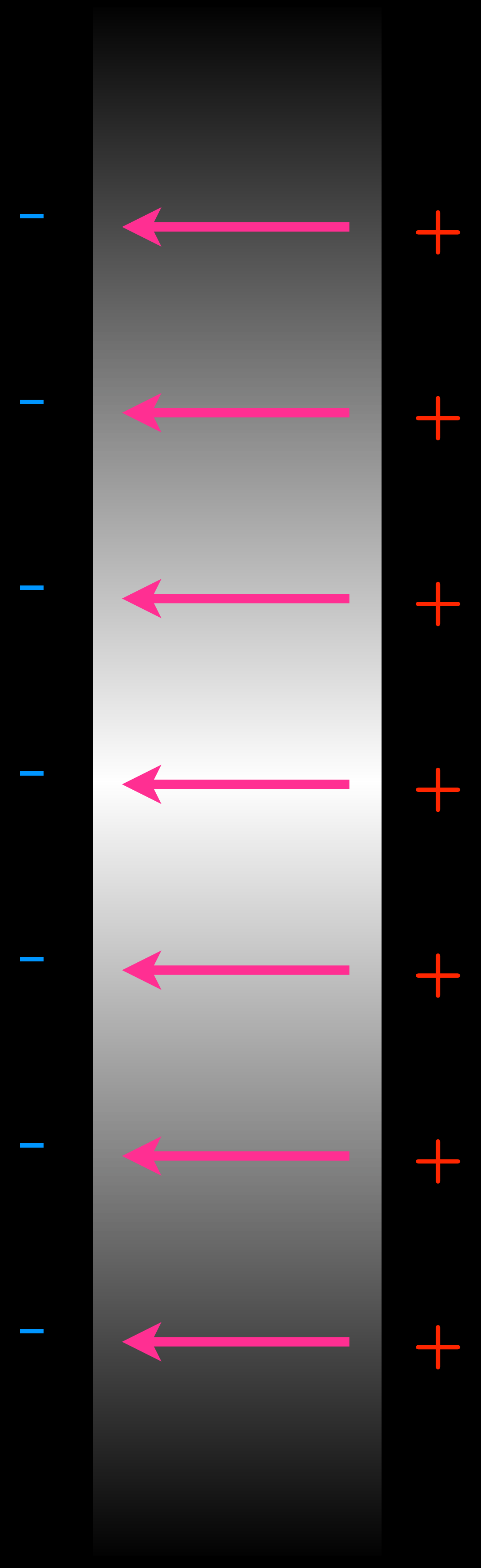
$$\begin{aligned} -P_c V' \phi_v^0 &= -\mathsf{E} \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle \\ &= -\mathsf{E} \sum_c \phi_c^0 \frac{\langle \phi_c^0 | [H_0, x] | \phi_v^0 \rangle}{\epsilon_c^0 - \epsilon_v^0} \equiv \psi_v' \end{aligned}$$

macroscopic electric fields

$\mathsf{E} = \mathrm{const}$



$$\phi_v^0(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r})$$
$$V'(\mathbf{r})\phi_v^0(\mathbf{r}) = ??$$

$$\langle\phi_v^0|x|\phi_u^0\rangle = \frac{\langle\phi_v^0|[H,x]|\phi_u^0\rangle}{\epsilon_v^0 - \epsilon_u^0} \qquad [H,x] = -\frac{\hbar^2}{m}\frac{\partial}{\partial x} + [H, V_{nl}]$$

$$-P_c V'\phi_v^0 = -\mathsf{E}\sum_c \phi_c^0\langle\phi_c^0|x|\phi_v^0\rangle$$
$$= -\mathsf{E}\sum_c \phi_c^0 \frac{\langle\phi_c^0|[H_0,x]|\phi_v^0\rangle}{\epsilon_c^0 - \epsilon_v^0} \equiv \psi_v'$$

$V'(\mathbf{r}) = \mathsf{E}\cdot\mathbf{r}$

$$\boxed{(H_0 - \epsilon_v^0)\psi_v' = -\mathsf{E} P_c [H_0, x]\phi_v^0}$$

DFPT rhs

phonons in polar materials

$$E(\mathbf{u}\quad) = \frac{1}{2} M \omega_0^2 u^2$$

phonons in polar materials

$$E(\mathbf{u}, \mathsf{E}) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \epsilon_\infty \mathsf{E}^2 - e Z^* \mathbf{u} \cdot \mathsf{E}$$

phonons in polar materials

$$E(\mathbf{u}, \mathsf{E}) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \epsilon_\infty \mathsf{E}^2 - e Z^* \mathbf{u} \cdot \mathsf{E}$$

$$\begin{aligned}
\mathbf{F} &\equiv -\frac{\partial E}{\partial \mathbf{u}} = -M\omega_0^2 \mathbf{u} + Z^* \mathsf{E} \\
\mathsf{D} &\equiv -\frac{4\pi}{\Omega} \frac{\partial E}{\partial \mathsf{E}} = \frac{4\pi}{\Omega} Z^* \mathbf{u} + \epsilon_\infty \mathsf{E}
\end{aligned}$$

phonons in polar materials

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\end{aligned}$$

$$\mathrm{rot}\ \boldsymbol{\mathsf{E}} \sim i\mathbf{q}\times\boldsymbol{\mathsf{E}} = 0$$

phonons in polar materials

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$$\mathrm{rot}\ \boldsymbol{\mathsf{E}} \sim i\mathbf{q} \times \boldsymbol{\mathsf{E}} = 0 \qquad\qquad \mathbf{u} \perp \mathbf{q} \Rightarrow \boldsymbol{\mathsf{E}} = 0$$

(T)

phonons in polar materials

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$$\begin{aligned} \mathbf{F} &\equiv -\frac{\partial E}{\partial \mathbf{u}} = -M\omega_0^2\mathbf{u} + Z^*\mathsf{E} \\ \mathsf{D} &\equiv -\frac{4\pi}{\Omega}\frac{\partial E}{\partial \mathsf{E}} = \frac{4\pi}{\Omega} Z^*\mathbf{u} + \epsilon_\infty \mathsf{E} \end{aligned}$$

$$\mathrm{rot}\ \mathsf{E} \sim i\mathbf{q}\times\mathsf{E} = 0 \qquad \mathbf{u}\perp\mathbf{q} \Rightarrow \mathsf{E} = 0 \qquad \text{(T)}$$

$$\mathbf{F}_T = -M\omega_0^2\mathbf{u}$$

phonons in polar materials

$$E(\mathbf{u},\mathsf{E}) = \frac{1}{2}M\omega_0^2 u^2 - \frac{\Omega}{8\pi}\epsilon_\infty \mathsf{E}^2 - eZ^*\mathbf{u}\cdot\mathsf{E}$$

$$\mathbf{F} \equiv -\frac{\partial E}{\partial \mathbf{u}} = -M\omega_0^2\mathbf{u} + Z^*\mathsf{E}$$

$$\mathsf{D} \equiv -\frac{4\pi}{\Omega}\frac{\partial E}{\partial \mathsf{E}} = \frac{4\pi}{\Omega}Z^*\mathbf{u} + \epsilon_\infty\mathsf{E}$$

$$\mathrm{rot}\ \mathsf{E} \sim i\mathbf{q}\times\mathsf{E} = 0 \qquad \mathbf{u}\perp\mathbf{q} \Rightarrow \mathsf{E} = 0 \qquad \text{(T)}$$

$$\mathrm{div}\ \mathsf{D} \sim i\mathbf{q}\cdot\mathsf{D} = 0$$

$$\mathbf{F}_T = -M\omega_0^2\mathbf{u}$$

phonons in polar materials

$$E(\mathbf{u},\mathsf{E}) = \frac{1}{2}M\omega_0^2 u^2 - \frac{\Omega}{8\pi}\epsilon_\infty \mathsf{E}^2 - eZ^*\mathbf{u}\cdot\mathsf{E}$$

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\mathsf{D} \quad &\equiv \quad -\frac{4\pi}{\Omega}\frac{\partial E}{\partial \mathsf{E}} = \frac{4\pi}{\Omega}Z^*\mathbf{u} + \epsilon_\infty\mathsf{E}
\end{aligned}$$

$\mathrm{rot}\ \mathsf{E} \sim i\mathbf{q}\times\mathsf{E} = 0$ $\qquad$ $\mathbf{u}\perp\mathbf{q} \Rightarrow \mathsf{E} = 0$ $\qquad$ (T)

$\mathrm{div}\ \mathsf{D} \sim i\mathbf{q}\cdot\mathsf{D} = 0$ $\qquad$ $\mathbf{u}\parallel\mathbf{q} \Rightarrow \mathsf{D} = 0$ $\qquad$ (L)

$$\mathbf{F}_T = -M\omega_0^2\mathbf{u}$$

phonons in polar materials

$$E(\mathbf{u},\mathsf{E}) = \frac{1}{2}M\omega_0^2u^2 - \frac{\Omega}{8\pi}\epsilon_\infty \mathsf{E}^2 - eZ^*\mathbf{u}\cdot\mathsf{E}$$

$$\mathbf{F} \equiv -\frac{\partial E}{\partial \mathbf{u}} = -M\omega_0^2\mathbf{u} + Z^*\mathsf{E}$$

$$\mathsf{D} \equiv -\frac{4\pi}{\Omega}\frac{\partial E}{\partial \mathsf{E}} = \frac{4\pi}{\Omega}Z^*\mathbf{u} + \epsilon_\infty\mathsf{E}$$

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$\mathbf{F}_T = -M\omega_0^2\mathbf{u}$ $\qquad$ $\mathbf{F}_L = -M\left(\omega_0^2 + \frac{4\pi Z^*}{M\Omega\epsilon_\infty}\right)\mathbf{u}$

interatomic force constants

$$\Phi_{st}^{\alpha\beta}(\mathbf{R}-\mathbf{R}') = -\frac{\partial^2 E}{\partial u_s^\alpha(\mathbf{R})\partial u_t^\beta(\mathbf{R}')}$$

interatomic force constants

$$
\begin{aligned}
\Phi_{st}^{\alpha\beta}(\mathbf{R}-\mathbf{R}') &= -\frac{\partial^2 E}{\partial u_s^\alpha(\mathbf{R})\partial u_t^\beta(\mathbf{R}')} \\
&= \frac{\Omega}{(2\pi)^3}\int \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} D_{st}^{\alpha\beta}(\mathbf{q})d\mathbf{q}
\end{aligned}
$$

interatomic force constants

$$\Phi^{\alpha\beta}_{st}(\mathbf{R}-\mathbf{R}') = -\frac{\partial^2 E}{\partial u^\alpha_s(\mathbf{R})\partial u^\beta_t(\mathbf{R}')}$$

$$= \frac{\Omega}{(2\pi)^3}\int \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} D^{\alpha\beta}_{st}(\mathbf{q})d\mathbf{q}$$

$$D^{\alpha\beta}_{st}(\mathbf{q}) = \bar{D}^{\alpha\beta}_{st}(\mathbf{q}) + \frac{4\pi e^2}{\Omega\epsilon_\infty} Z^\star_s Z^\star_t \frac{q^\alpha q^\beta}{q^2}$$

short ranged +
dipole-dipole

interatomic force constants

$$\Phi_{st}^{\alpha\beta}(\mathbf{R}-\mathbf{R}') = -\frac{\partial^2 E}{\partial u_s^\alpha(\mathbf{R})\partial u_t^\beta(\mathbf{R}')}$$

