PHY 712 Electrodynamics
12-12:50 AM MWF Olin 103

Plan for Lecture 10:

Complete reading of Chapter 4

A. Microscopic ←→macroscopic polarizability

B. Clausius-Mossotti equation

C. Electrostatic energy in dielectric media

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Colloquium this week --

Colloquium: "2D Materials in the Spot 'Light': The Emergence of Advanced Optical and Electronic Functionalities"

Dr. Sharmila Shirodkar
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Department of Materials Science
and NanoEngineering
Rice University, Houston, TX
George P. Williams, Jr. Lecture Hall, (Olin 101)
Wednesday, February 5, 2020 at 3:00 PM

There will be a reception in Olin Lounge at approximately 4 PM following the colloquium. All interested persons are cordially invited to attend.

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Course schedule for Spring 2020

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	JDJ Reading	Topic	HW	Due date
1	Mon: 01/13/2020	Chap. 1 & Appen.	Introduction, units and Poisson equation	#1	01/17/2020
2	Wed: 01/15/2020	Chap. 1	Electrostatic energy calculations	#2	01/22/2020
3	Fri: 01/17/2020	Chap. 1	Electrostatic potentials and fields	#3	01/24/2020
	Mon: 01/20/2020	No class	Martin Luther King Holiday		
4	Wed: 01/22/2020	Chap. 1 - 3	Poisson's equation in 2 and 3 dimensions	#4	01/27/2020
5	Fri: 01/24/2020	Chap. 1 - 3	Brief introduction to numerical methods	#5	01/31/2020
6	Mon: 01/27/2020	Chap. 2 & 3	Image charge constructions	#6	02/03/2020
7	Wed: 01/29/2020	Chap. 2 & 3	Cylindrical and spherical geometries	#7	02/05/2020
8	Fri: 01/31/2020	Chap. 3 & 4	Spherical geometry and multipole moments	#8	02/07/2020
9	Mon: 02/03/2020	Chap. 4	Dipoles and Dielectrics	#9	02/10/2020
10	Wed: 02/05/2020	Chap. 4	Polarization and Dielectrics		
11	Fri: 02/07/2020	Chap. 5	Magnetostatics		
12	Mon: 02/10/2020	Chap. 5	Magnetic dipoles and hyperfine interaction		
13	Wed: 02/12/2020	Chap. 5	Magnetic dipoles and dipolar fields		

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Focus on dipolar fields:

Dipole moment $\mathbf{p}$:

$$\mathbf{p} \equiv \int d^3r' \, \mathbf{r}' \rho(\mathbf{r}')$$

For r outside the extent of $\rho(\mathbf{r})$:

Electrostatic potential from single dipole:

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{\mathbf{p}\cdot\mathbf{r}}{r^3}\right)$$

Electrostatic field from single dipole:

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{3\mathbf{r}\,(\mathbf{p}\cdot\mathbf{r}) - r^2\mathbf{p}}{r^5} - \frac{4\pi}{3}\mathbf{p}\delta^3(\mathbf{r})\right)$$

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Coarse grain representation of macroscopic distribution of dipoles -- continued:

Many materials are polarizable and produce a polarization field in the presence of an electric field with a proportionality constant χ_e:

$$\mathbf{P}(\mathbf{r}) = \varepsilon_0 \chi_e \mathbf{E}(\mathbf{r})$$

$$\mathbf{D}(\mathbf{r}) \equiv \varepsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r}) = \varepsilon_0 (1+\chi_e)\mathbf{E}(\mathbf{r}) \equiv \varepsilon \mathbf{E}(\mathbf{r})$$

ε represents the dielectric function of the material

Boundary value problems in dielectric materials

For $\rho_{\text{mono}}(\mathbf{r}) = 0$

$\nabla \cdot \mathbf{D}(\mathbf{r}) = 0$ and $\nabla \times \mathbf{E}(\mathbf{r}) = 0$

$\Rightarrow$ At a surface between two dielectrics, in terms of surface normal $\hat{\mathbf{r}}$:

$\hat{\mathbf{r}} \cdot \mathbf{D}(\mathbf{r}) = \text{continuous} = \hat{\mathbf{r}} \times \mathbf{E}(\mathbf{r})$

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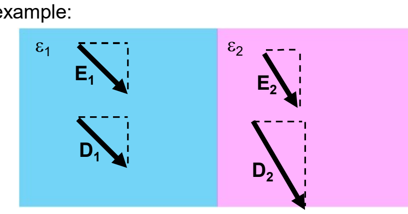
Boundary value problems in the presence of dielectrics – example:



For $\frac{\varepsilon_2}{\varepsilon_1} = 2$

For $\rho_{\text{mono}}(\mathbf{r}) = 0$: $\nabla \cdot \mathbf{D}(\mathbf{r}) = 0$ and $\nabla \times \mathbf{E}(\mathbf{r}) = 0$

