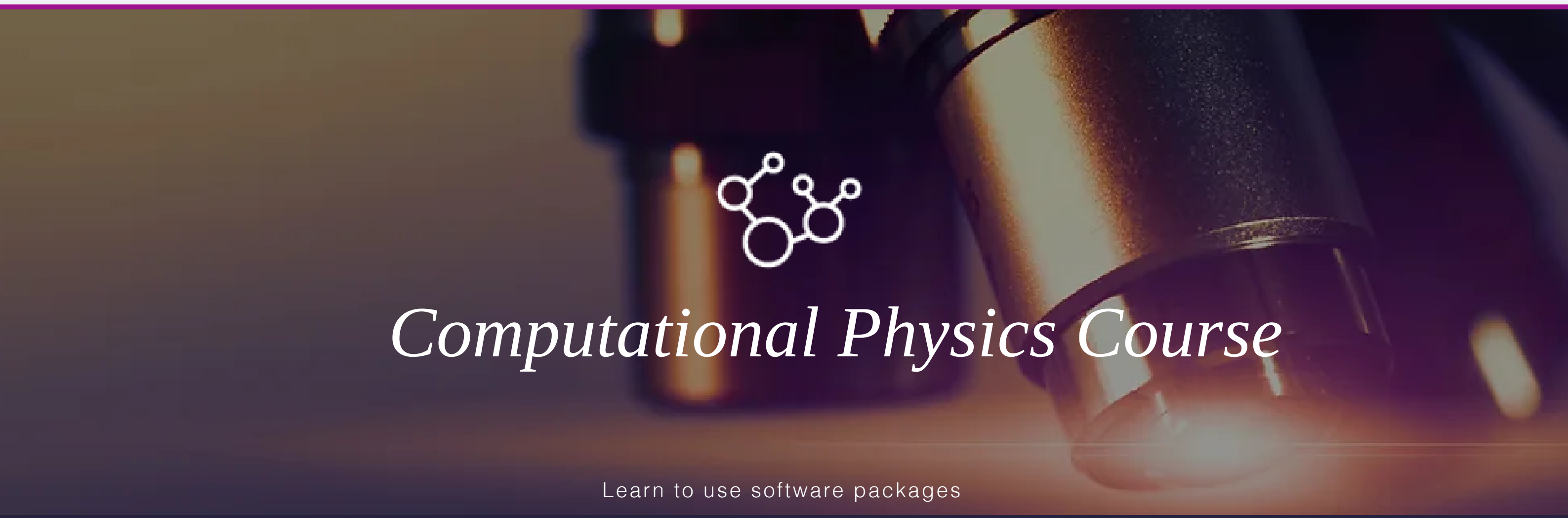

Day 6-7 (Ferroelectricity)

Unperturbed system and Perturbation

$$H^{(0)}\left|\psi_i^{(0)}\right\rangle = \varepsilon_i^{(0)}\left|\psi_i^{(0)}\right\rangle$$

$$V_{ext}(\lambda) = V_{ext}^{(0)} + \lambda V_{ext}^{(1)} + \lambda^2 V_{ext}^{(2)} + \cdots$$

$$\Rightarrow \quad H(\lambda)|\psi_i(\lambda)\rangle = \varepsilon_i(\lambda)|\psi_i(\lambda)\rangle$$

Perturbation series

$$\left(H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \ldots\right)\left(|\psi_i^{(0)}\rangle + \lambda|\psi_i^{(1)}\rangle + \lambda^2|\psi_i^{(2)}\rangle + \ldots\right) =$$
$$\left(\varepsilon_i^{(0)} + \lambda\varepsilon_i^{(1)} + \lambda^2\varepsilon_i^{(2)} + \ldots\right)\left(|\psi_i^{(0)}\rangle + \lambda|\psi_i^{(1)}\rangle + \lambda^2|\psi_i^{(2)}\rangle + \ldots\right)$$

Perturbed energy

$$\varepsilon_i^{(1)} = \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle \quad \textit{Helmann-Feynman theorem}$$

$$\varepsilon_i^{(2)} = \langle\psi_i^{(0)}|H^{(2)}|\psi_i^{(0)}\rangle + \frac{1}{2}\left(\langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(1)}\rangle + \langle\psi_i^{(1)}|H^{(1)}|\psi_i^{(0)}\rangle\right)$$

Let us learn the density functional perturbation and then the linear response

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Perturbed wave function

$$\left(H^{(0)} - \varepsilon_i^{(0)}\right)|\psi_i^{(1)}\rangle = -\left(H^{(1)} - \varepsilon_i^{(1)}\right)|\psi_i^{(0)}\rangle \quad \textit{Sternheimer equation}$$

