TDDFT of magneto-optical response of solids

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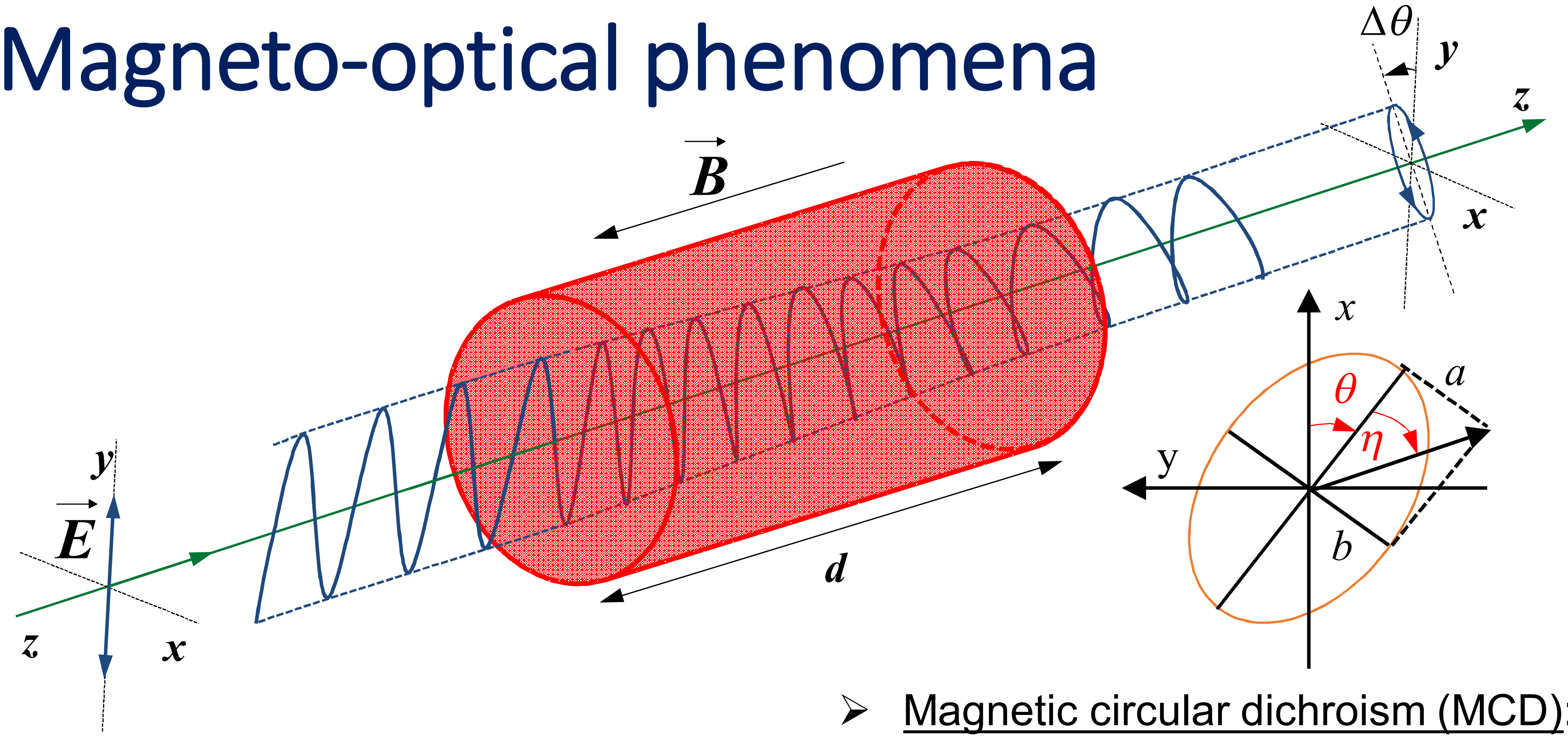
MARIE CURIE ACTIONS

Ouline

- Magneto-optical phenomena
- Magneto-optical response of finite systems
- Green function in arbitrary electromagnetic fields
- Expression for magneto-optical response of extended systems
- Computational scheme for calculation of magneto-optical response

Magneto-optical phenomena



- <u>Faraday effect</u>: Different refractive indices for left and right-circularly polarized light => Rotation of the polarization plane of linearly polarized light.

