TDDFT of magneto-optical response of solids

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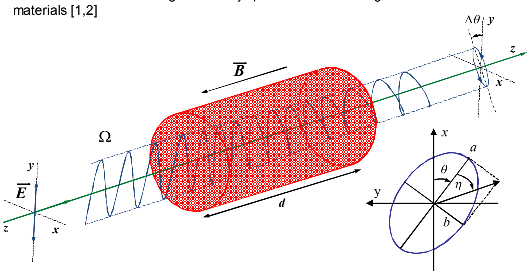
Magneto-optical phenomena

A magnetic field applied along the wave propagation leads to differences in the interaction of left and right-circularly polarized electromagnetic waves with materials [1,2]



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

$$\Delta\theta \approx -2\pi\frac{\Omega d}{c} Im\left[\left\langle\tilde{\alpha}_{XY}(-\Omega;\Omega)\right\rangle\right]$$

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

$$\eta \approx 2\pi\frac{\Omega d}{c} Re\left[\left\langle\tilde{\alpha}_{XY}(-\Omega;\Omega)\right\rangle\right]$$

c is the speed of light

$\left\langle\tilde{\alpha}_{XY}(-\Omega;\Omega)\right\rangle$ is the orientational average of asymmetrized polarizability for the sample subjected to the electric field in the XY plane

To the first order in magnetic field $\quad \tilde{\alpha}_{\nu\mu} = \tilde{\alpha}^0_{\nu\mu} + \tilde{\alpha}^B_{\nu\mu\gamma}B_\gamma$

For closed shell systems, $\quad \left\langle\tilde{\alpha}_{XY}\right\rangle = \frac{1}{6}B_z e_{\nu\mu\gamma}\tilde{\alpha}^B_{\nu\mu\gamma}$

Magneto-optical response of finite systems

Interactions with the electromagnetic wave and magnetic field can be considered as perturbations [1,2]

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

$$\alpha_{\nu\mu\gamma} = \varepsilon_{\alpha\beta\gamma}\sum_{l,n,m}\left\{\bar{\mu}^\nu_{ln}\bar{\mu}^\mu_{nm}\bar{M}^{\alpha\beta}_{ml}\left(G^<_l G^R_{n,+\Omega}G^R_{m,0} + G^A_{l,-\Omega}G^<_n G^A_{m,-\Omega} + G^A_{l,0}G^R_{n,+\Omega}G^<_m\right)\right.$$
$$\left.\bar{\mu}^\mu_{ln}\bar{\mu}^\nu_{nm}\bar{M}^{\alpha\beta}_{ml}\left(G^<_l G^A_{n,-\Omega}G^R_{m,0} + G^R_{l,+\Omega}G^<_n G^R_{m,+\Omega} + G^A_{l,0}G^A_{n,+\Omega}G^<_m\right)\right\}$$

$$G^<_l = \begin{cases}1, & l=\text{occ}\\ 0, & l=\text{unocc}\end{cases} \qquad G^<_l G^R_{n,+\Omega} = \frac{G^<_l}{\varepsilon_l - \varepsilon_n + \hbar\Omega + i\delta} \qquad G^<_l G^A_{n,-\Omega} = \frac{G^<_l}{\varepsilon_l - \varepsilon_n - \hbar\Omega - i\delta}$$

$$\bar{\mu}^\nu_{ln}\bar{\mu}^\mu_{nm}\bar{M}^{\alpha\beta}_{ml}G^<_l = \left\langle\psi_l\left|\mu_\nu - \mu^\nu_{ll}\right|\psi_n\right\rangle\left\langle\psi_n\left|\mu_\mu - \mu^\mu_{ll}\right|\psi_m\right\rangle\left\langle\psi_m\left|M_{\alpha\beta} - M^{\alpha\beta}_{ll}\right|\psi_l\right\rangle G^<_l$$

$$\mu^\nu_{ll} = \left\langle\psi_l\left|\mu_\nu\right|\psi_l\right\rangle = e\left\langle\psi_l\left|x_\nu\right|\psi_l\right\rangle \qquad M^{\alpha\beta}_{ll} = \left\langle\psi_l\left|M_{\alpha\beta}\right|\psi_l\right\rangle = \frac{e}{2c}\left\langle\psi_l\left|x_\alpha V_\beta\right|\psi_l\right\rangle$$

