Density Functional Perturbation Theory

KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

KS self-consistent equations

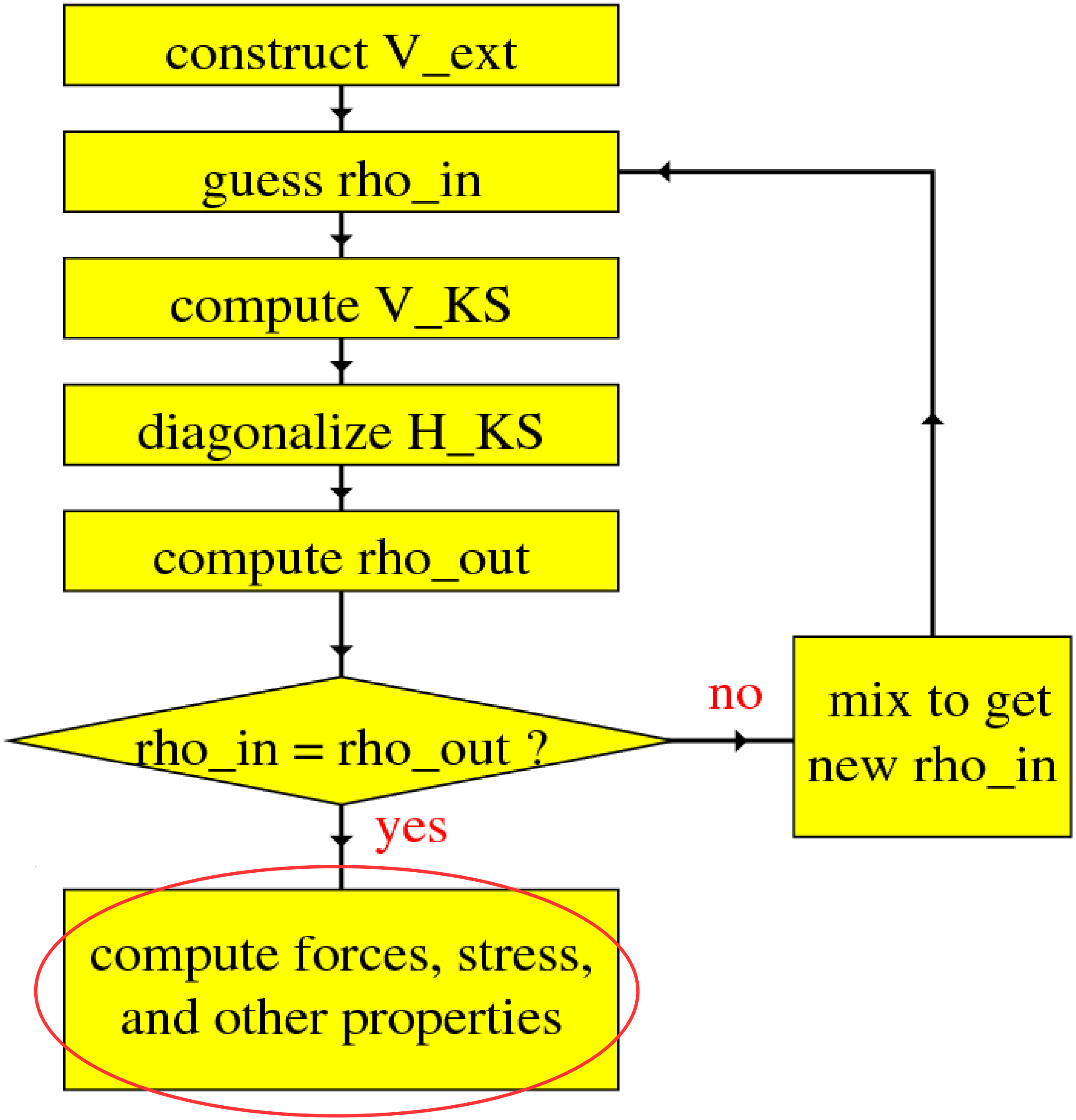
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

$$V_{KS}(r) \rightarrow \varphi_i(r) \rightarrow \rho(r)$$

Structure of a self-consistent type code



Total KS energy

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle\varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

Total KS energy

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle \varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