- <u>Magnetic circular dichroism (MCD)</u>: Different adsorption of left and right-circularly polarized light => Transformation of linearly polarized light to elliptically polarized light

$$\Delta\theta \approx -\pi \frac{\Omega d}{c} Im\left[\frac{\tilde{\boldsymbol{\alpha}}_{\mathrm{M}}^{xy} - \tilde{\boldsymbol{\alpha}}_{\mathrm{M}}^{yx}}{n}\right]$$

polarizability

refractive index

frequency

$$\eta \approx \pi \frac{\Omega d}{c} Re\left[\frac{\tilde{\boldsymbol{\alpha}}_{\mathrm{M}}^{xy} - \tilde{\boldsymbol{\alpha}}_{\mathrm{M}}^{yx}}{n}\right]$$

speed of light

L. D. Barron, *Molecular Light Scattering and Optical Activity*, 2nd ed. Cambridge University Press, Cambridge, 2004.

Finite systems

$$H = H_0 + V_E + V_B \qquad H_0 = \frac{p^2}{2m} + V(\vec{x}) \qquad V_E = \mu_\mu E_\mu \qquad V_B = M_\gamma B_\gamma$$

<u>Second-order perturbation theory</u> $\mu_\nu = \sum_{l=occ} \left[\left\langle \varphi_l^{(2)} \middle| \hat{\mu}_\nu \middle| \varphi_l^{(0)} \right\rangle + c.c. + \left\langle \varphi_l^{(1)} \middle| \hat{\mu}_\nu \middle| \varphi_l^{(1)} \right\rangle \right] = \alpha_{\nu\mu\gamma} E_\mu B_\gamma$

$$\begin{aligned}\alpha_{\nu\mu\gamma} = \sum_{l,n,m} \Big\{ & \bar{\mu}^\nu_{ln} \bar{\mu}^\mu_{nm} \bar{M}^\gamma_{ml} \left(G^<_l G^R_{n,+\Omega} G^R_{m,0} + G^A_{l,-\Omega} G^<_n G^A_{m,-\Omega} + G^A_{l,0} G^R_{n,+\Omega} G^<_m \right) \\ & + \bar{\mu}^\mu_{ln} \bar{\mu}^\nu_{nm} \bar{M}^\gamma_{ml} \left(G^<_l G^A_{n,-\Omega} G^R_{m,0} + G^R_{l,+\Omega} G^<_n G^R_{m,+\Omega} + G^A_{l,0} G^A_{n,+\Omega} G^<_m \right) \\ & + \left(\mu^\mu_{nn} - \mu^\mu_{ll} \right) G^<_l \left(\bar{\mu}^\nu_{ln} \bar{M}^\gamma_{nl} G^R_{n,+\Omega} G^R_{n,0} + \bar{M}^\gamma_{ln} \bar{\mu}^\nu_{nl} G^A_{n,0} G^A_{n,+\Omega} \right) \\ & + \left(\mu^\nu_{nn} - \mu^\nu_{ll} \right) G^<_l \left(\bar{M}^\gamma_{ln} \bar{\mu}^\mu_{nl} G^A_{n,0} G^R_{n,+\Omega} + \bar{\mu}^\mu_{ln} \bar{M}^\gamma_{nl} G^A_{n,-\Omega} G^R_{n,0} \right) \\ & + \left(M^\gamma_{nn} - M^\nu_{ll} \right) G^<_l \left(\bar{\mu}^\mu_{ln} \bar{\mu}^\nu_{nl} G^A_{l,-\Omega} G^A_{m,-\Omega} + \bar{\mu}^\nu_{ln} \bar{\mu}^\mu_{nl} G^R_{n,+\Omega} G^R_{n,+\Omega} \right) \end{aligned}$$

$$G^<_l = \begin{cases} 1, & l = \text{occ} \\ 0, & l = \text{unocc} \end{cases}$$

$$G^<_l G^{R(A)}_{n,\pm\Omega} = G^<_l \left(\varepsilon_l - \varepsilon_n \pm \hbar\Omega \pm i\delta \right)^{-1}$$

translational invariance in direction ν

$$\bar{\mu}^\nu_{ln} = \left\langle l \middle| \hat{\mu}_\nu - \mu^\nu_{ll} \middle| n \right\rangle \qquad \mu^\nu_{ll} = \left\langle l \middle| \hat{\mu}_\nu \middle| l \right\rangle = e \left\langle l \middle| \hat{x}_\nu \middle| l \right\rangle$$

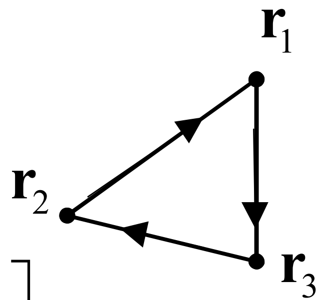
translational invariance in direction β

$$M^\gamma_{nm} G^<_l = \left\langle n \middle| \hat{M}_\gamma \middle| m \right\rangle G^<_l \rightarrow e_{\alpha\beta\gamma} \frac{e}{2c} \left(\left\langle n \middle| \hat{V}_\alpha \bar{x}_\beta \middle| m \right\rangle + \left\langle n \middle| \hat{V}_\alpha \left(x^\beta_{mm} - x^\beta_{ll} \right) \middle| m \right\rangle \right) G^<_l$$

<u>Periodic systems:</u> $\left\langle l \middle| \hat{x}_\nu \middle| l \right\rangle = ?$