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$$D_{st}^{\alpha\beta}(\mathbf{q}) = \bar{D}_{st}^{\alpha\beta}(\mathbf{q}) + \frac{4\pi e^2}{\Omega\epsilon_\infty}Z_s^\star Z_t^\star \frac{q^\alpha q^\beta}{q^2}$$

short ranged +
dipole-dipole

- **remove singularities** in D(**q**) → D_{SR}(**q**)
- **do FFT's** (# R's = # q's - the shorter the range, the coarser the grid)
- **store information**
- **interpolate** D_{SR}(**q**) on any finer mesh (pad Φ with 0's and do FFT^{-1}: # q's = # R's)
- add back D_{dd}(**q**) analytically
- **calculate phonon bands**

DFPT: the main features

☛ response functions calculated in terms of response orbitals, $\{\phi'_v\}$

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- ☛ non-periodic perturbations: OK

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- response functions calculated in terms of response orbitals, $\{\phi'_v\}$
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- calculate the response to the perturbation you want, only
- non-local perturbations: OK
- non-periodic perturbations: OK
- macroscopic electric fields: OK

Piezoelectric Properties of III-V Semiconductors from First-Principles Linear-Response Theory

Stefano de Gironcoli[(a)]
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Scuola Internazionale Superiore di Studi Avanzati (SISSA), Strada Costiera 11, I-34014 Trieste, Italy

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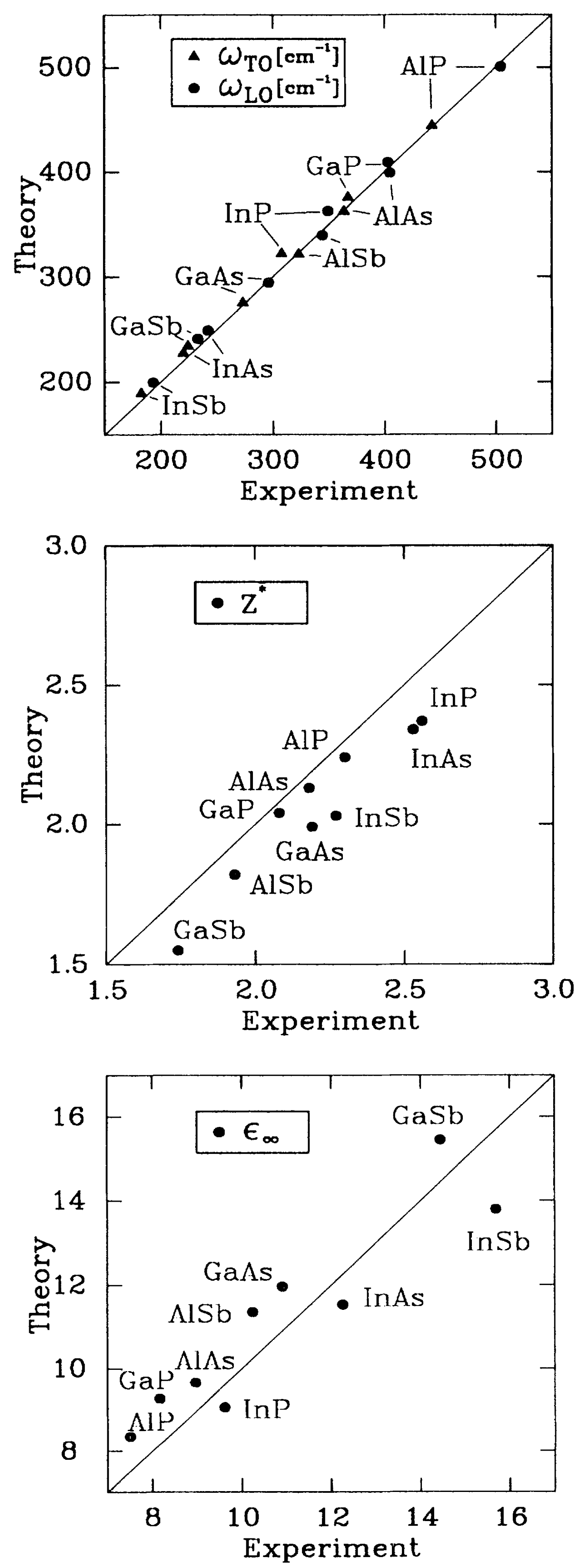
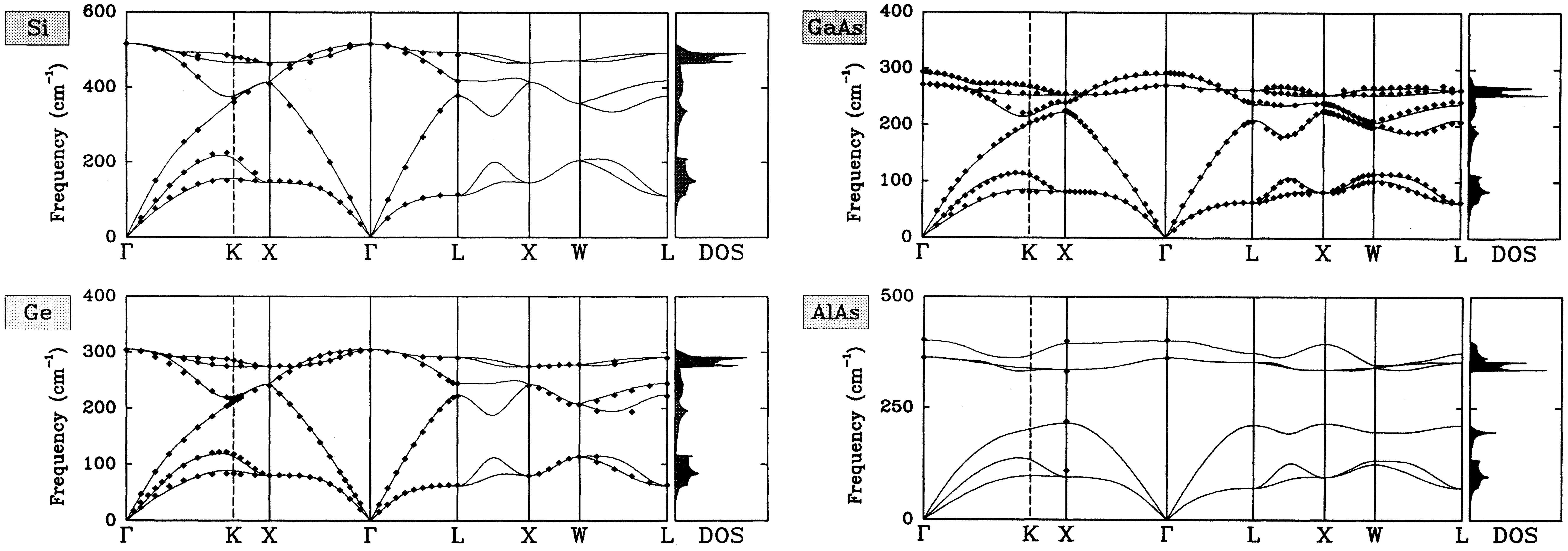
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), Ecole Polytechnique Fédérale de Lausanne, CH-1015, Lausanne, Switzerland
(Received 7 November 1988)



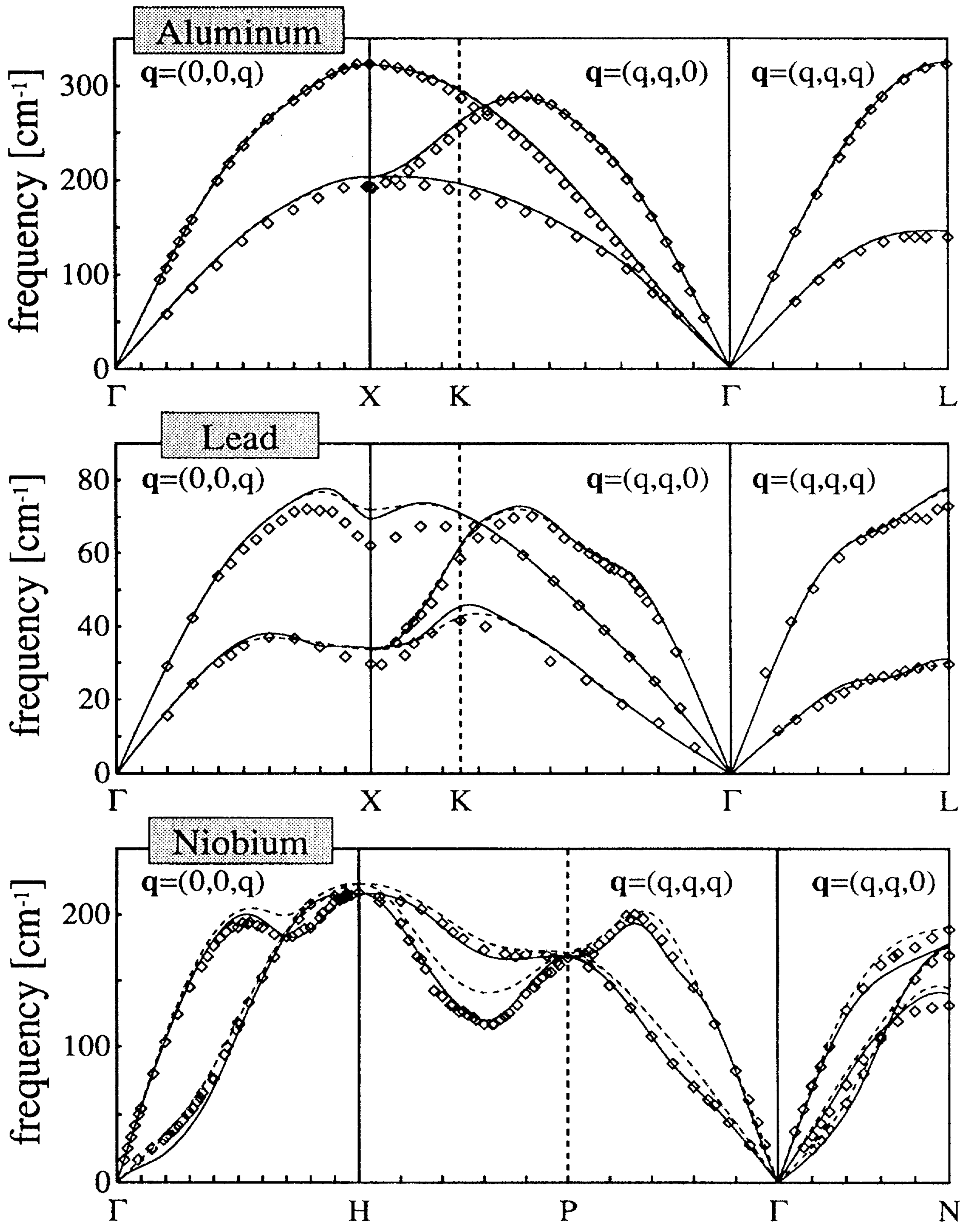
$\bar{\gamma}_{14}$	P	As	Sb
Al	0.11 (· · ·)	−0.03 (· · ·)	−0.13 (−0.16)
Ga	−0.18 (−0.18)	−0.35 (−0.32)	−0.40 (−0.39)
In	0.12 (|0.09|)	−0.08 (−0.10)	−0.20 (−0.18)