Hellmann-Feynman Theorem

$$F_{I\alpha} = -\frac{\partial E_{el+ion}}{\partial R_{I\alpha}} = -\int \frac{\partial V_{ext}(r)}{\partial R_{I\alpha}}\rho(r)dr \; - \; \frac{\partial E_{WLD}}{\partial R_{I\alpha}}$$

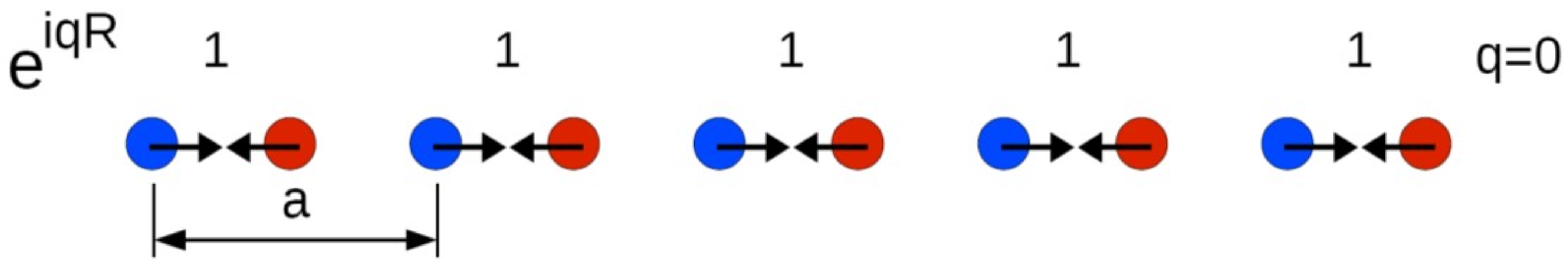
$$\frac{\partial E_{el+ion}}{\partial \lambda} = \int \frac{\partial V_{ext}(r)}{\partial \lambda}\rho(r)dr \; + \; \frac{\partial E_{WLD}}{\partial \lambda}$$

the linear variation of the GS density is not needed

Vibrational properties

$$(\mathbf{R}+\tau_s)_{eq} \longrightarrow (\mathbf{R}+\tau_s)_{eq} + \mathbf{u}_{\mathbf{R}s}$$

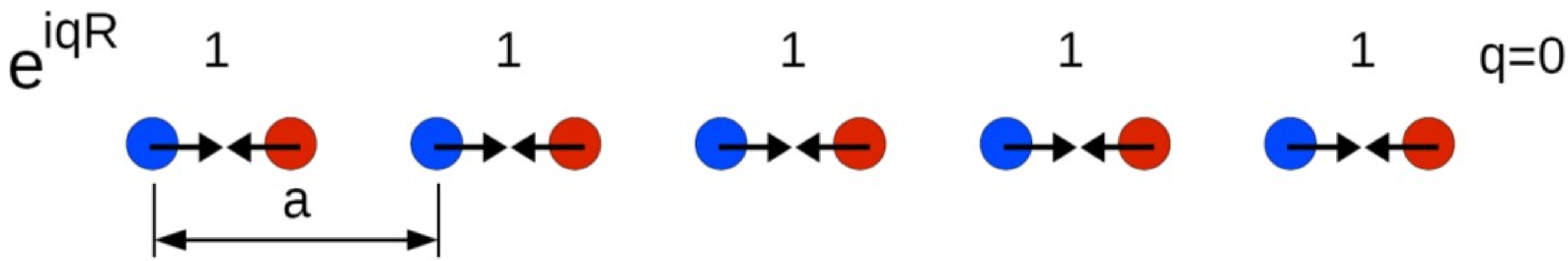
$$\sum_{Rs\alpha} \frac{\mathbf{P}^2_{Rs\alpha}}{2M_s} + \frac{1}{2} \sum_{\substack{Rs\alpha \\ R's'\alpha'}} \mathbf{u}_{Rs\alpha} \frac{\partial^2 E_{el+ion}}{\partial \mathbf{u}_{Rs\alpha} \partial \mathbf{u}_{R's'\alpha'}} \mathbf{u}_{R's'\alpha'}$$