Green function in static uniform magnetic field

$$\left(\hbar\omega - H\right)_{\mathbf{r}_1\mathbf{r}_2} G_{\mathbf{r}_2\mathbf{r}_3} = \delta_{\mathbf{r}_1\mathbf{r}_3} \qquad f_{\mathbf{r}_1\mathbf{r}_2} = \tilde{f}_{\mathbf{r}_1\mathbf{r}_2}\, exp\left[i\frac{e}{\hbar c}\int_{\mathbf{r}_2}^{\mathbf{r}_1} \mathbf{A}(\xi)\,d\xi \right]$$



with lattice translational symmetry

$$\left(\hbar\omega - \tilde{H}\right)_{\mathbf{r}_1\mathbf{r}_2} \tilde{G}_{\mathbf{r}_2\mathbf{r}_3}\, exp\left[i\frac{e}{\hbar c}\int_{\mathbf{r}_3\to\mathbf{r}_2\to\mathbf{r}_1} \mathbf{A}(\xi)\,d\xi \right] = \delta_{\mathbf{r}_1\mathbf{r}_3}\, exp\left[\int_{\mathbf{r}_3\to\mathbf{r}_1} \mathbf{A}(\xi)\,d\xi \right]$$

Chen et al. Phys. Rev. B 84, 205137 (2011)

$$\tilde{H}_{\mathbf{r}_1\mathbf{r}_2} = H_{0\mathbf{r}_1\mathbf{r}_2}$$

$$\int_{\Delta} \mathbf{A}(\xi)\,d\xi = -\frac{1}{2}\mathbf{B}\left[(\mathbf{r}_2 - \mathbf{r}_1)\times(\mathbf{r}_3 - \mathbf{r}_2)\right]$$

<u>To the first order in B</u> $\left(\hbar\omega - \tilde{H}_0\right)\delta\tilde{G} = \frac{ie}{2\hbar c} e_{\alpha\beta\gamma} B_\gamma \left[H_0, r_\alpha\right]\left[\tilde{G}, r_\beta\right]$ $\quad \mathbf{V}_0 = -i\left[\mathbf{r}, H_0\right]/\hbar$

<u>In crystal-momentum representation</u> $\left[\mathbf{r}, \tilde{G}\right] = i\partial\tilde{G}/\partial\mathbf{k}$

$$\delta\tilde{G}_{\mathrm{B}}(\omega) = -\frac{ie}{2c} e_{\alpha\beta\gamma} B_\gamma G_0(\omega) V_{0\alpha} \frac{\partial G_0(\omega)}{\partial k_\beta} \qquad G_0(\omega) = \sum_n \frac{|n\rangle\langle n|}{\hbar\omega - \varepsilon_n}$$

<u>Change in density of states</u> <u>Chern number</u>

$$\delta\rho_{\mathrm{B}} = \int \frac{d\omega\, d\vec{k}}{(2\pi)^4 i} \mathrm{Tr}\left(\delta G_B\right) = e_{\alpha\beta\gamma} \frac{eB_\gamma}{\hbar c} \int \frac{d\vec{k}}{(2\pi)^3} \sum_{l=\mathrm{occ}} \left\langle \frac{\partial l}{\partial k_\alpha} \middle| \frac{\partial l}{\partial k_\beta} \right\rangle = \frac{e}{\hbar c}\frac{BC_1}{2\pi}$$

Green function in magnetic field

$$\delta\tilde{G}_{\mathrm{B}}(\omega) = -\frac{ie}{2c} e_{\alpha\beta\gamma} B_\gamma G_0(\omega) V_{0\alpha} \frac{\partial G_0(\omega)}{\partial k_\beta}$$

$$M_\gamma = e_{\alpha\beta\gamma} \frac{e}{2c} \tilde{V}_\alpha \bar{x}_\beta$$

Matrix elements of magnetic moment

$$\delta G^<_{\mathrm{B}}(\omega) = -\frac{ie}{2c} e_{\alpha\beta\gamma} B_\gamma \Big\{ (A)\ G^R_n G^<_l \langle n|\tilde{V}_\alpha \bar{x}_\beta|l\rangle + G^<_n G^A_l \langle n|\bar{x}_\beta \tilde{V}_\alpha|l\rangle - \partial_\omega G^<_l \langle l|\tilde{V}_\alpha \bar{x}_\beta|l\rangle$$

$$(B)\ -\sum_m G^<_m \langle n|\bar{x}_\alpha|m\rangle\langle m|\bar{x}_\beta|l\rangle - \delta_{ln} G^<_l \langle l|\bar{x}_\alpha \bar{x}_\beta|l\rangle$$

$$(C)\ +2\delta_{ln} G^<_l \langle l|\bar{x}_\alpha \bar{x}_\beta|l\rangle + 2\partial_\omega G^<_l\, \partial_{k_\alpha} \varepsilon_{l\mathbf{k}} \langle n|\bar{x}_\beta|l\rangle \Big\}$$