phonons from DFPT



P. Giannozzi, S. de Gironcoli, P. Pavone, and SB, Phys. Rev. B **43**, 7231 (1991)

DFPT phonons in metals



Stefano de Gironcoli, Phys. Rev. B **51**, 6773 (1995)

applications done so far

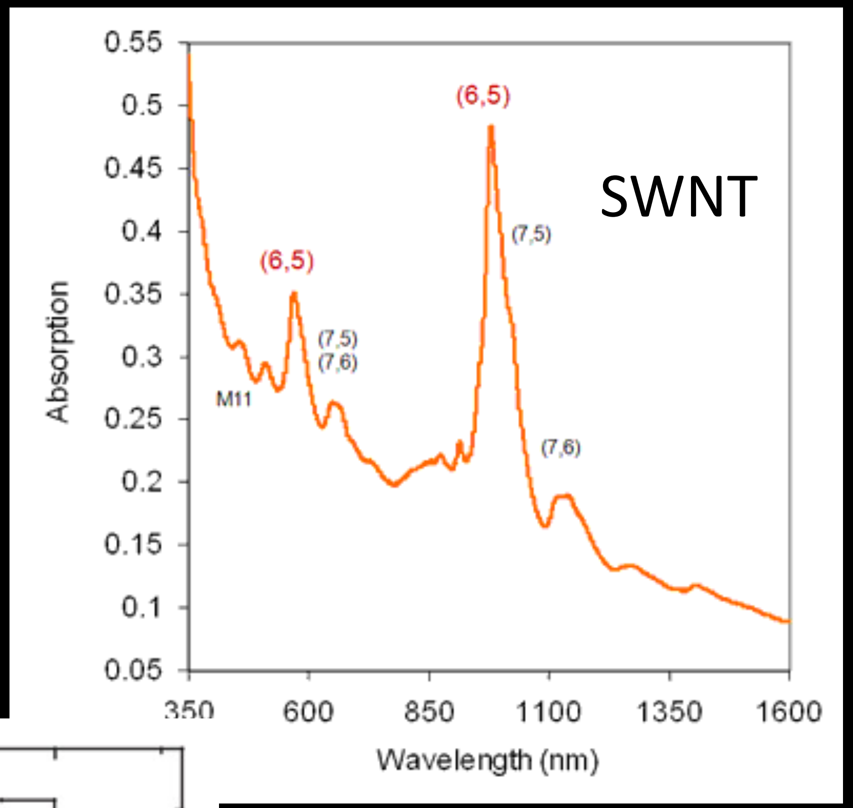
- Dielectric properties
- Piezoelectric properties
- Elastic properties
- Phonon in crystals and alloys
- Phonon at surfaces, interfaces, super-lattices, and nano-structures
- Raman and infrared activities
- Anharmonic couplings and vibrational line widths
- Mode softening and structural transitions
- Electron-phonon interaction and superconductivity
- Thermal expansion
- Isotopic effects on structural and dynamical properties
- Thermo-elasticity and other thermal properties of minerals
- ...

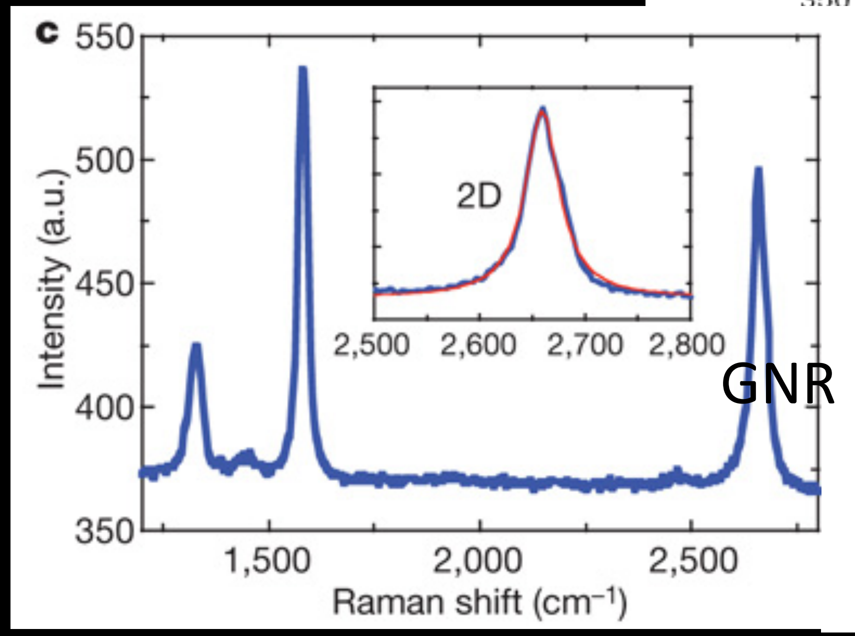
SB, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, *Phonons and related crystal properties from density-functional perturbation theory*, Rev. Mod. Phys. **73**, 515 (2001)

DFPT goes time-dependent

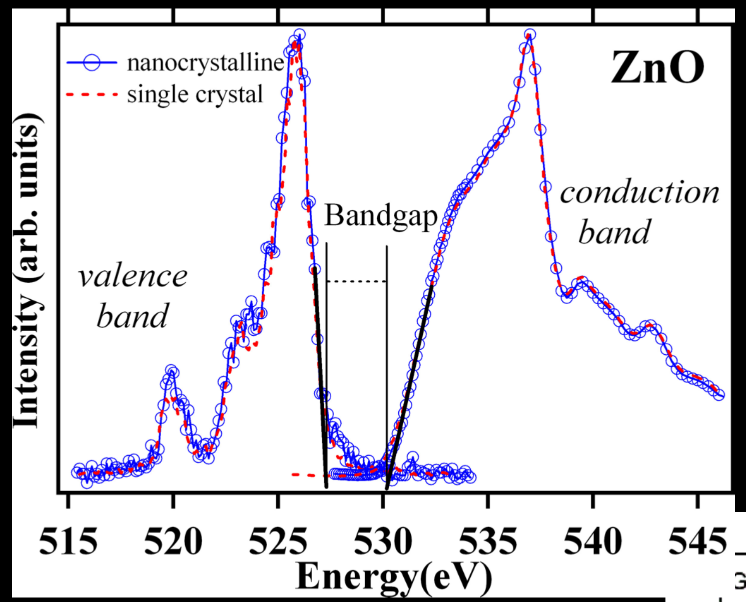
simulating materials spectroscopy with TDDFT absorption