Problem for periodic systems: $\langle l|x_\nu|l\rangle = ?$

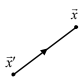
The position operator $\hat{x}$ and, consequently, operators of momenta $\hat{\mu}$ and $\hat{M}$ are ill defined under periodic conditions =>

A new unified approach using a gauge-invariant expression for the position operator should be developed.

Green function in electromagnetic fields

Uniform magnetic field

$$\left[\hbar\omega - \frac{1}{2m_e}\left(i\hbar\partial_\alpha + \frac{e}{c}A_\alpha\right)^2 - V(\vec{x})\right]G(\vec{x},\vec{x}') = \delta(\vec{x}-\vec{x}')$$



$$G(\vec{x},\vec{x}') = exp\left[i\frac{e}{\hbar c}\int_0^1\vec{A}(\vec{\xi})\frac{d\vec{\xi}}{d\lambda}d\lambda\right]\tilde{G}(\vec{x},\vec{x}') \qquad \vec{\xi} = \vec{x}' + \lambda(\vec{x}-\vec{x}')$$

Green function with lattice translational symmetry

$$-\frac{\partial}{\partial x_\alpha}\int_0^1 A_\nu(\vec{\xi})\frac{d\xi^\nu}{d\lambda}d\lambda = -A_\alpha(\vec{x}) + \int_0^1 F_{\nu\beta}(\vec{\xi})\frac{\partial\xi_\nu}{\partial x_\alpha}\frac{d\xi_\beta}{d\lambda}d\lambda$$

$$\boxed{\begin{gathered}F_{\alpha\beta} = \partial_\alpha A_\beta - \partial_\beta A_\alpha\\ F_{\alpha\beta} = e_{\alpha\beta\gamma}B_\gamma\end{gathered}}$$

$$= -A_\alpha(\vec{x}) + (x_\beta - x'_\beta)\int_0^1 F_{\alpha\beta}(\vec{\xi})\lambda d\lambda \approx -A_\alpha(\vec{x}) + \frac{1}{2}F_{\alpha\beta}(x_\beta - x'_\beta)$$

$$\left[\hbar\omega - H_0 - \frac{i\hbar e}{2m_e c}F_{\alpha\beta}(x_\beta - x'_\beta)\partial_{x_\alpha}\right]\tilde{G}(\vec{x},\vec{x}') = \delta(\vec{x}-\vec{x}')$$

$$\delta\tilde{G}_B(\vec{x},\vec{x}') = \frac{\hbar e}{2m_e c}F_{\alpha\beta}\int d\vec{x}_1 G_0(\vec{x},\vec{x}_1)(x_{1\beta} - x'_\beta)i\partial_{x_{1\alpha}}G(\vec{x}_1,\vec{x}')$$

In crystal momentum representation $\quad V_\alpha = \frac{\partial H_0(\vec{k})}{\hbar\partial k_\alpha} \qquad G_0(\omega) = \sum_n\frac{|n\rangle\langle n|}{\hbar\omega - \varepsilon_n}$

$$\delta\tilde{G}_B = -\frac{e}{2c}e_{\alpha\beta\gamma}B_\gamma G_0(\omega)V_\alpha\left[x_\beta, G_0(\omega)\right] = -\frac{ie}{2c}e_{\alpha\beta\gamma}B_\gamma G_0(\omega)V_\alpha\frac{\partial G(\omega)}{\partial k_\beta}$$

in agreement with [3]

Density of states

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

Chern number

Electromagnetic wave $\quad \vec{E} = \vec{E}_\Omega exp(i\vec{q}\vec{r} - i\Omega t) \qquad \vec{B} = \frac{\vec{q}}{\omega}\times\vec{E} \qquad q\to 0$