= 0 for finite systems

$$G^<_l \tilde{V}_\alpha = \frac{\partial(H_0 + \varepsilon_{l\mathbf{k}})}{\hbar \partial k_\alpha}$$

$$x_\mu \to i\partial / \partial k_\mu \ \textbf{?}$$

$$\langle n|\bar{x}_\mu|l\rangle = \frac{\langle n|[H_0, x_\mu]|l\rangle}{\varepsilon_{n\mathbf{k}} - \varepsilon_{l\mathbf{k}}} = i\langle n|\left(\frac{\partial}{\partial k_\mu} - \langle l|\frac{\partial}{\partial k_\mu}|l\rangle\right)|l\rangle$$

$$G^<_l G^{R(A)}_{n,\pm\Omega} = \frac{G^<_l}{\varepsilon_{l\mathbf{k}} - \varepsilon_{n\mathbf{k}} \pm \hbar\Omega \pm i\delta}$$

Green function in electromagnetic wave

$$\tilde{\mathbf{E}} = \mathbf{E}_\Omega \, exp\left(i\mathbf{qr} - i\Omega t\right) \qquad \tilde{\mathbf{B}} = \mathbf{B}_\Omega \, exp\left(i\mathbf{qr} - i\Omega t\right) \qquad q \rightarrow 0$$

$$\mathbf{B}_\Omega << \mathbf{B} \qquad \mathbf{B}_\Omega \propto \left|\mathbf{E}_\Omega\right|\left(V/c\right) << \left|\mathbf{E}_\Omega\right|$$

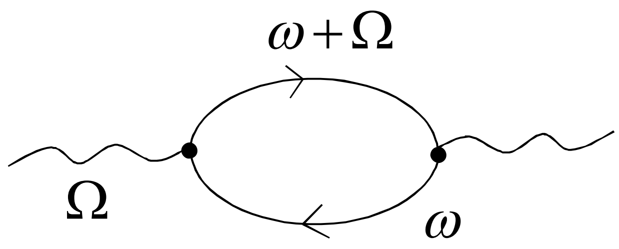
$$\left(\hbar\left(\omega+\Omega\right)+i\hbar\partial_t - H\right)_{\mathbf{r}_1\mathbf{r}_2} G_{\mathbf{r}_2\mathbf{r}_3} = \delta_{\mathbf{r}_1\mathbf{r}_3} \qquad G_{\mathbf{r}_1\mathbf{r}_2} = \tilde{G}_{\mathbf{r}_1\mathbf{r}_2} \, exp\left[i\frac{e}{\hbar c}\int_{\mathbf{r}_2}^{\mathbf{r}_1} \mathbf{A}(\xi)\, d\xi \right]$$

$$\frac{\partial}{\partial t}\int_{\mathbf{r}_2}^{\mathbf{r}_1} \mathbf{A}(\xi)\, d\xi \approx -c\left(r_{1\mu} - r_{2\mu}\right)E_\mu \qquad \left(\hbar\omega + \hbar\Omega - \tilde{H}_0\right)\delta\tilde{G} = eE_\mu\left[r_\mu, \tilde{G}\right]$$

In crystal-momentum representation

$$\delta\tilde{G}_E(\omega) = ieE_\mu G_0(\omega+\Omega)\frac{\partial G_0(\omega)}{\partial k_\mu}$$

Optical response



$$j_\nu(\Omega) = e\mathrm{Tr}\int \frac{d\omega}{2\pi i}\left\{V_{0\nu}\delta\tilde{G}_E^<\right\} = \sigma_{\nu\mu}E_\mu$$

$$\Rightarrow \quad \alpha_{\nu\mu} = i\sigma_{\nu\mu}/\Omega$$

$x_\mu \to i\partial/\partial k_\mu$ **?**

position operator = d/dk for $n \neq l$

1. $$\langle n|\bar{x}_\mu|l\rangle = i\langle n|\left(\frac{\partial}{\partial k_\mu} - \langle l|\frac{\partial}{\partial k_\mu}|l\rangle\right)|l\rangle \qquad n \neq l \qquad \left[\bar{x}_\mu, \bar{x}_\nu\right] \neq 0$$