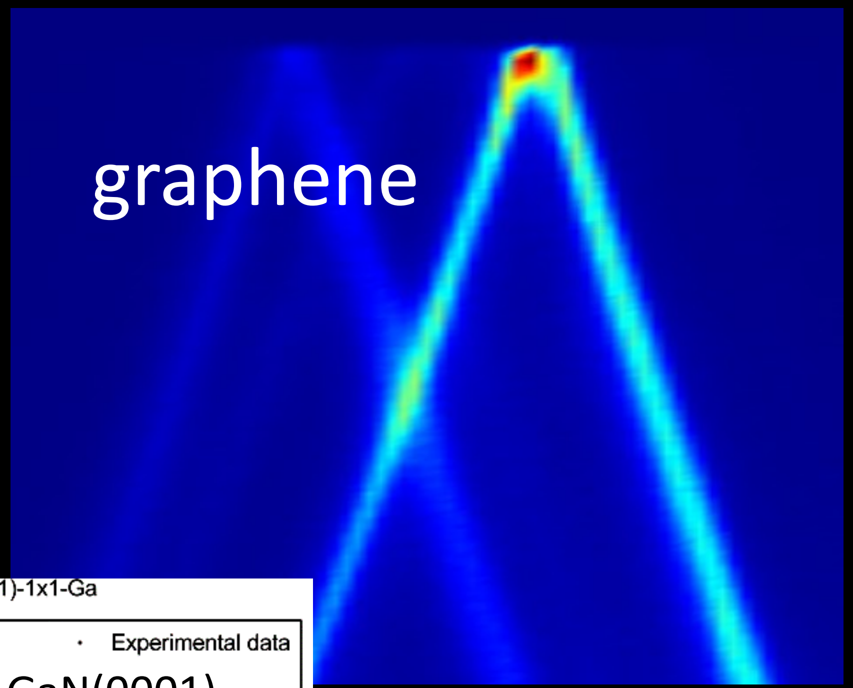
lattice and molecular vibrations





Raman

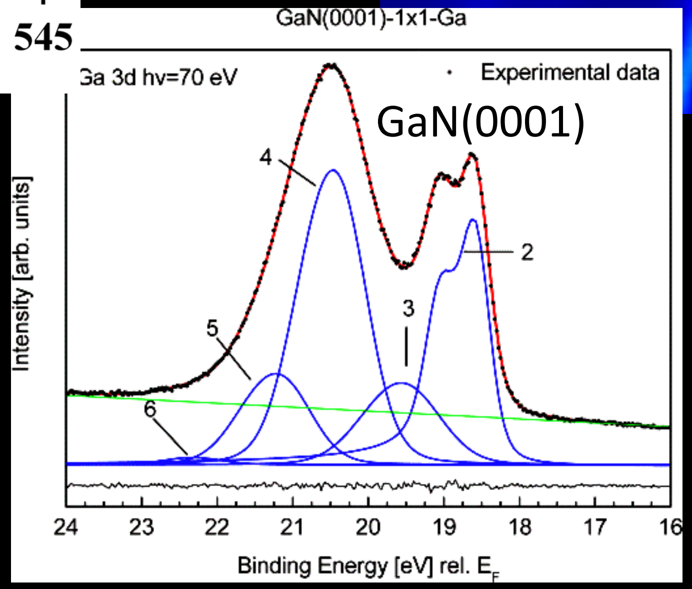




XAS/XES

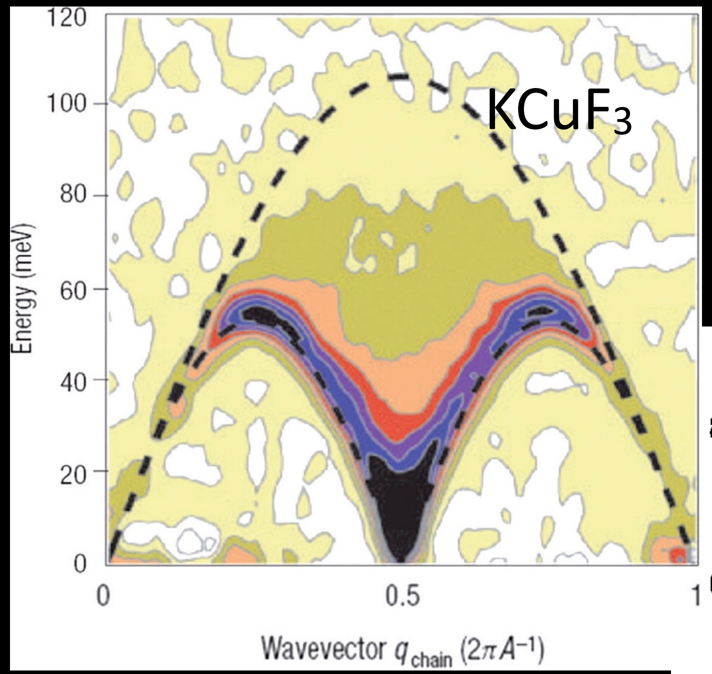
ARPES

electronic transitions

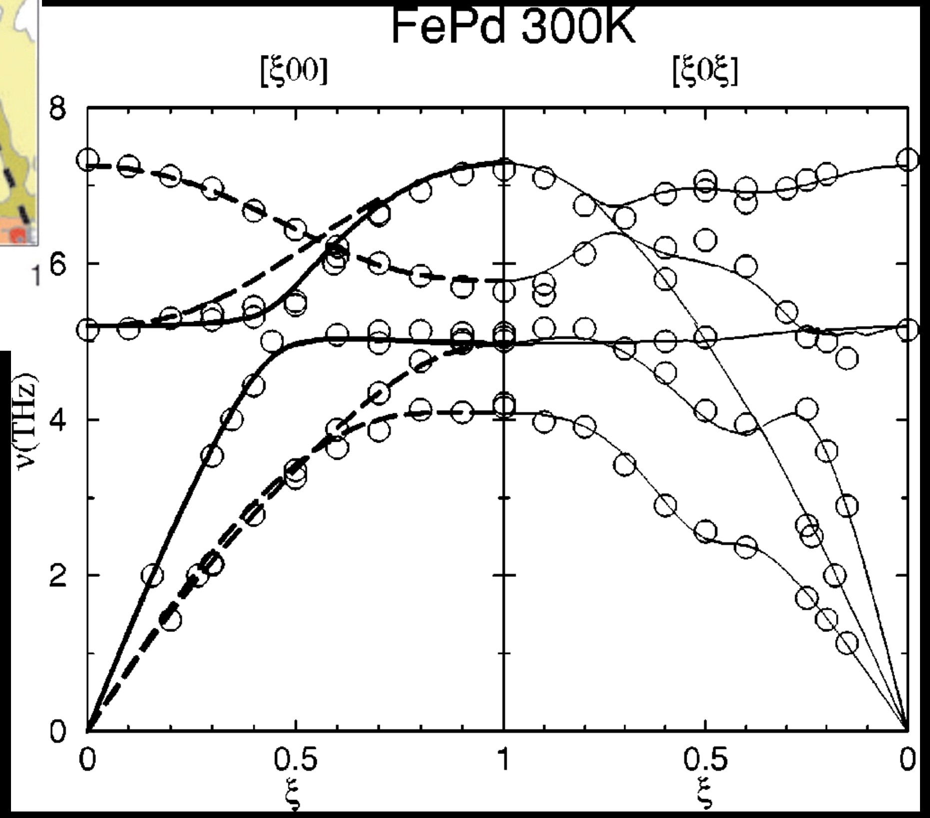


XPS

spectroscopies



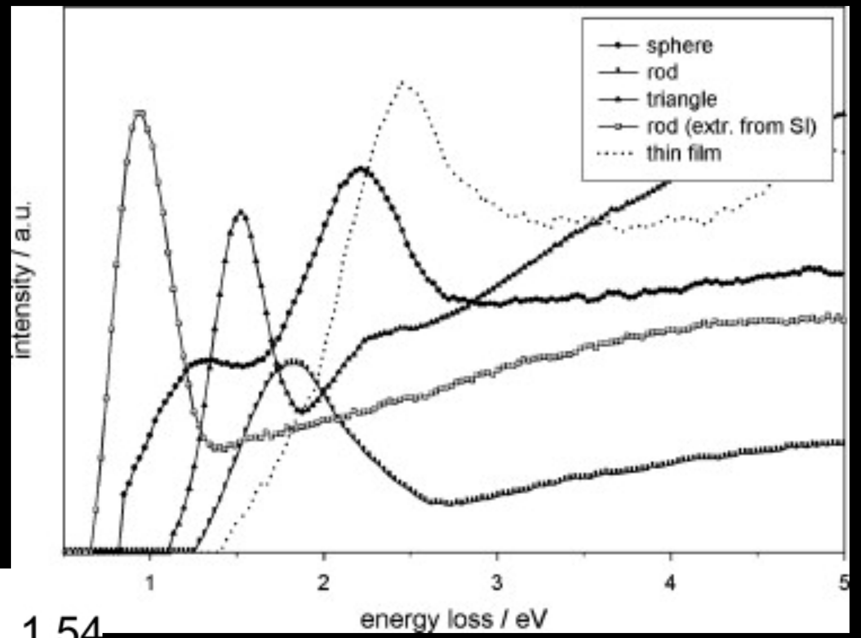
spin fluctuations

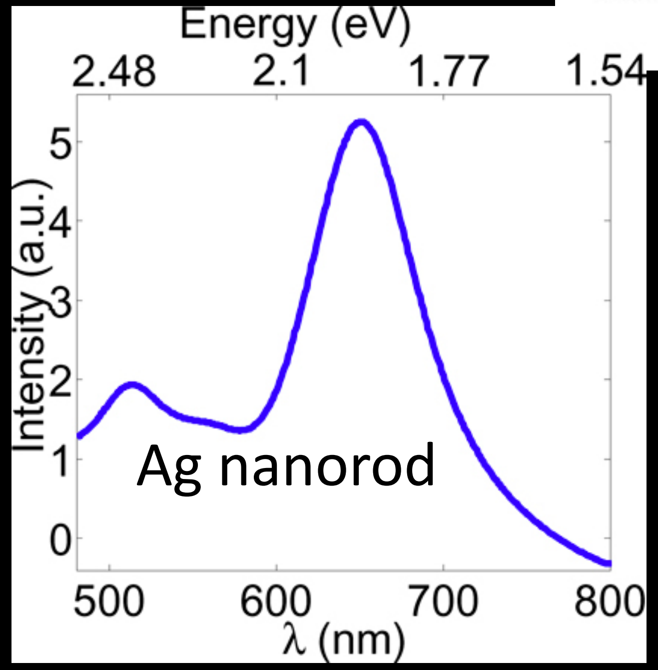


inelastic neutron scattering

lattice vibrations

eels



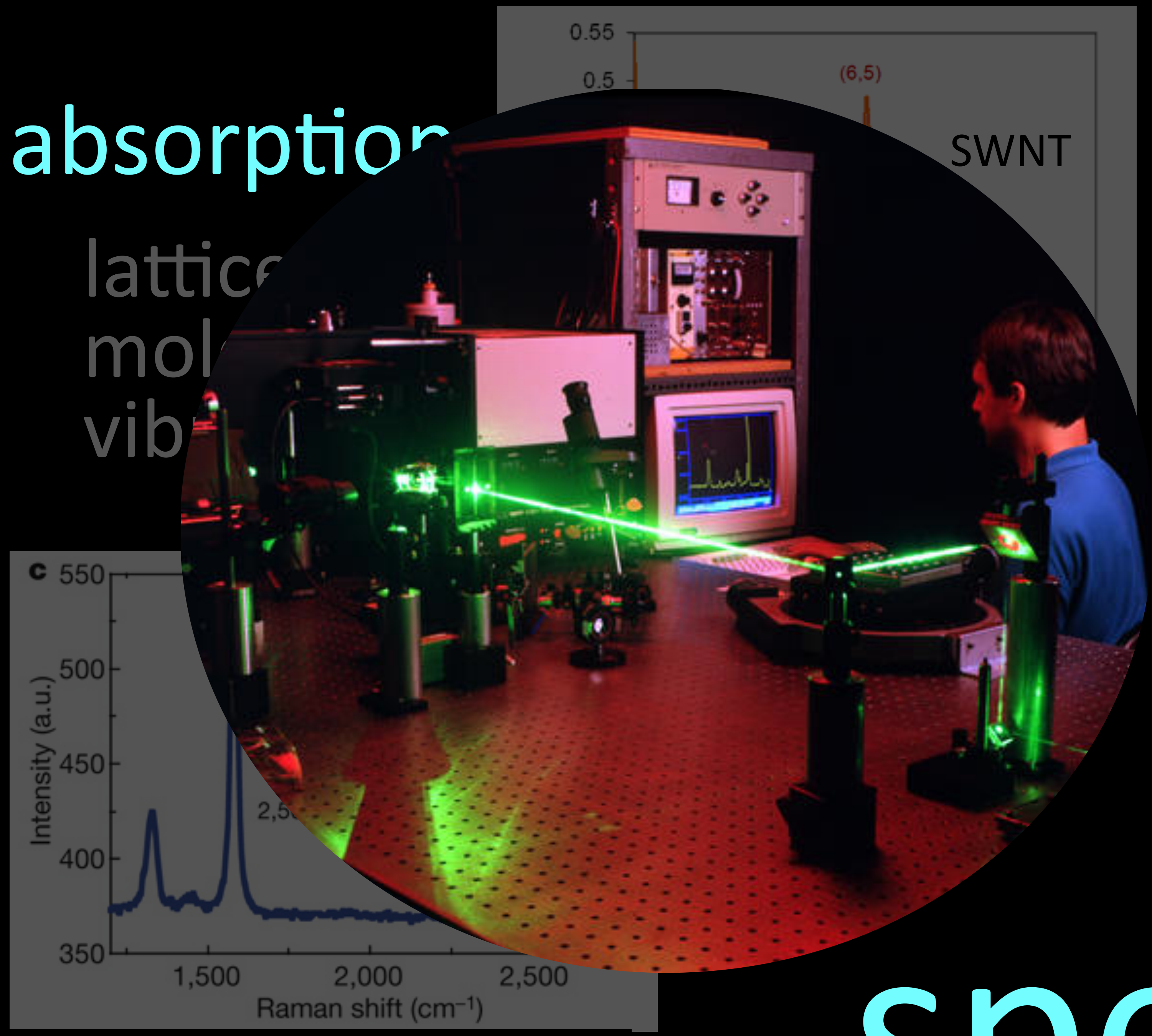


charge fluctuations

• • •

absorption

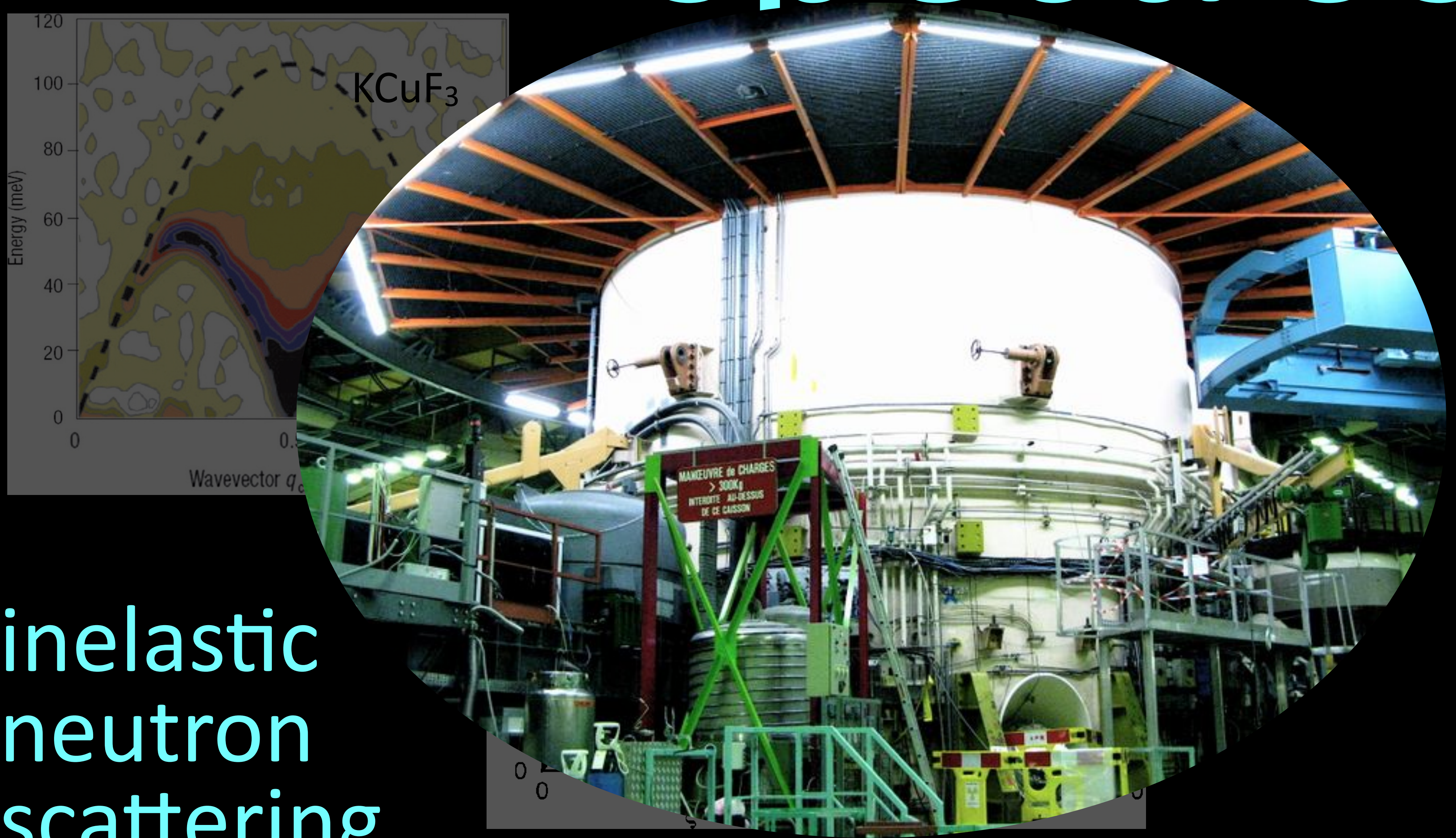
lattice
mol
vib



XAS/XES

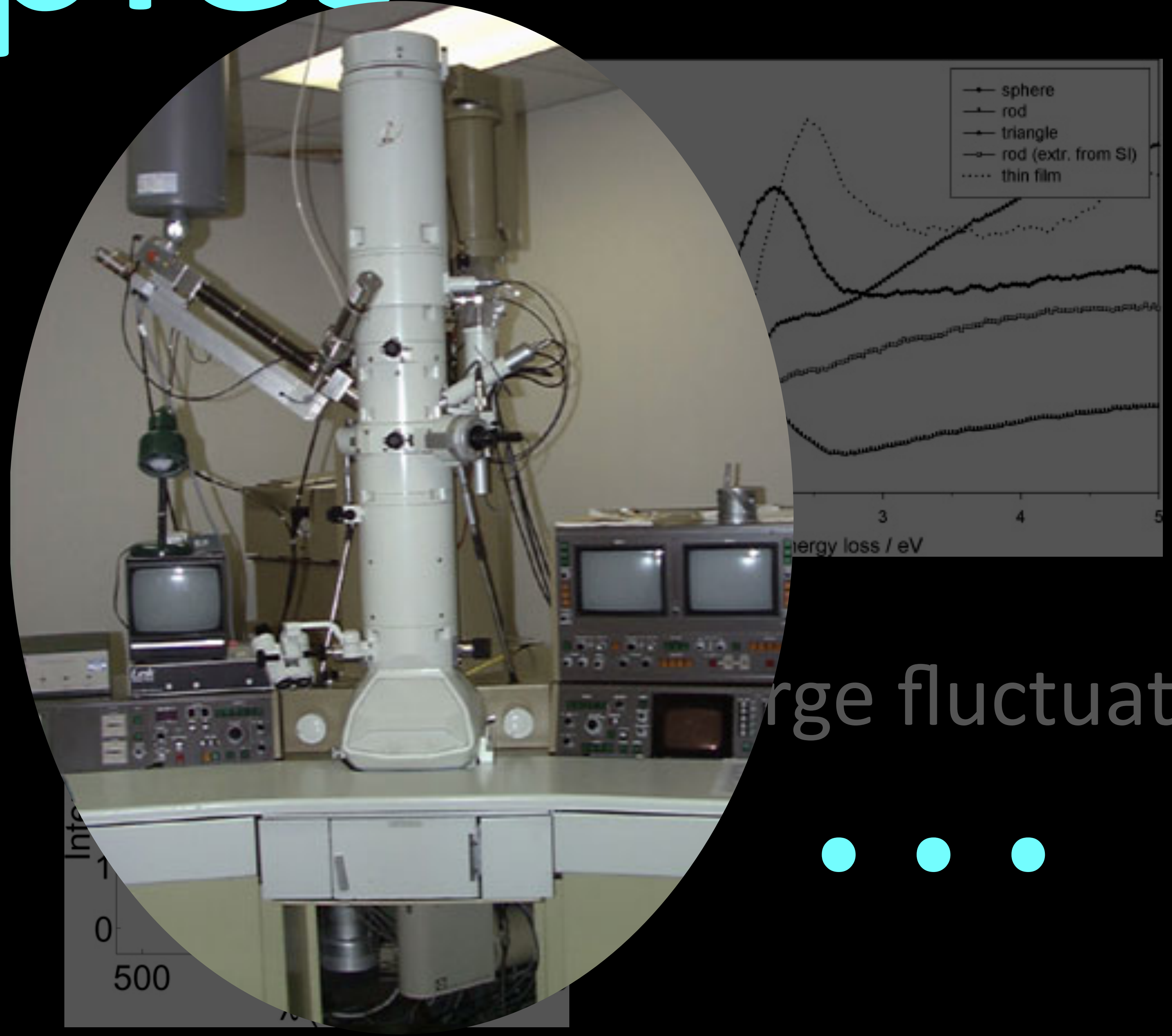
elect
transitio

spectroscopies



inelastic
neutron
scattering

lattice vibrations



rge fluctuations

• • •

probing the flickers of matter

flicker	probe
molecular vibration	IR, Raman, INS, HREELS, ···
spin fluctuation	INS, EPR, MCD, ···
charge fluctuation	optical and PE spectra, EELS, ···
···	···

probing the flickers of matter

flicker	probe	theory
molecular vibration	IR, Raman, INS, HREELS, ⋯	DF(p)T
spin fluctuation	INS, EPR, MCD, ⋯	constrained DFT, TDDFT, MBPT
charge fluctuation	optical and PE spectra, EELS, ⋯	TDDFT, MBPT, ⋯
⋯	⋯	⋯

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$$\mathsf{R}(\omega) = \chi_{RP}(\omega)\mathsf{P}(\omega)$$