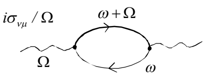
$$\frac{\partial}{\partial t}\int_0^1 A_\mu(\vec{\xi})\frac{d\xi_\mu}{d\lambda}d\lambda = -c(x_\mu - x'_\mu)\int_0^1 E_\mu(\vec{\xi})d\lambda \approx -c(x_\mu - x'_\mu)E_\mu$$

$$\delta\tilde{G}_E = -eE_\mu G_0(\omega+\Omega)\left[x_\mu, G(\omega)\right] = -ieE_\mu G_0(\omega+\Omega)\frac{\partial G(\omega)}{\partial k_\mu}$$

Optical response

The polarizability can be extracted from the current response

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



Traditionally, it is assumed that $x_\mu \to i\partial/\partial k_\mu$
Indeed for $n \neq l$

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

However, as $\left[\bar{x}_\mu,\bar{x}_\nu\right] \neq 0$, it is more convinient to derive the response using a different formulation.

According to the properties of Fourier transform, for any function F

$$\left[x_\mu, F(\omega)\right] = i\frac{\partial F(\omega)}{\partial k_\mu}$$

Let us introduce the position "superoperator" that acts on whole matrix elements

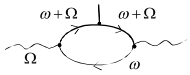
$$X_\mu R(\omega)|n\rangle = i\frac{\partial R(\omega)|n\rangle}{\partial k_\mu} \qquad \left[X_\mu, X_\nu\right] = 0 \qquad \left[V_\mu, X_\nu\right] = -\frac{i\hbar}{m}\delta_{\mu\nu}$$

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

$$= i\frac{e^2}{\hbar}\int\frac{d\vec{k}}{(2\pi)^3}\sum_{l,n}G^<_l\left\{\underbrace{\left\langle\frac{\partial l}{\partial k_\nu}\middle|\frac{\partial l}{\partial k_\mu}\right\rangle - \left\langle\frac{\partial l}{\partial k_\mu}\middle|\frac{\partial l}{\partial k_\nu}\right\rangle}_{\text{Berry curvature => Anomalous Hall effect [4]}} + \underbrace{\hbar\Omega\langle l|\left(\bar{x}_\nu G^R_{n,+\Omega}\bar{x}_\mu + \bar{x}_\mu G^A_{n,-\Omega}\bar{x}_\nu\right)|l\rangle}_{\text{Optical response for finite systems}}\right\}$$

Magneto-optical response

Electromagnetic wave +uniform magnetic field



$$\delta\tilde{G}_{EB} = -\frac{e}{2c}e_{\alpha\beta\gamma}B_\gamma G_0(\omega)V_\alpha\left[x_\beta,\delta\tilde{G}_E(\omega)\right] - eE_\mu G_0(\omega+\Omega)\left[x_\mu,\delta\tilde{G}_B(\omega)\right]$$

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

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

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

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

$$-iG^<_l\langle l|\tilde{V}_\alpha|\partial l/\partial k_\beta\rangle\langle l|X_\nu\left(G^R_{n,+\Omega}\right)^2 X_\mu + X_\mu\left(G^A_{n,-\Omega}\right)^2 X_\nu|l\rangle$$
$$\underbrace{-2iG^<_l\langle\partial l/\partial k_\alpha|\partial l/\partial k_\beta\rangle}_{\text{Berry curvature => Density of states in magnetic field}}\underbrace{\langle l|X_\nu G^R_{n,+\Omega}X_\mu + X_\mu G^A_{n,-\Omega}X_\nu|l\rangle\}}_{\text{Optical response}}$$