2. $$\left[x_\mu, F(\omega)\right] = i\frac{\partial F(\omega)}{\partial k_\mu} \qquad X_\mu R(\omega)|n\rangle = i\frac{\partial R(\omega)|n\rangle}{\partial k_\mu}$$

position "superoperator"

$$\left[X_\mu, X_\nu\right] = 0$$

$$\left[V_\mu, X_\nu\right] = -\frac{i\hbar}{m}\delta_{\mu\nu}$$

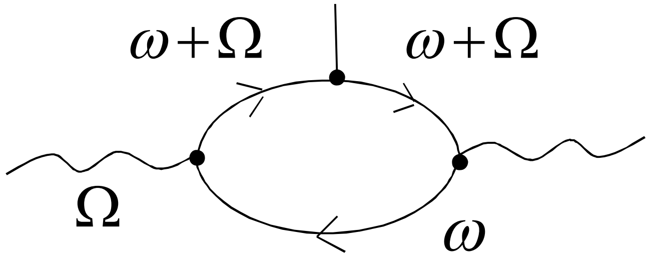
$$\sigma_{\nu\mu} = i\frac{e^2\Omega}{\hbar}\int\frac{d\vec{k}}{(2\pi)^3}\sum_{l,n}G_l^<\langle l|\left\{X_\nu G^R_{n,+\Omega}X_\mu + X_\mu G^A_{n,-\Omega}X_\nu|l\rangle\right\}$$

$$= i\frac{e^2}{\hbar}\int\frac{d\vec{k}}{(2\pi)^3}\sum_{l,n}G_l^<\left\{\left\langle\partial_{k_\nu}l\middle|\partial_{k_\mu}l\right\rangle - \left\langle\partial_{k_\mu}l\middle|\partial_{k_\nu}l\right\rangle + \hbar\Omega\langle l|\left(\bar{x}_\nu G^R_{n,+\Omega}\bar{x}_\mu + \bar{x}_\mu G^A_{n,-\Omega}\bar{x}_\nu\right)|l\rangle\right\}$$

Berry curvature = $\delta\rho_B$ =>
Anomalous Hall effect

Optical response
of finite systems

Magneto-optical response



$$j_\nu(\Omega) = e\mathrm{Tr}\int\frac{d\omega}{2\pi i}\left\{V_{0\nu}\delta\tilde{G}^<_{EB}\right\} = \sigma_{\nu\mu\gamma}E_\mu B_\gamma$$

$$\Rightarrow \quad \alpha_{\nu\mu\gamma} = i\sigma_{\nu\mu\gamma}/\Omega$$

$$\delta\tilde{G}_{EB} = -\frac{e}{2c}e_{\alpha\beta\gamma}B_\gamma G^0 V_\alpha\left[x_\beta,\delta\tilde{G}_E(\omega)\right] + eE_\mu G^0_{+\Omega}\left[x_\mu,\delta\tilde{G}_B(\omega)\right]$$

$$= -\frac{e^2}{2c}e_{\alpha\beta\gamma}E_\mu B_\gamma\left\{G^0_{+\Omega}V_\alpha\left[x_\beta,G^0_{+\Omega}\left[x_\mu,G\right]\right] + G^0_{+\Omega}\left[x_\mu,G^0V_\alpha\left[x_\beta,G\right]\right]\right\}$$

$$\sigma_{\nu\mu\gamma} = -i\frac{e^3\Omega}{2c}e_{\alpha\beta\gamma}\int\frac{d\vec{k}}{(2\pi)^3}\sum_{l,n,m}G^<_l\langle l|\{X_\nu G^R_{n,+\Omega}X_\mu G^R_{m,+0}\tilde{V}_\alpha X_\beta + X_\mu G^A_{n,-\Omega}\tilde{V}_\alpha X_\beta G^A_{m,-\Omega}X_\nu$$
$$\tilde{V}_\alpha X_\beta G^A_{n,0}X_\nu G^R_{m,+\Omega}X_\mu + X_\mu G^A_{n,-\Omega}X_\nu G^R_{m,+0}\tilde{V}_\alpha X_\beta$$
$$X_\nu G^R_{n,+\Omega}\tilde{V}_\alpha X_\beta G^R_{m,+\Omega}X_\mu + \tilde{V}_\alpha X_\beta G^A_{n,0}X_\mu G^A_{m,-\Omega}X_\nu\}|l\rangle$$
$$-i\langle l|\tilde{V}_\alpha|\partial l/\partial k_\beta\rangle\langle l|X_\nu\left(G^R_{n,+\Omega}\right)^2X_\mu + X_\mu\left(G^A_{n,-\Omega}\right)^2X_\nu|l\rangle$$
$$-2i\langle\partial l/\partial k_\alpha|\partial l/\partial k_\beta\rangle\langle l|X_\nu G^R_{n,+\Omega}X_\mu + X_\mu G^A_{n,-\Omega}X_\nu|l\rangle\}$$