Simplify the Sternheimer eq.

$$|\psi_i^{(1)}\rangle = \sum_j c_{ij}^{(1)}|\psi_j^{(0)}\rangle = \sum_{j\in I} c_{ij}^{(1)}|\psi_j^{(0)}\rangle + \sum_{j\in I^\perp} c_{ij}^{(1)}|\psi_j^{(0)}\rangle$$

Linear combination of the unperturbed WF

Decompose into degenerated states $\in I$ and others $\in I^\perp$

Left-hand side of the Sternheimer eq. becomes $= \sum_{j\in I^\perp} c_{ij}^{(1)}\left(\varepsilon_j^{(0)} - \varepsilon_i^{(0)}\right)|\psi_j^{(0)}\rangle$

Thus $c_{ij}^{(1)} = \dfrac{1}{\varepsilon_i^{(0)} - \varepsilon_j^{(0)}}\langle\psi_j^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle$ for $j \in I^\perp$

Simplify the Sternheimer eq.

There is a gauge freedom to choose $c_{ij}^{(1)} = 0$ for $j \in I$. Then

$$|\psi_i^{(1)}\rangle = \sum_{j \in I^\perp} |\psi_j^{(0)}\rangle \frac{1}{\varepsilon_i^{(0)} - \varepsilon_j^{(0)}} \langle \psi_j^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle$$

Or

$$P_{I^\perp} \left(H^{(0)} - \varepsilon_i^{(0)} \right) P_{I^\perp} |\psi_i^{(1)}\rangle = -P_{I^\perp} H^{(1)} |\psi_i^{(0)}\rangle \quad \text{with} \quad P_{I^\perp} \equiv \sum |\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|$$

Density functional perturbation theory

In DFT, one needs to minimize the electronic energy functional:

$$E_{el}[\rho^{(0)}] = \sum_{i=1}^{N_e} \left\langle \psi_i^{(0)} \middle| T + V_{ext}^{(0)} \middle| \psi_i^{(0)} \right\rangle + E_{Hxc}^{(0)}[\rho^{(0)}]$$

$$\rho^{(0)}(\mathbf{r}) = \sum_{i=1}^{N_e} \left[\psi_i^{(0)}(\mathbf{r}) \right]^* \psi_i^{(0)}(\mathbf{r})$$

$$\left\langle \psi_i^{(0)} \middle| \psi_j^{(0)} \right\rangle = \delta_{ij}$$

Or to solve the KS equation

$$H^{(0)} \left| \psi_i^{(0)} \right\rangle = \left[-\frac{1}{2}\nabla^2 + V_{ext}^{(0)} + V_{Hxc}^{(0)} \right] \left| \psi_i^{(0)} \right\rangle = \varepsilon_i^{(0)} \left| \psi_i^{(0)} \right\rangle$$

$$V_{Hxc}^{(0)}(\mathbf{r}) = \frac{\delta E_{Hxc}^{(0)}[\rho^{(0)}]}{\delta \rho(\mathbf{r})}$$

First order energy in DFPT

$$E_{el}^{(1)} = \sum_{i=1}^{N_e} \left\langle \psi_i^{(0)} \middle| (T + V_{ext})^{(1)} \middle| \psi_i^{(0)} \right\rangle + \frac{d}{d\lambda} E_{Hxc}[\rho^{(0)}] \Big|_{\lambda=0} \quad \textit{Helmann-Feynman}$$

$$\left\langle \psi_i^{(0)} \middle| \psi_j^{(1)} \right\rangle + \left\langle \psi_i^{(1)} \middle| \psi_j^{(0)} \right\rangle = 0$$

Second order energy in DFPT

$$E_{el}^{(2)} = \sum_{i=1}^{N_e} \left[\left\langle \psi_i^{(1)} \middle| (T + V_{ext})^{(1)} \middle| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(0)} \middle| (T + V_{ext})^{(1)} \middle| \psi_i^{(1)} \right\rangle \right]$$

$$+ \sum_{i=1}^{N_e} \left[\left\langle \psi_i^{(0)} \middle| (T + V_{ext})^{(2)} \middle| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(1)} \middle| (H - \varepsilon_i)^{(0)} \middle| \psi_i^{(1)} \right\rangle \right]$$

$$+ \frac{1}{2} \int\int \frac{\delta^2 E_{Hxc}[\rho^{(0)}]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$+ \int \frac{d}{d\lambda} \frac{E_{Hxc}[\rho^{(0)}]}{\delta\rho(\mathbf{r})} \Bigg|_{\lambda=0} \rho^{(1)}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \frac{d^2}{d\lambda^2} E_{Hxc}[\rho^{(0)}] \Big|_{\lambda=0}$$

with

$$\rho^{(1)}(\mathbf{r}) = \sum_{i=1}^{N_e} \left(\left[\psi_i^{(1)}(\mathbf{r}) \right]^* \psi_i^{(0)}(\mathbf{r}) + \left[\psi_i^{(0)}(\mathbf{r}) \right]^* \psi_i^{(1)}(\mathbf{r}) \right)$$