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probe → system → response

TDDFT: Time-Dependent DFT

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$$\forall \qquad n(\mathbf{r},t)\ \&\ \Psi(t=0) : \langle\Psi(0)|\hat{n}(\mathbf{r})|\Psi(0)\rangle = n(\mathbf{r},0)$$

$$\exists! \qquad v(\mathbf{r},t) : v(\mathbf{r},t) \mapsto n(\mathbf{r},t)$$

E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

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$$v_{KS}(\mathbf{r},t) = v(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}[n](\mathbf{r},t)$$

time-dependent DFpT

$$i|\dot{\phi}_v(t)\rangle = H_{KS}(t)|\phi_v(t)\rangle$$

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$$\begin{aligned} \rho^2 &= \rho \\ \langle A(t)\rangle &= \mathsf{Tr}\big(\rho(t)A\big) \end{aligned}$$

excited states from TDDFpT

$$i \; \dot{\rho}(t) = [H_{KS}(t), \rho(t)]$$

excited states from TDDFpT

$$i\ \dot{\rho}(t) = [H_{KS}(t), \rho(t)]$$

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$$i\ \dot{\rho}' = [H^\circ, \rho'] + [V'_{HXC}, \rho^\circ] + [V'_{ext}, \rho^\circ] + \mathcal{O}\left(V'^2\right)$$

excited states from TDDFpT

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$$i\ \dot{\rho}' = \mathcal{L}\ \rho' + [V'_{ext}, \rho^\circ]$$