Finite system

Berry curvature $=\delta\rho_B$

Optical response

Magneto-optical response

$$M^{\alpha\beta} = \frac{e}{2c}\tilde{V}_{\alpha}\bar{x}_{\beta}$$

$$\sigma_{\nu\mu\gamma} = -i\Omega e_{\alpha\beta\gamma}\int\frac{d\vec{k}}{(2\pi)^3}\sum_{l,n,m} G_l^{<}\left\{\bar{\mu}_{ln}^{\nu}\bar{\mu}_{nm}^{\mu}\bar{M}_{ml}^{\alpha\beta}G_{n,+\Omega}^{R}G_{m,0}^{R} + \left(\mu_{nn}^{\mu} - \mu_{ll}^{\mu}\right)\bar{\mu}_{ln}^{\nu}\bar{M}_{nl}^{\gamma}G_{n,+\Omega}^{R}G_{n,0}^{R}\right.$$

$$+ieG_l^{<}\bar{\mu}_{ln}^{\nu}G_{n,+\Omega}^{R}\partial_{k_\mu}\left(\bar{M}_{nl}^{\alpha\beta}G_{n,+0}^{R}\right)$$

finite systems

integral of k-derivative

$$-\frac{ie}{\hbar\Omega}\partial_{k_\mu}\left(G_l^{<}\bar{\mu}_{ln}^{\nu}G_{n,+0}^{R}\bar{M}_{nl}^{\alpha\beta}\right)$$

$$x_{nn}^{\mu} = \langle n|\partial_{k_\mu}|n\rangle$$

$$+\{\nu \leftrightarrow \mu\} + c.c.$$

$$\langle n|\left[\hat{x}_\mu, |n\rangle G_n \langle n|f|l\rangle\langle l|\right]|l\rangle =$$

$$\left(x_{nn}^{\mu} - x_{ll}^{\mu}\right)G_n\langle n|f|l\rangle +$$

$$i\partial_{k_\mu}\left(G_n\langle n|f|l\rangle\right)$$

$$\bar{\mu}_{ln}^{\nu}\bar{M}_{nm}^{\alpha\beta}\bar{\mu}_{ml}^{\mu}G_{n,+\Omega}^{R}G_{m,+\Omega}^{R} + \left(M_{nn}^{\alpha\beta} - M_{ll}^{\alpha\beta}\right)\bar{\mu}_{ln}^{\nu}\bar{\mu}_{nl}^{\mu}G_{n,+\Omega}^{R}G_{n,+\Omega}^{R}$$

$$+\frac{ie}{2c}\bar{\mu}_{ln}^{\nu}G_{n,+\Omega}^{R}\tilde{V}_{nm}^{\alpha}\partial_{k_\beta}\left(\bar{\mu}_{ml}^{\mu}G_{m,+\Omega}^{R}\right)$$

$$+\frac{ie}{2c}\partial_{k_\beta}\left(G_l^{<}\tilde{V}_{ln}^{\alpha}G_{n+,0}^{A}\bar{\mu}_{nm}^{\nu}G_{m,+\Omega}^{R}\bar{\mu}_{ml}^{\mu}\right)$$

$$G_l^{<}\tilde{V}_{\alpha} = \frac{\partial\left(H_0 + \varepsilon_{l\mathbf{k}}\right)}{\hbar\partial k_\alpha}$$

$$+\frac{e}{2c}\left[2\langle l|\bar{x}_\alpha\bar{x}_\beta|l\rangle\bar{\mu}_{ln}^{\nu}\bar{\mu}_{nl}^{\mu}G_{n,+\Omega}^{R}\right.$$

$$+\left(\langle l|\bar{x}_\beta\bar{x}_\nu|l\rangle - \langle l|\bar{x}_\nu\bar{x}_\beta|l\rangle\right)\bar{\mu}_{ln}^{\alpha}\bar{\mu}_{nl}^{\mu}G_{n,+\Omega}^{R}$$

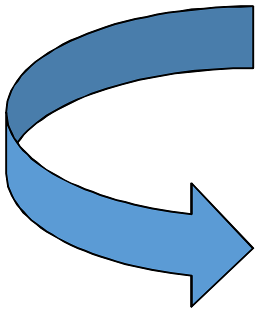
$$\left.\left.+\left(\langle l|\bar{x}_\beta\bar{x}_\mu|l\rangle - \langle l|\bar{x}_\mu\bar{x}_\beta|l\rangle\right)\bar{\mu}_{ln}^{\nu}\bar{\mu}_{nl}^{\alpha}G_{n,+\Omega}^{R}\right] + c.c.\right\}$$

= density of states in magnetic field x optical response

Dipole moment matrix elements

$$\tilde{\mu}^{\mu}_{nm} G^<_l = e\left\langle \psi_n \middle| x_\mu - \langle \psi_l | x_\mu | \psi_l \rangle \middle| \psi_m \right\rangle G^<_l \qquad \tilde{M}^{\alpha\beta}_{nm} G^<_l = \left(M^{\alpha\beta}_{nm} - M^{\alpha\beta}_{ll} \right) G^<_l$$

$$M^{\alpha\beta}_{nm} G^<_l = \frac{e}{2c}\left\langle \psi_n \middle| V_\alpha \left(x_\beta - \langle \psi_l | x_\beta | \psi_l \rangle \right) \middle| \psi_m \right\rangle G^<_l$$



finite system

periodic system

$$\tilde{\mu}^{\mu}_{nm} G^<_l = e\left\langle n \middle| \partial_{k_\mu} - \langle l | \partial_{k_\mu} l \rangle \middle| m \right\rangle G^<_l \qquad \tilde{M}^{\alpha\beta}_{nm} G^<_l = \left(M^{\alpha\beta}_{nm} - M^{\alpha\beta}_{ll} \right) G^<_l$$

$$M^{\alpha\beta}_{nm} G^<_l = \frac{e}{2c\hbar}\left\langle n \middle| \partial_{k_\alpha} \left(H + \varepsilon_{l\mathbf{k}} \right) \left(\partial_{k_\beta} - \langle l | \partial_{k_\beta} l \rangle \right) \middle| m \right\rangle G^<_l$$