In terms of standard operators, the same expression is derived as follows

$$\sigma_{\nu\mu\gamma} = e^2\text{Tr}\int\frac{d\vec{k}}{(2\pi)^3}\left\{G^R_{B,+\Omega}\left[\bar{x}_\mu, G^<\right]V_\nu - \left[\bar{x}_\mu, G^R_{B,+\Omega}\right]G^<_B V_\nu + G^<_B\left[\bar{x}_\mu, G^A_{-\Omega}\right]V_\nu\right.$$
$$-\left[\bar{x}_\mu, G^<\right]G^A_{B,-\Omega}V_\nu - \delta_{\mu\nu}\left(G^R_{+\Omega}G^<_B + G^<G^A_{B,-\Omega}\right)$$
$$+\delta_{\alpha\nu}\left(G^R_{B',+\Omega}\left[\bar{x}_\mu, G^<\right] + G^<_{B'}\left[\bar{x}_\mu, G^A_{-\Omega}\right]\right)$$
$$\left.-\partial_{k_\alpha}\left(G^R_{B',+\Omega}\left[\bar{x}_\mu, G^<\right]V_\nu + G^<_{B'}\left[\bar{x}_\mu, G^A_{-\Omega}\right]V_\nu\right)\right\}$$

$$G^<_B(\omega) = (A)\ G^R_n G^<_l\langle n|\tilde{V}_\alpha\bar{x}_\beta|l\rangle + G^<_n G^A_l\langle n|\bar{x}_\beta\tilde{V}_\alpha|l\rangle - \partial G^<_l/\partial\omega\langle l|\tilde{V}_\alpha\bar{x}_\beta|l\rangle$$
$$(B)\ -\sum_m G^<_m\langle n|\bar{x}_\alpha|m\rangle\langle m|\bar{x}_\beta|l\rangle - \delta_{ln}G^<_l\langle l|\bar{x}_\alpha\bar{x}_\beta|l\rangle$$
$$(C)\ +2\delta_{ln}G^<_l\langle l|\bar{x}_\alpha\bar{x}_\beta|l\rangle + 2\partial_\omega G^<_l\partial_{k_\alpha}E_l\langle n|\bar{x}_\beta|l\rangle$$

Matrix elements of magnetic moment

$$G^R_B(\omega) = (A)\ G^R_n G^R_l\langle n|\tilde{V}_\alpha\bar{x}_\beta|l\rangle \qquad G^A_B(\omega) = (A)\ G^A_n G^A_l\langle n|\bar{x}_\beta\tilde{V}_\alpha|l\rangle$$
$$(B)\ -\sum_m\left(G^R_m - G^R_n\right)\langle n|\bar{x}_\alpha|m\rangle\langle m|\bar{x}_\beta|l\rangle \qquad (B)\ -\sum_m\left(G^A_m - G^A_l\right)\langle n|\bar{x}_\alpha|m\rangle\langle m|\bar{x}_\beta|l\rangle$$
$$(D)\ -\langle n|\bar{x}_\beta|l\rangle\left(\left(G^R_n\right)^2\partial_{k_\alpha}E_n + \left(G^A_l\right)^2\partial_{k_\alpha}E_l\right) \qquad (D)\ -\langle n|\bar{x}_\beta|l\rangle\left(\left(G^A_n\right)^2\partial_{k_\alpha}E_n + \left(G^R_l\right)^2\partial_{k_\alpha}E_l\right)$$
$$G^<_{B'}(\omega) = (B)\ \langle n|\bar{x}_\beta|l\rangle\left(G^<_l - G^<_n\right) \qquad G^R_{B'}(\omega) = (B)\ \langle n|\bar{x}_\beta|l\rangle\left(G^R_l - G^R_n\right)$$
$$(D)\ \left(G^R_l\right)^2\partial_{k_\beta}E_l$$