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$$(\omega - \mathcal{L})\tilde{\rho}' = [\tilde{V}'_{ext}, \rho^\circ]$$

excited states from TDDFpT

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$$(\omega - \mathcal{L})\tilde{\rho}' = \cancel{[\tilde{V}'_{ext}, \rho^\circ]}$$

free oscillations

$$\mathcal{L}\ \tilde{\rho}' = \omega\tilde{\rho}' \longrightarrow$$

excitation energies
and oscillator strenghts

the Liouville-Lanczos algorithm

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^\circ]$$

the Liouville-Lanczos algorithm

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^\circ]$$

$$\boldsymbol{\alpha}(\omega) \quad = \quad \mathsf{Tr}\big(\mathbf{d}\tilde{\rho}'(\omega)\big)$$

the Liouville-Lanczos algorithm

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$$\begin{aligned}\boldsymbol{\alpha}(\omega) &= \mathrm{Tr}\big(\mathbf{d}\tilde{\rho}'(\omega)\big) \\ &= \big(\mathbf{d}, (\omega - \mathcal{L})^{-1} \cdot [\tilde{V}'_{ext}(\omega), \rho^\circ]\big)\end{aligned}$$

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the batch representation

$$\tilde{\rho}'(\omega) = \sum_{cv} \Big(X_{cv}(\omega) |\varphi_c^\circ\rangle\langle\varphi_v^\circ| + Y_{cv}(\omega) |\varphi_v^\circ\rangle\langle\varphi_c^\circ| \Big)$$

the batch representation

$$
\begin{aligned}
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&= \sum_{v} \Big(|x_v\rangle\langle\varphi_v^\circ| + |\varphi_v^\circ\rangle\langle y_v| \Big)
\end{aligned}
$$

the batch representation

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$$= \sum_{v}\Big(|x_v\rangle\langle\varphi_v^\circ| + |\varphi_v^\circ\rangle\langle y_v|\Big) \longrightarrow \begin{pmatrix}\{x_v\}\\ \{y_v\}\end{pmatrix}$$

$$P_v x_v = P_v y_v = 0$$

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$$P_v x_v = P_v y_v = 0$$

$$x_v(\mathbf{r}) \xrightarrow{\mathcal{L}} (H^\circ - \epsilon_v) x_v(\mathbf{r}) + P_c \sum_{v'} \int K_{vv'}(\mathbf{r}, \mathbf{r}') \big(x_{v'}(\mathbf{r}') + y_{v'}(\mathbf{r}') \big) d\mathbf{r}'$$

the batch representation

$$\tilde{\rho}'(\omega) = \sum_{cv}\Big(X_{cv}(\omega)|\varphi_c^\circ\rangle\langle\varphi_v^\circ| + |\varphi_v^\circ\rangle\langle\varphi_c^\circ|Y_{cv}(\omega)\Big)$$

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$$P_v x_v = P_v y_v = 0$$

$$2\varphi_v^\circ(\mathbf{r})\varphi_{v'}^\circ(\mathbf{r}') \times \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \kappa_{XC}(\mathbf{r}-\mathbf{r}')\right)$$

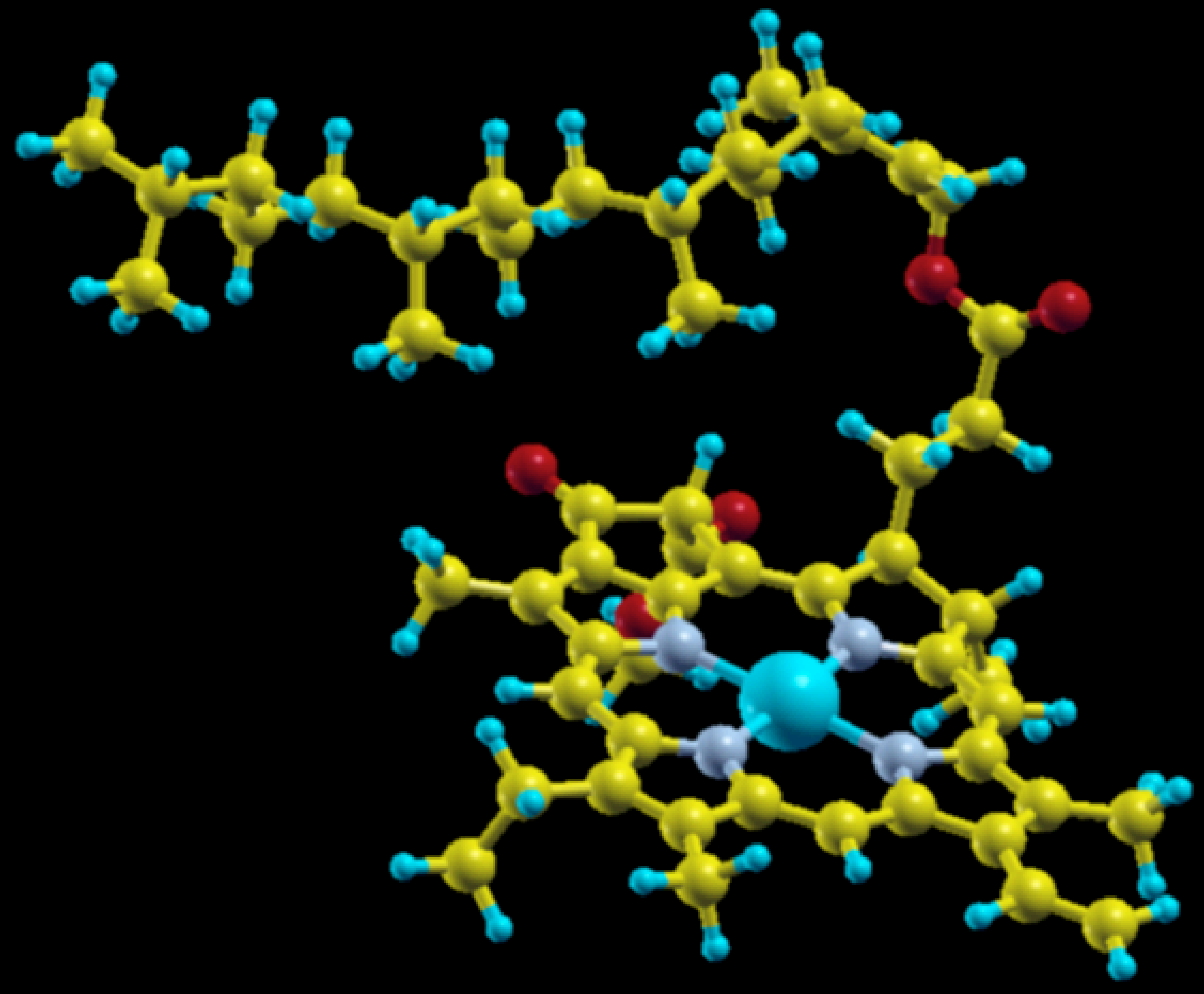
$$x_v(\mathbf{r}) \xrightarrow{\mathcal{L}} (H^\circ - \epsilon_v)x_v(\mathbf{r}) + P_c \sum_{v'} \int K_{vv'}(\mathbf{r},\mathbf{r}')\big(x_{v'}(\mathbf{r}') + y_{v'}(\mathbf{r}')\big)d\mathbf{r}'$$

$$= (H^\circ - \epsilon_v)x_v(\mathbf{r}) + P_c V'_{HXC}(\mathbf{r})\varphi_v^\circ(\mathbf{r})$$

B. Walker, A.M. Saitta, R. Gebauer, and SB, Phys. Rev. Lett. **96**, 1130001 (2006)

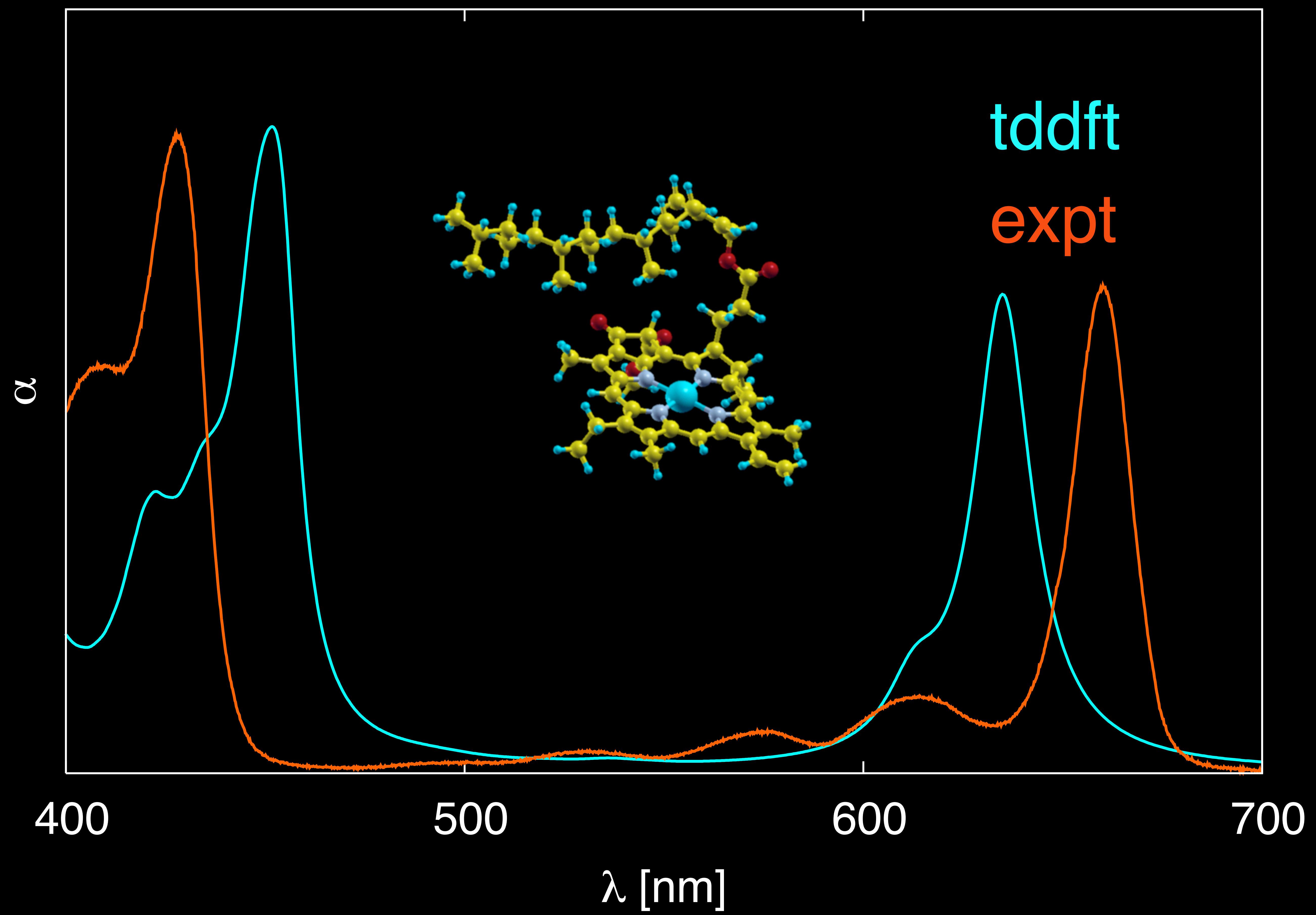
D. Rocca, R. Gebauer, Y. Saad, and SB, J. Chem. Phys. **128**, 154105 (2008)