<u>In agreement with</u>

Essin et al Phys. Rev. B 81, 205104 (2010)

Shi et al. Phys. Rev. Lett. 99, 197202 (2007)

Computational scheme

1. Liouville equation

$$i\hbar\partial_t\rho - [H_0,\rho] = [H_1,\rho] \qquad \rho_{\mathbf{r}_1\mathbf{r}_2} = \tilde{\rho}_{\mathbf{r}_1\mathbf{r}_2}\, exp\left[i\frac{e}{\hbar c}\int_{\mathbf{r}_2}^{\mathbf{r}_1} \mathbf{A}(\boldsymbol{\xi})\, d\boldsymbol{\xi} \right]$$

<u>Electromagnetic wave</u>

$$\pm\hbar\Omega\delta\tilde{\rho}_{\mathbf{k},\pm\Omega} \pm \left[H_0, \delta\tilde{\rho}_{\mathbf{k},\pm\Omega} \right] = ieE_\mu \frac{\partial\tilde{\rho}_{\mathbf{k},\pm\Omega}}{\partial k_\mu}$$

<u>Uniform magnetic field</u>

$$\left[H_0, \delta\tilde{\rho}_{\mathbf{k}} \right] = \frac{ie}{2c} e_{\alpha\beta\gamma} B_\gamma \left(\frac{\partial\tilde{\rho}_{\mathbf{k}}}{\partial k_\alpha} V_\beta - V_\alpha \frac{\partial\tilde{\rho}_{\mathbf{k}}}{\partial k_\beta} \right)$$

2. Idempotency

$$\rho = \rho\rho$$

$$\delta\tilde{\rho}_D = \frac{ie}{2c\hbar} e_{\alpha\beta\gamma} B_\gamma \frac{\partial\tilde{\rho}_{\mathbf{k}}}{\partial k_\alpha} \frac{\partial\tilde{\rho}_{\mathbf{k}}}{\partial k_\beta}$$

Gonze&Zwanziger, Phys. Rev. B 84, 064445 (2011)

There is no need to solve Liouville equation for density matrix elements within occupied and unoccupied subspaces

First-order corrections

B

$$\tilde{\rho}_D^{(1)} = \frac{ie}{2c\hbar} e_{\alpha\beta\gamma} B_\gamma \frac{\partial \rho^{(0)}}{\partial k_\alpha} \frac{\partial \rho^{(0)}}{\partial k_\beta}$$

"diagonal" terms

$$\tilde{\rho}_B^{(1)}(CC) = \left(1-\rho^{(0)}\right) \tilde{\rho}_D^{(1)} \left(1-\rho^{(0)}\right)$$

$$\tilde{\rho}_B^{(1)}(VV) = -\rho^{(0)} \tilde{\rho}_D^{(1)} \rho^{(0)}$$

$$\left|\eta_{v\mathbf{k}}^{(1)}\right\rangle = P_c \tilde{\rho}_B^{(1)} \left|u_{v\mathbf{k}}^{(0)}\right\rangle \qquad P_c = \left(1-\rho^{(0)}\right)$$

Lazzeri&Mauri, Phys. Rev. B 68, 161101 (2003)

terms between CV subspaces

$$\left(H_0 - \varepsilon_{v\mathbf{k}}^{(0)}\right)\left|\eta_{v\mathbf{k}}^{(1)}\right\rangle = P_c \frac{ie}{2c} e_{\alpha\beta\gamma} B_\gamma \left(V_\alpha \frac{\partial \rho^{(0)}}{\partial k_\beta} - \frac{\partial \rho^{(0)}}{\partial k_\alpha} V_\beta \right) \left|u_{v\mathbf{k}}^{(0)}\right\rangle$$

$$\tilde{\rho}_B^{(1)}(CV) = \sum_v \left|\eta_{v\mathbf{k}}^{(1)}\right\rangle \left\langle u_{v\mathbf{k}}^{(0)}\right| \qquad \tilde{\rho}_B^{(1)}(VC) = \sum_v \left|u_{v\mathbf{k}}^{(0)}\right\rangle \left\langle \eta_{v\mathbf{k}}^{(1)}\right|$$