$$\alpha_{\nu\mu\gamma} = e_{\alpha\beta\gamma}\int\frac{d\vec{k}}{(2\pi)^3}\sum_{l,n,m}\{$$
$$\left.\begin{aligned}&\bar{\mu}^\nu_{ln}\bar{\mu}^\mu_{nm}\bar{M}^{\alpha\beta}_{ml}\left(G^<_l G^R_{n,+\Omega}G^R_{m,0} + G^A_{l,-\Omega}G^<_n G^A_{m,-\Omega} + G^A_{l,0}G^R_{n,+\Omega}G^<_m\right)\\ &+\bar{\mu}^\mu_{ln}\bar{\mu}^\nu_{nm}\bar{M}^{\alpha\beta}_{ml}\left(G^<_l G^A_{n,-\Omega}G^R_{m,0} + G^R_{l,+\Omega}G^<_n G^R_{m,+\Omega} + G^A_{l,0}G^A_{n,+\Omega}G^<_m\right)\end{aligned}\right\}\text{Finite system}$$

$$+G^<_l\bar{\mu}^\nu_{ln}G^R_{n,+\Omega}\partial_{k_\mu}\left(\bar{M}^{\alpha\beta}_{nl}G^R_{n,+0}\right) - G^A_{l,-\Omega}\bar{\mu}^\nu_{ln}G^<_n\partial_{k_\mu}\left(\bar{M}^{\alpha\beta}_{nl}G^A_{l,+0}\right)$$
$$+G^<_l\bar{\mu}^\mu_{ln}G^A_{n,-\Omega}\partial_{k_\nu}\left(\bar{M}^{\alpha\beta}_{nl}G^R_{n,+0}\right) - G^R_{l,+\Omega}\bar{\mu}^\mu_{ln}G^<_n\partial_{k_\nu}\left(\bar{M}^{\alpha\beta}_{nl}G^A_{l,+0}\right)$$
$$+G^<_l\bar{\mu}^\nu_{ln}G^R_{n,+\Omega}\tilde{V}^\alpha_{nm}\partial_{k_\beta}\left(\bar{\mu}^\mu_{ml}G^R_{m,+\Omega}\right) + G^<_l\bar{\mu}^\mu_{ln}G^A_{n,-\Omega}\tilde{V}^\alpha_{nm}\partial_{k_\beta}\left(\bar{\mu}^\nu_{ml}G^A_{m,-\Omega}\right)$$
$$-\frac{ie}{\hbar\Omega}\partial_{k_\mu}\left(G^<_l\bar{\mu}^\nu_{ln}G^R_{n,+0}\bar{M}^{\alpha\beta}_{nl} + G^<_l\bar{M}^{\alpha\beta}_{ln}G^A_{n,-\Omega}\bar{\mu}^\nu_{nl}\right) + \frac{ie}{\hbar\Omega}\partial_{k_\nu}\left(G^<_l\bar{\mu}^\mu_{ln}G^R_{n,+0}\bar{M}^{\alpha\beta}_{nl} + G^<_l\bar{M}^{\alpha\beta}_{ln}G^R_{n,+\Omega}\bar{\mu}^\mu_{nl}\right)$$
$$+\frac{ie}{2c}\partial_{k_\beta}\left(G^<_l\tilde{V}^\alpha_{ln}G^A_{n+,0}\bar{\mu}^\nu_{nm}G^R_{m,+\Omega}\bar{\mu}^\mu_{ml} + G^<_l\tilde{V}^\alpha_{ln}G^A_{n,+0}\bar{\mu}^\mu_{nm}G^A_{m,+\Omega}\bar{\mu}^\nu_{ml}\right)$$

$$\left.\begin{aligned}&+2\langle l|\bar{x}_\alpha\bar{x}_\beta|l\rangle\left(\bar{\mu}^\nu_{ln}\bar{\mu}^\mu_{nl}G^R_{n,+\Omega}G^<_l + \bar{\mu}^\mu_{ln}\bar{\mu}^\nu_{nl}G^<_l G^A_{n,-\Omega}\right)\\ &+\left(\langle l|\bar{x}_\beta\bar{x}_\nu|l\rangle - \langle l|\bar{x}_\nu\bar{x}_\beta|l\rangle\right)\left(\bar{\mu}^\alpha_{ln}\bar{\mu}^\mu_{nl}G^R_{n,+\Omega}G^<_l + \bar{\mu}^\mu_{ln}\bar{\mu}^\alpha_{nl}G^<_l G^A_{n,-\Omega}\right)\end{aligned}\right\}\text{Modified density of states}$$
$$+\left(\langle l|\bar{x}_\beta\bar{x}_\mu|l\rangle - \langle l|\bar{x}_\mu\bar{x}_\beta|l\rangle\right)\left(\bar{\mu}^\nu_{ln}\bar{\mu}^\alpha_{nl}G^R_{n,+\Omega}G^<_l + \bar{\mu}^\alpha_{ln}\bar{\mu}^\nu_{nl}G^<_l G^A_{n,-\Omega}\right)$$