Vibrational properties

$$(\mathbf{R}+\tau_s)_{eq} \longrightarrow (\mathbf{R}+\tau_s)_{eq} + \mathbf{u}_s^{\mathbf{q}} \frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

$$\sum_{s\alpha} \frac{\mathbf{P}_{s\alpha}^2}{2M_s} + \frac{1}{2}\sum_{\substack{s\alpha\\ 's'\alpha'}} \mathbf{u}_{s\alpha}^{\mathbf{q}}{}^* \frac{\partial^2 E_{el+ion}}{\partial \mathbf{u}_{s\alpha}^{\mathbf{q}}{}^*\partial \mathbf{u}_{'s'\alpha'}^{\mathbf{q}}} \mathbf{u}_{'s'\alpha'}^{\mathbf{q}}$$

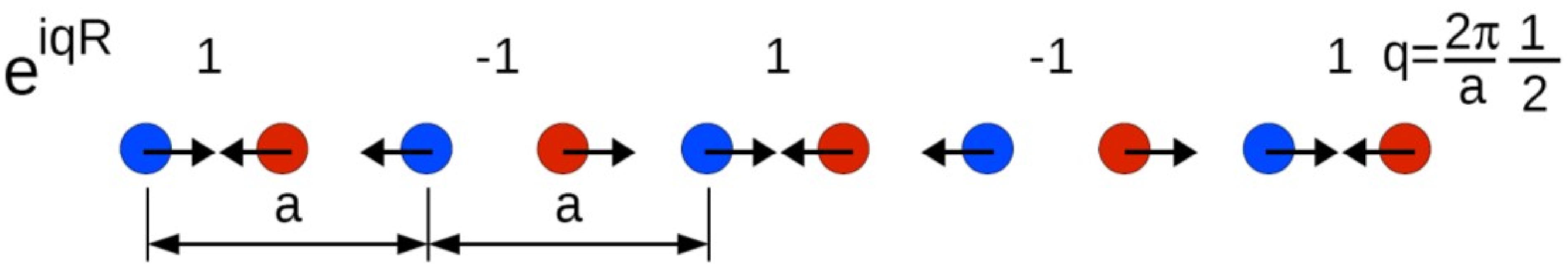


$$\Delta V_{ext}(r) = \sum_{\mathbf{R}s} \frac{\partial V_s}{\partial \mathbf{R}}(|r-\mathbf{R}-\tau_s|)\ \mathbf{u}_s^{\mathbf{q}} \frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

Vibrational properties

$$(\mathbf{R}+\tau_s)_{eq} \longrightarrow (\mathbf{R}+\tau_s)_{eq} + \mathbf{u}_s^{\mathbf{q}} \frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

$$\sum_{s\alpha} \frac{\mathbf{P}^2_{s\alpha}}{2M_s} + \frac{1}{2}\sum_{\substack{s\alpha \\ {}'s'\alpha'}} \mathbf{u}^{\mathbf{q}}_{s\alpha}{}^* \frac{\partial^2 E_{el+ion}}{\partial \mathbf{u}^{\mathbf{q}}_{s\alpha}{}^*\partial \mathbf{u}^{\mathbf{q}}_{{}'s'\alpha'}} \mathbf{u}^{\mathbf{q}}_{{}'s'\alpha'}$$

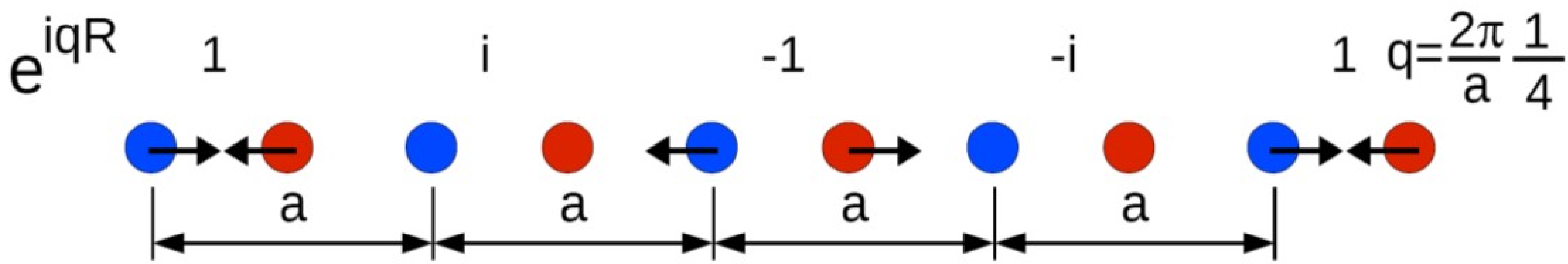


$$\Delta V_{ext}(r) = \sum_{\mathbf{R}s} \frac{\partial V_s}{\partial \mathbf{R}}(|r-\mathbf{R}-\tau_s|)\;\mathbf{u}_s^{\mathbf{q}}\;\frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