E

$$\left|\xi_{v\mathbf{k},\pm\Omega}^{(1)}\right\rangle = P_c \tilde{\rho}_{E,\pm\Omega}^{(1)} \left|u_{v\mathbf{k}}^{(0)}\right\rangle$$

terms between CV subspaces

$$\left(\pm\hbar\Omega + H_0 - \varepsilon_{v\mathbf{k}}^{(0)}\right)\left|\xi_{v\mathbf{k},\pm\Omega}^{(1)}\right\rangle = P_c ie E_{\mu,\pm\Omega} \frac{\partial \rho^{(0)}}{\partial k_\mu} \left|u_{v\mathbf{k}}^{(0)}\right\rangle$$

$$\tilde{\rho}_{E,\pm\Omega}^{(1)}(CV) = \sum_v \left|\xi_{v\mathbf{k},\pm\Omega}^{(1)}\right\rangle \left\langle u_{v\mathbf{k}}^{(0)}\right| \qquad \tilde{\rho}_{E,\pm\Omega}^{(1)}(VC) = \sum_v \left|u_{v\mathbf{k}}^{(0)}\right\rangle \left\langle \xi_{v\mathbf{k},\mp\Omega}^{(1)}\right|$$

Second-order corrections

$$\tilde{\rho}^{(2)}_{D,\pm\Omega} = \tilde{\rho}^{(1)}_{B}\tilde{\rho}^{(1)}_{E,\pm\Omega} + \tilde{\rho}^{(1)}_{E,\pm\Omega}\tilde{\rho}^{(1)}_{B} + \frac{ie}{2c\hbar}e_{\alpha\beta\gamma}B_\gamma\left(\frac{\partial\tilde{\rho}^{(1)}_{E,\pm\Omega}}{\partial k_\alpha}\frac{\partial\rho^{(0)}}{\partial k_\beta} + \frac{\partial\rho^{(0)}}{\partial k_\alpha}\frac{\partial\tilde{\rho}^{(1)}_{E,\pm\Omega}}{\partial k_\beta}\right)$$

"diagonal" terms

$$\tilde{\rho}^{(2)}_{EB,\pm\Omega}(VV) = -\rho^{(0)}\tilde{\rho}^{(2)}_{D,\pm\Omega}\rho^{(0)} \qquad \tilde{\rho}^{(2)}_{EB,\pm\Omega}(CC) = \left(1-\rho^{(0)}\right)\tilde{\rho}^{(2)}_{D,\pm\Omega}\left(1-\rho^{(0)}\right)$$

$$\left|\eta^{(2)}_{v\mathbf{k},\pm\Omega}\right\rangle = P_c\tilde{\rho}^{(2)}_{EB,\pm\Omega}\left|u^{(0)}_{v\mathbf{k}}\right\rangle$$

terms between CV subspaces

$$\left(\pm\hbar\Omega + \varepsilon^{(0)}_{v\mathbf{k}} - H_0\right)\left|\eta^{(2)}_{v\mathbf{k},\pm\Omega}\right\rangle = P_c\left\{\frac{ie}{2c\hbar}e_{\alpha\beta\gamma}B_\gamma\left(V_\alpha\frac{\partial\tilde{\rho}^{(1)}_{E,\pm\Omega}}{\partial k_\beta} - \frac{\partial\tilde{\rho}^{(1)}_{E,\pm\Omega}}{\partial k_\alpha}V_\beta\right) - ieE_{\mu,\pm\Omega}\frac{\partial\tilde{\rho}^{(1)}_{B}}{\partial k_\mu}\right\}\left|u^{(0)}_{v\mathbf{k}}\right\rangle$$

$$\tilde{\rho}^{(2)}_{EB,\pm\Omega}(VC) = \sum_v\left|u^{(0)}_{v\mathbf{k}}\right\rangle\left\langle\eta^{(2)}_{v\mathbf{k},\mp\Omega}\right| \qquad \tilde{\rho}^{(2)}_{EB,\pm\Omega}(CV) = \sum_v\left|\eta^{(2)}_{v\mathbf{k},\pm\Omega}\right\rangle\left\langle u^{(0)}_{v\mathbf{k}}\right|$$

$$j_{\nu,\pm\Omega} = e\int\frac{d\vec{k}}{(2\pi)^3}\mathrm{Tr}\left\{V_{0\nu}\tilde{\rho}^{(2)}_{EB,\pm\Omega}\right\} = \sigma_{\nu\mu\gamma}E_{\mu,\pm\Omega}B_\gamma$$

Conclusions

- Non-equilibrium Green functions offer a unified approach to calculation of all-order response to arbitrary electromagnetic fields both for periodic and molecular systems
- The expression for the magneto-optical response of insulating solids in the approximation of non-interacting electrons is obtained
- Gauge invariant expressions for the magnetic and electric dipole moments are suggested
- A computational scheme based on density matrix-perturbation theory is developed

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SEVENTH FRAMEWORK PROGRAMME

DYNAMO

MARIE CURIE ACTIONS