First order wave function in DFPT

Sternheimer equation

Since

$$\left(\varepsilon_{i,\mathbf{k}}^{(0)}-\varepsilon_{j,\mathbf{k}}^{(0)}\right)\left\langle u_{i,\mathbf{k}}^{(0)}\middle| r_\alpha \middle| u_{j,\mathbf{k}}^{(0)}\right\rangle=\left\langle u_{i,\mathbf{k}}^{(0)}\middle| H_{\mathbf{kk}}^{(0)} r_\alpha - r_\alpha H_{\mathbf{kk}}^{(0)} \middle| u_{j,\mathbf{k}}^{(0)}\right\rangle$$

$$=\left\langle u_{i,\mathbf{k}}^{(0)}\middle| -i\frac{\partial H_{\mathbf{kk}}^{(0)}}{\partial k_\alpha} \middle| u_{j,\mathbf{k}}^{(0)}\right\rangle$$

$\Downarrow$

$$P_c\left(H_{\mathbf{kk}}^{(0)}-\varepsilon_{j,\mathbf{k}}^{(0)}\right)P_c r_\alpha\left|u_{j,\mathbf{k}}^{(0)}\right\rangle=-P_c i\frac{\partial H_{\mathbf{kk}}^{(0)}}{\partial k_\alpha}\left|u_{j,\mathbf{k}}^{(0)}\right\rangle$$

$$P_{I\perp}\left(H^{(0)}-\varepsilon_i^{(0)}\right)P_{I\perp}|\psi_i^{(1)}\rangle=-P_{I\perp}H^{(1)}|\psi_i^{(0)}\rangle$$

Application to phonon

Unperturbed system and Perturbation

$$V_{ext}^{(0)}(\mathbf{r}+\mathbf{R}_a)=V_{ext}^{(0)}(\mathbf{r}) \quad \Rightarrow \quad V_{ext}^{(1)}(\mathbf{r}+\mathbf{R}_a)=e^{i\mathbf{q}\cdot\mathbf{R}_a}V_{ext}^{(1)}(\mathbf{r})$$

$$\rho^{(1)}(\mathbf{r}+\mathbf{R}_a)=e^{i\mathbf{q}\cdot\mathbf{R}_a}\rho^{(1)}(\mathbf{r})$$

$$\psi_{i,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a)=e^{i\mathbf{q}\cdot\mathbf{R}_a}\psi_{i,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r})$$

$\cdots$

Application to dielectric response

Unperturbed system and Perturbation

$$V_{ext}^{(0)}(\mathbf{r}+\mathbf{R}_a)=V_{ext}^{(0)}(\mathbf{r}) \quad \Rightarrow \quad V_{ext}^{(1)}(\mathbf{r})=\mathscr{E}\cdot\mathbf{r}$$

The applied electric field $\vec{\mathcal{E}}$ is modified by the linearly induced polarization $\vec{P}$ as $\vec{\mathcal{E}}-4\pi\vec{P}$ with

$$P_\alpha=-\frac{1}{\Omega}\int_\Omega r_\alpha\rho^{(1)}(\vec{r})d^3r$$

This requires computation of matrix elements of the type

$$\left\langle u_{c,\mathbf{k}}^{(0)}\middle| r_{\alpha'} \middle| u_{v,\mathbf{k}}^{E_\alpha}\right\rangle \text{ and } \left\langle u_{c,\mathbf{k}}^{E_\alpha}\middle| r_{\alpha'} \middle| u_{v,\mathbf{k}}^{(0)}\right\rangle$$

Mixed perturbation

You may want to know how a uniform electric field $\vec{\mathcal{E}}$ and an atomic displacement $\vec{u}_\tau$ will change the polarization $\vec{P}$.

$$Z^*\equiv\Omega\frac{\partial P_\alpha}{\partial u_{\tau\alpha}} \qquad \vec{P}=\frac{1}{\Omega}\sum_\tau Z_\tau^*\vec{u}_\tau+\frac{\epsilon_\infty-1}{4\pi}\vec{E}$$

Z* is called the *Born effective charge*, which describes the linear relation between the force and the electric field. This important quantity can be obtained by perturb the system with the electric field and the atomic displacement.

Having learned DFT, let us move to learning program packages. We begin by learning Quantum Espresso

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