Vibrational properties

$$(\mathbf{R}+\tau_s)_{eq} \longrightarrow (\mathbf{R}+\tau_s)_{eq} + \mathbf{u}_s^{\mathbf{q}} \frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

$$\sum_{s\alpha} \frac{\mathbf{P}_{s\alpha}^2}{2M_s} + \frac{1}{2}\sum_{\substack{s\alpha \\ 's'\alpha'}} \mathbf{u}_{s\alpha}^{\mathbf{q}}{}^{*} \frac{\partial^2 E_{el+ion}}{\partial \mathbf{u}_{s\alpha}^{\mathbf{q}}{}^{*}\,\partial \mathbf{u}_{'s'\alpha'}^{\mathbf{q}}} \mathbf{u}_{'s'\alpha'}^{\mathbf{q}}$$



$$\Delta V_{ext}(r) = \sum_{\mathbf{R}s} \frac{\partial V_s}{\partial \mathbf{R}}(|r-\mathbf{R}-\tau_s|)\; \mathbf{u}_s^{\mathbf{q}} \frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

KS energy expansion

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle\varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

$$\frac{\partial E_{el+ion}}{\partial\lambda} = \int \frac{\partial V_{ext}(r)}{\partial\lambda}\rho(r)dr \; + \; \frac{\partial E_{WLD}}{\partial\lambda}$$

KS energy expansion

$$E_{el+ion} = -\frac{\hbar^2}{2m}\sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD}$$

$$\frac{\partial E_{el+ion}}{\partial \lambda} = \int \frac{\partial V_{ext}(r)}{\partial \lambda}\rho(r)dr \; + \; \frac{\partial E_{WLD}}{\partial \lambda}$$

$$\frac{\partial^2 E_{el+ion}}{\partial \lambda \partial \mu} = \int \frac{\partial^2 V_{ext}(r)}{\partial \lambda \partial \mu}\rho(r)dr + \int \frac{\partial V_{ext}(r)}{\partial \lambda}\frac{\partial \rho(r)}{\partial \mu}dr + \frac{\partial^2 E_{WLD}}{\partial \lambda \partial \mu}$$

the linear variation of the GS density is needed

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\varphi_i(r) = -\left(\Delta V_{KS} - \Delta\varepsilon_i\right)\varphi_i(r)$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\varphi_i(r) = -\left(\Delta V_{KS} - \Delta\varepsilon_i\right)\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\varphi_i(r)$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + \Delta V_H(r) + \Delta v_{xc}(r)$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2\int\frac{\Delta\rho(r')}{|r-r'|}dr' + \int\frac{\delta v_{xc}(r)}{\delta\rho(r')}\Delta\rho(r')dr'$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2\int\frac{\Delta\rho(r')}{|r-r'|}dr' + \int f_{xc}\Delta\rho(r')dr'$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2\int\frac{\Delta\rho(r')}{|r-r'|}dr' + \int f_{xc}\Delta\rho(r')dr'$$

$$\Delta V_{KS} \rightarrow \Delta\tilde{\varphi}_i(r) \rightarrow \Delta\rho(r)$$

DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\Delta\tilde{\varphi}_i(r) = -P_c\,\Delta V_{KS}(r)\,\varphi_i(r)$$

$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2\int\frac{\Delta\rho(r')}{|r-r'|}dr' + \int f_{xc}\Delta\rho(r')dr'$$

$$\Delta V_{KS} \rightarrow \Delta\tilde{\varphi}_i(r) \rightarrow \Delta\rho(r)$$

Evaluate the dynamical matrix

$$\frac{\partial^2 E_{el+ion}}{\partial\lambda\partial\mu} = \int \frac{\partial^2 V_{ext}(r)}{\partial\lambda\partial\mu}\rho(r)dr + \int \frac{\partial V_{ext}(r)}{\partial\lambda}\frac{\partial\rho(r)}{\partial\mu}dr + \frac{\partial^2 E_{WLD}}{\partial\lambda\partial\mu}$$

THE END