Matrix elements of electic and magnetic dipole moments of Bloch states (in agreement with [5,6])

finite system

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

periodic system

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

Computational scheme

Corrections to density matrix

$$i\hbar\partial_t\rho - \left[H_0,\rho\right] = \left[H_1,\rho\right] \qquad \rho(\vec{x},\vec{x}') = exp\left[i\frac{e}{\hbar c}\int_{\vec{x}'}^{\vec{x}}\vec{A}(\vec{\xi})d\vec{\xi}\right]\tilde{\rho}(\vec{x},\vec{x}')$$

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

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

Terms within conduction or valence bands do not need solution of Liouville equation $\quad \rho = \rho\rho \Rightarrow \delta\tilde{\rho}_D = -\frac{ie}{2c\hbar}e_{\alpha\beta\gamma}B_\gamma\frac{\partial\tilde{\rho}_{\mathbf{k}}}{\partial k_\alpha}\frac{\partial\tilde{\rho}_{\mathbf{k}}}{\partial k_\beta}$

based on approaches [5,7,8]

1. First-order corrections

B *Terms within conduction (CC) and valence (VV) bands*

$$\tilde{\rho}^{(1)}_D = -\frac{ie}{2c\hbar}e_{\alpha\beta\gamma}B_\gamma\frac{\partial\rho^{(0)}}{\partial k_\alpha}\frac{\partial\rho^{(0)}}{\partial k_\beta} \qquad \tilde{\rho}^{(1)}_B(VV) = -\rho^{(0)}\tilde{\rho}^{(1)}_D\rho^{(0)} \qquad \tilde{\rho}^{(1)}_B(CC) = \left(1-\rho^{(0)}\right)\tilde{\rho}^{(1)}_D\left(1-\rho^{(0)}\right)$$

Terms between conduction and valence bands (CV, VC)

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

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

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

E *Only terms between conduction and valence bands (CV, VC) are non-zero*

$$\left|\xi^{(1)}_{v\mathbf{k},\pm\Omega}\right\rangle = P_c\tilde{\rho}^{(1)}_{E,\pm\Omega}\left|u^{(0)}_{v\mathbf{k}}\right\rangle \qquad \left(\pm\hbar\Omega - H_0 + \varepsilon^{(0)}_{v\mathbf{k}}\right)\left|\xi^{(1)}_{v\mathbf{k},\pm\Omega}\right\rangle = -P_c ieE_{\mu,\pm\Omega}\frac{\partial\rho^{(0)}}{\partial k_\mu}\left|u^{(0)}_{v\mathbf{k}}\right\rangle$$

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

2. Second-order corrections

EB

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

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

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

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

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

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

Conclusions

- A unified approach to calculation of all-order response to arbitrary electromagnetic fields both for periodic and molecular systems is developed within the formalism of non-equilibrium Green functions.
- The approach is applied to derive the expression for the magneto-optical response of insulating solids in the approximation of non-interacting electrons. The obtained formula is identical to the expression for molecular systems if the proper position and orbital magnetization operators are chosen.
- A computational scheme based on density matrix-perturbation theory is suggested. The scheme involves direct calculation of corrections to the density matrix elements within the occupied and unoccupied subspaces on the basis of lower-order corrections and solution of the Liouville equation for corrections to the density matrix elements between the occupied and unoccupied subspaces.

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