why grass is green

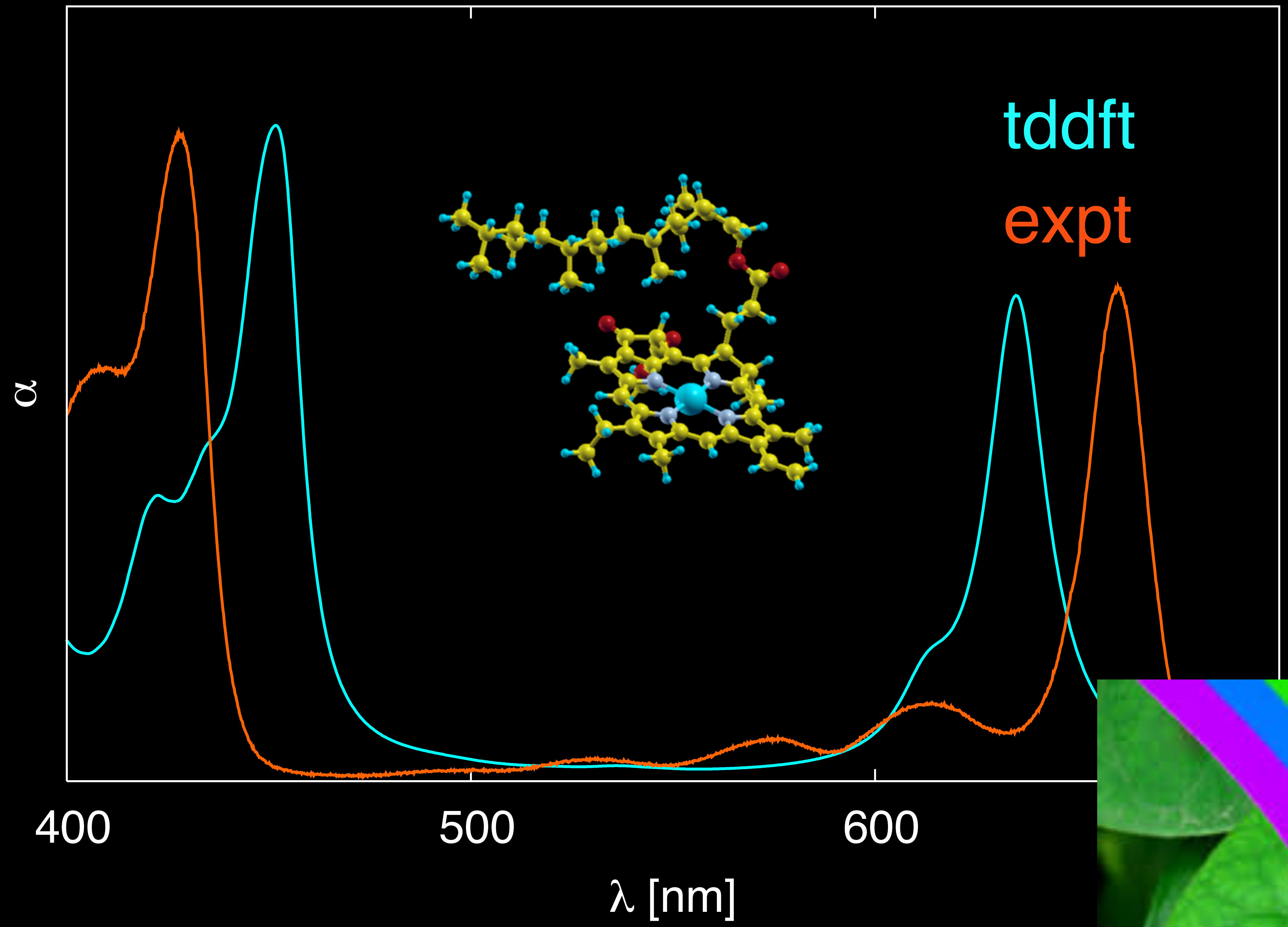


$C_{55}H_{72}MgN_4O$

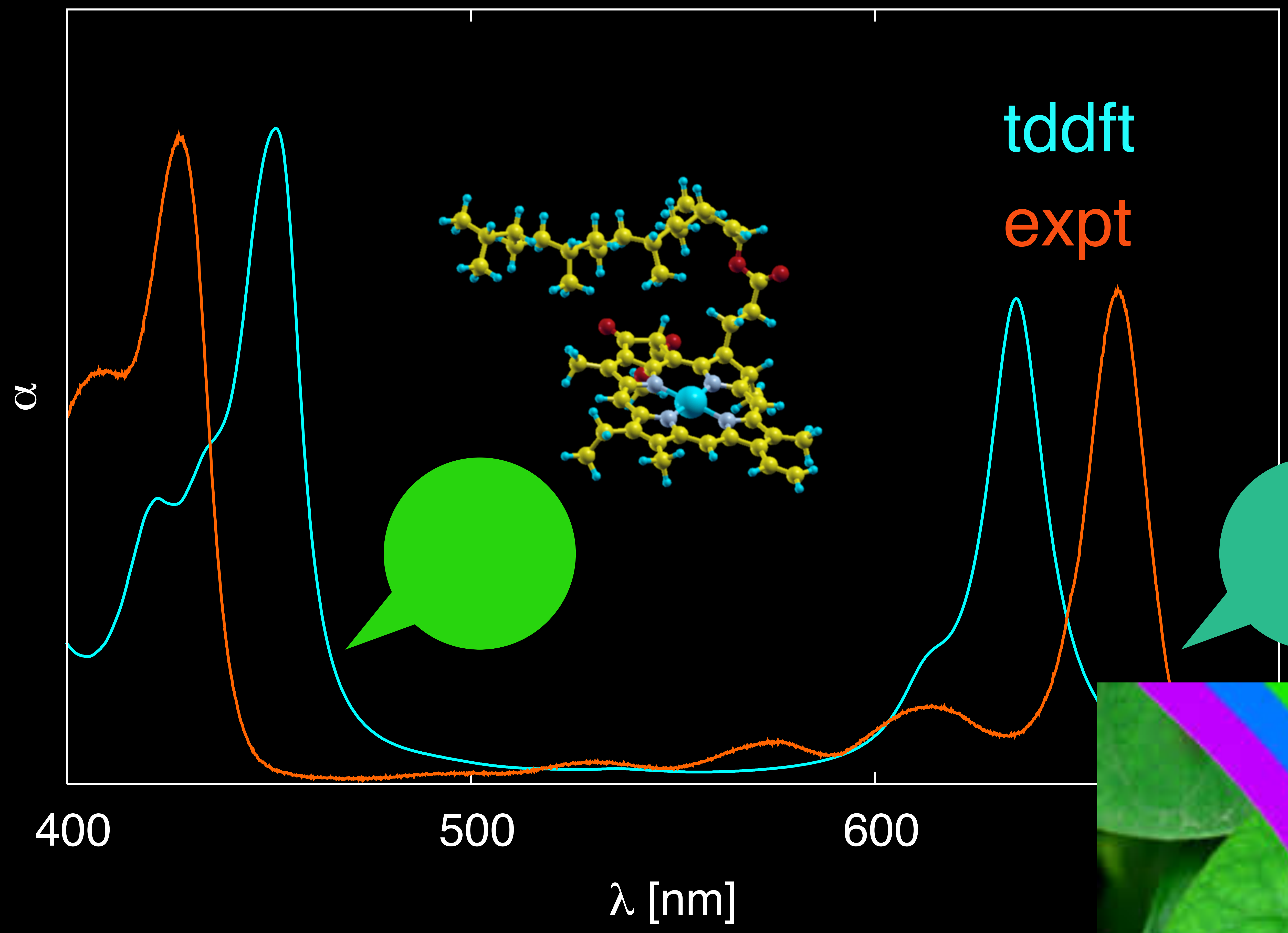
why grass is green



why grass is green

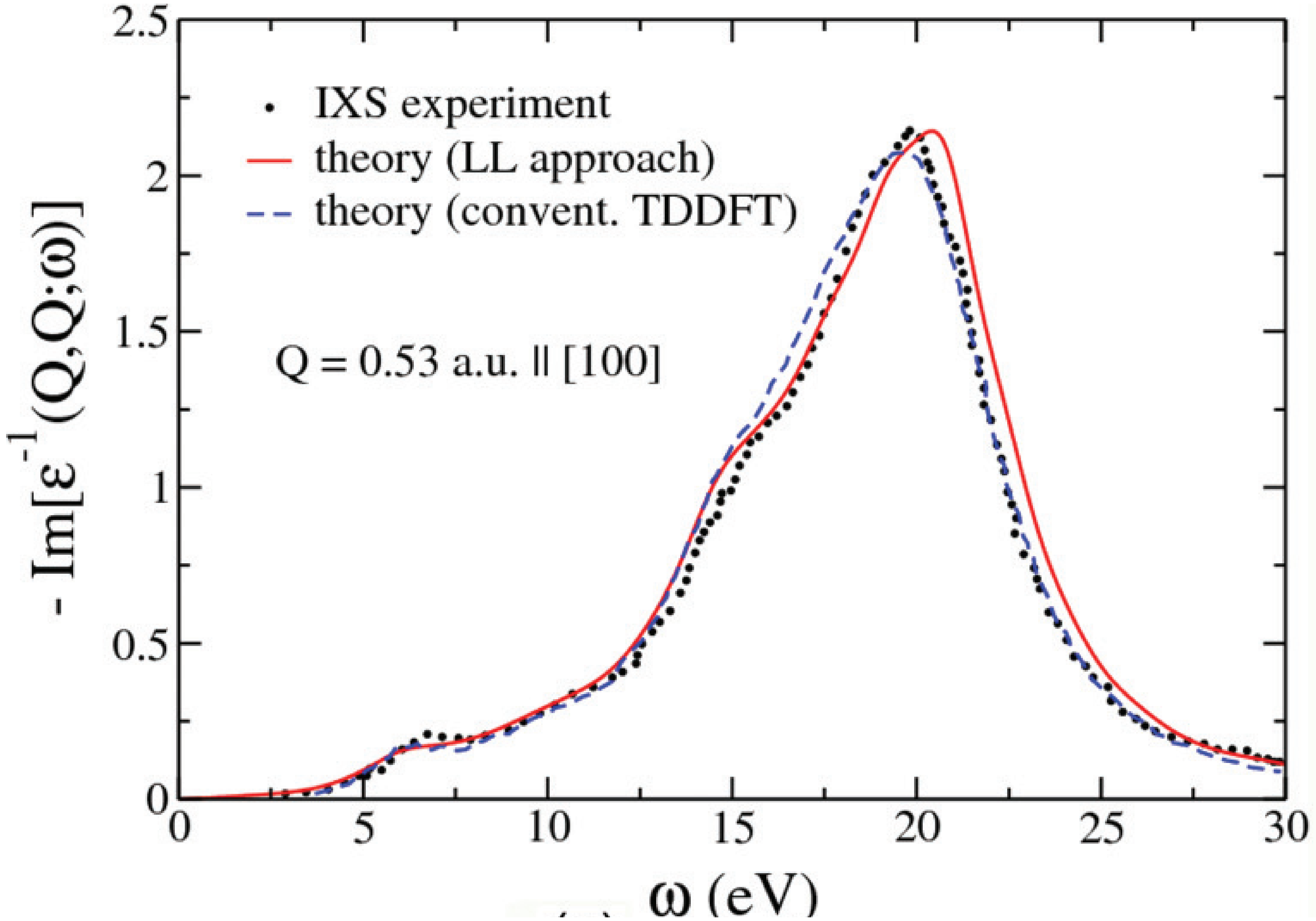


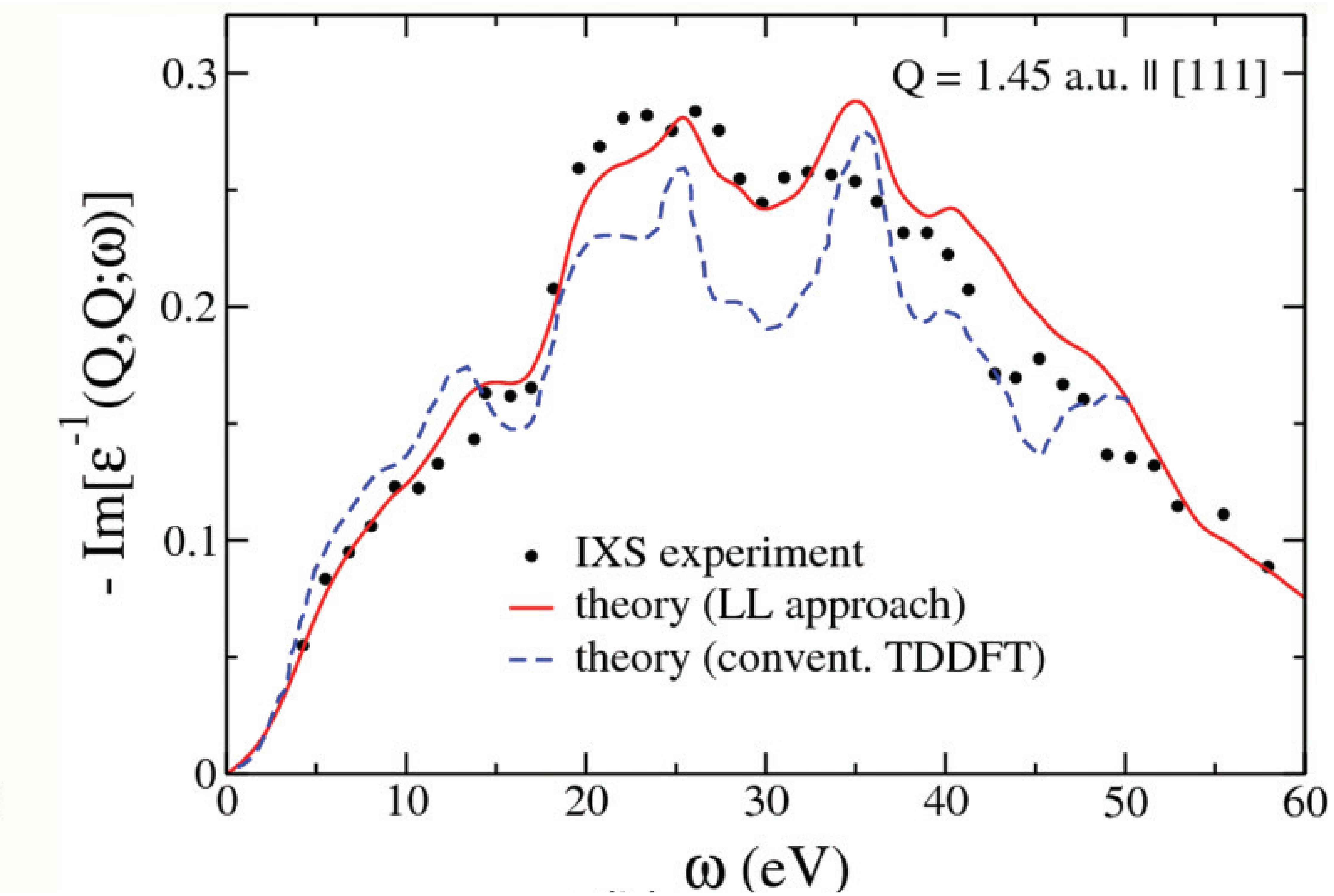
why grass is green



EELS & IXS spectra in Silicon from TDDFpT

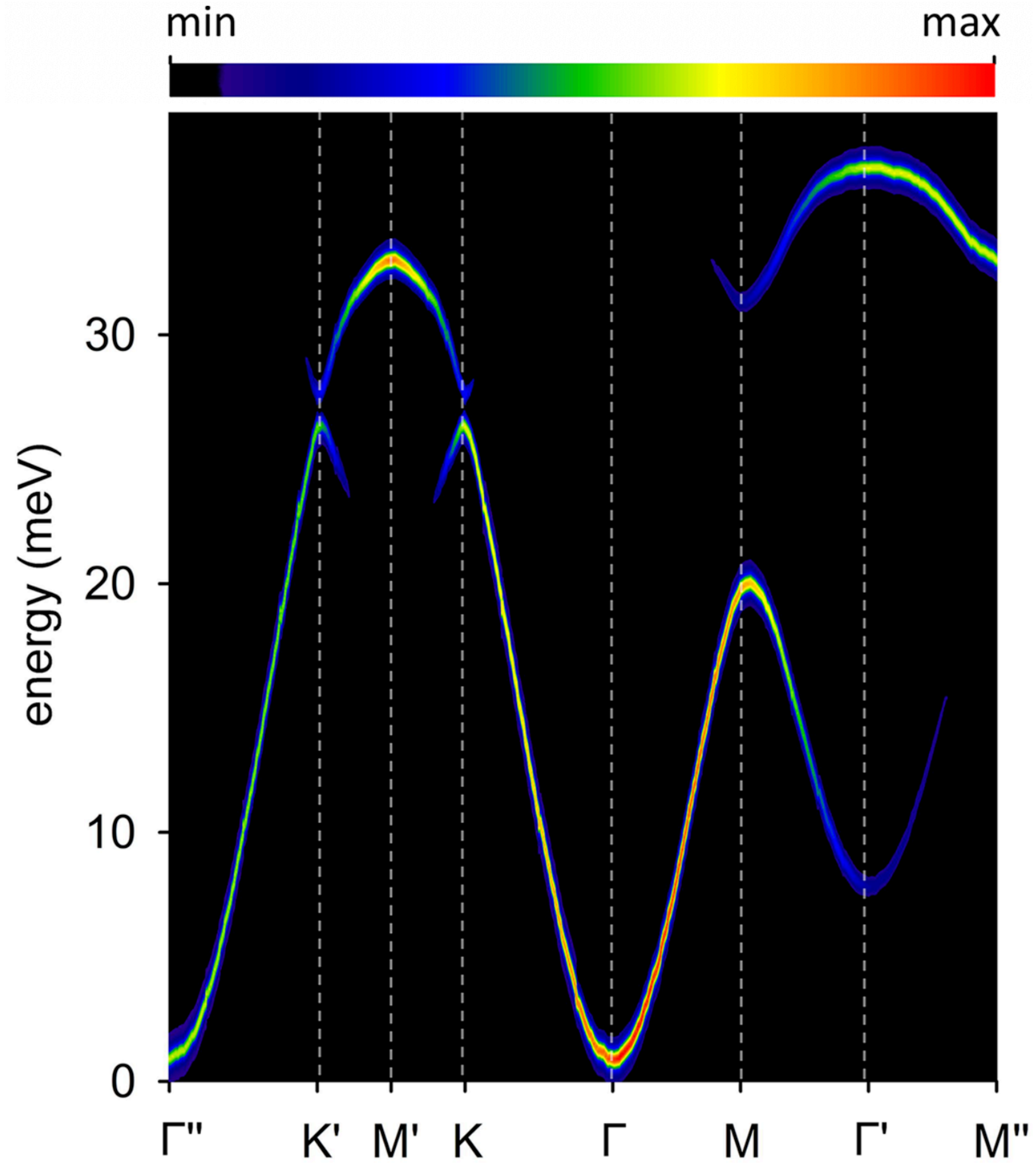
Si





I. Timrov, N. Vast, R. Gebauer & SB, Phys. Rev. B **88**, 64301 (2013)

spin-fluctuation (magnon) dispersions in CrI_3



T. Gorni, O. Baseggio, P. Delugas, I. Timrov & SB, PRB **107**, L220410 (2023)

these slides shortly at
http://talks.baroni.me