$\Rightarrow$ At a surface between two dielectrics, in terms of surface normal $\hat{\mathbf{r}}$:

$\hat{\mathbf{r}} \cdot \mathbf{D}(\mathbf{r}) = \text{continuous} = \hat{\mathbf{r}} \times \mathbf{E}(\mathbf{r})$

$D_{1n} = D_{2n}$ $\quad \varepsilon_1 E_{1n} = \varepsilon_2 E_{2n}$

For isotropic dielectrics: $E_{1t} = E_{2t}$ $\quad \frac{D_{1t}}{\varepsilon_1} = \frac{D_{2t}}{\varepsilon_2}$

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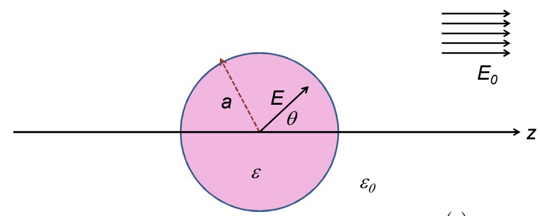
Boundary value problems in the presence of dielectrics – example:



$\nabla \cdot \mathbf{D}(\mathbf{r}) = 0$ and $\nabla \times \mathbf{E}(\mathbf{r}) = 0$

For $r \le a$ $\quad \mathbf{D}(\mathbf{r}) = -\varepsilon \nabla \Phi(\mathbf{r})$

For $r > a$ $\quad \mathbf{D}(\mathbf{r}) = -\varepsilon_0 \nabla \Phi(\mathbf{r})$

At $r = a$: $\quad \varepsilon \frac{\partial \Phi_<(\mathbf{r})}{\partial r} = \varepsilon_0 \frac{\partial \Phi_>(\mathbf{r})}{\partial r}$

$\frac{\partial \Phi_<(\mathbf{r})}{\partial \theta} = \frac{\partial \Phi_>(\mathbf{r})}{\partial \theta}$

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Boundary value problems in the presence of dielectrics – example -- continued:

$$\Phi_<(\mathbf{r}) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta)$$

$$\Phi_>(\mathbf{r}) = \sum_{l=0}^{\infty} \left(B_l r^l + \frac{C_l}{r^{l+1}} \right) P_l(\cos\theta)$$

At $r = a$: $\quad \varepsilon \frac{\partial \Phi_<(\mathbf{r})}{\partial r} = \varepsilon_0 \frac{\partial \Phi_>(\mathbf{r})}{\partial r}$

$\frac{\partial \Phi_<(\mathbf{r})}{\partial \theta} = \frac{\partial \Phi_>(\mathbf{r})}{\partial \theta}$

For $r \to \infty$ $\quad \Phi_>(\mathbf{r}) = -E_0 r \cos\theta$

Solution -- only $l = 1$ contributes

$B_1 = -E_0$

$$A_1 = -\left(\frac{3}{2 + \varepsilon / \varepsilon_0} \right) E_0 \qquad C_1 = \left(\frac{\varepsilon / \varepsilon_0 - 1}{2 + \varepsilon / \varepsilon_0} \right) a^3 E_0$$

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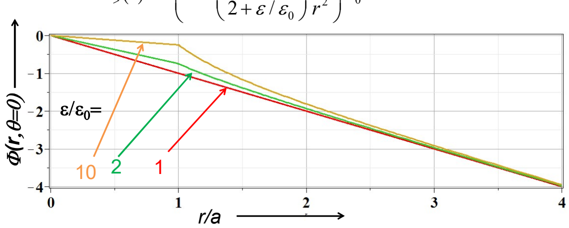
Boundary value problems in the presence of dielectrics – example -- continued:

$$\Phi_<(\mathbf{r}) = -\left(\frac{3}{2 + \varepsilon / \varepsilon_0} \right) E_0 \, r \cos\theta$$

$$\Phi_>(\mathbf{r}) = -\left(r - \left(\frac{\varepsilon / \varepsilon_0 - 1}{2 + \varepsilon / \varepsilon_0} \right) \frac{a^3}{r^2} \right) E_0 \cos\theta$$



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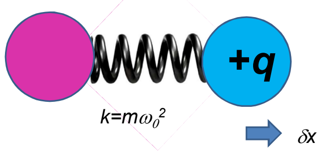
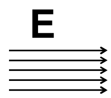
Microscopic origin of dipole moments
- Polarizable atoms/molecules
- Anisotropic charged molecules

Polarizable isotropic atoms/molecules





At equilibrium:

$$q\mathbf{E} - m\omega_0^2\delta\mathbf{x} = 0$$

$$\delta\mathbf{x} = \frac{q\mathbf{E}}{m\omega_0^2}$$

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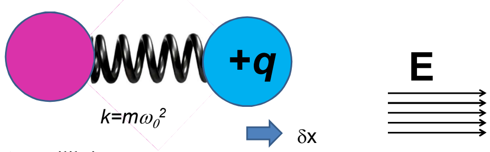
Polarizable isotropic atoms/molecules – continued:



At equilibrium:

$$q\mathbf{E} - m\omega_0^2\delta\mathbf{x} = 0$$

$$\delta\mathbf{x} = \frac{q\mathbf{E}}{m\omega_0^2}$$

Induced dipole moment:

$$p = q\delta\mathbf{x} = \frac{q^2}{m\omega_0^2}\mathbf{E} \equiv \varepsilon_0\gamma_{mol}\mathbf{E} \quad \Rightarrow \gamma_{mol} = \frac{q^2}{m\omega_0^2\varepsilon_0}$$

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Alignment of molecules with permanent dipoles $\mathbf{p}_0$:

For a freely rotating dipole its average moment in an electric field, estimated assuming a Boltzmann distribution:

$$\langle \mathbf{p}_{mol} \rangle = \frac{\int d\Omega\; p_0 \cos\theta e^{p_0 E\cos\theta/kT}}{\int d\Omega e^{p_0 E\cos\theta/kT}} \approx \frac{1}{3}\frac{p_0^2}{kT}\mathbf{E} \text{ for } \frac{p_0 E}{kT} \ll 1$$

$$\langle \mathbf{p}_{mol} \rangle \approx \frac{1}{3}\frac{p_0^2}{kT}\mathbf{E} \equiv \varepsilon_0\gamma_{mol}\mathbf{E} \qquad \Rightarrow \gamma_{mol} \approx \frac{1}{3}\frac{p_0^2}{kT\varepsilon_0}$$

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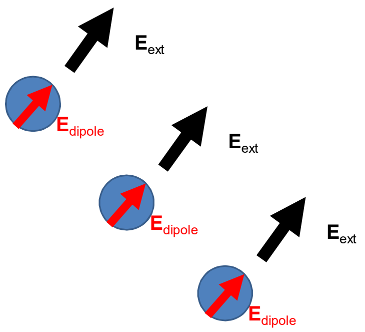
Superposition of dipoles



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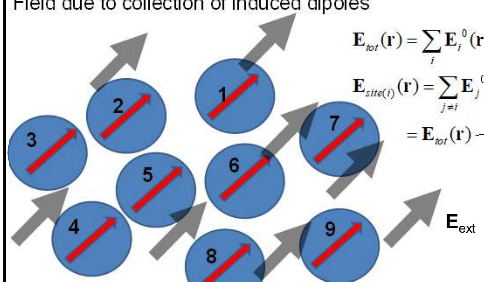
Field due to collection of induced dipoles



$$\mathbf{E}_{tot}(\mathbf{r}) = \sum_i \mathbf{E}_i^{\,0}(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$\mathbf{E}_{site(i)}(\mathbf{r}) = \sum_{j \neq i} \mathbf{E}_j^{\,0}(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$= \mathbf{E}_{tot}(\mathbf{r}) - \mathbf{E}_i^{\,0}(\mathbf{r})$$

Electrostatic field from single dipole:

$$\mathbf{E}_i^0(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{3\mathbf{r}\,(\mathbf{p}_i \cdot \mathbf{r}) - r^2\mathbf{p}_i}{r^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right)$$

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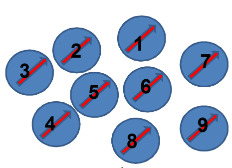
Field due to collection of induced dipoles -- continued



$$\mathbf{E}_{tot}(\mathbf{r}) = \sum_i \mathbf{E}_i^{\,0}(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$\mathbf{E}_{site(i)}(\mathbf{r}) = \sum_{j \neq i} \mathbf{E}_j^{\,0}(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$= \mathbf{E}_{tot}(\mathbf{r}) - \mathbf{E}_i^{\,0}(\mathbf{r})$$

$$\mathbf{E}(\mathbf{r})_{tot} = \frac{1}{4\pi\varepsilon_0}\sum_i\left(\frac{3\mathbf{r}\,(\mathbf{p}_i \cdot \mathbf{r}) - r^2\mathbf{p}_i}{r^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right) + \mathbf{E}_{ext}(\mathbf{r})$$

$$\mathbf{E}(\mathbf{r})_{site(i)} = \frac{1}{4\pi\varepsilon_0}\left(\sum_{j\neq i}\frac{3\mathbf{r}\,(\mathbf{p}_j \cdot \mathbf{r}) - r^2\mathbf{p}_j}{r^5}\right) + \mathbf{E}_{ext}(\mathbf{r}) = \mathbf{E}(\mathbf{r})_{tot} - \left(\mathbf{E}_i^0(\mathbf{r})\right)_{site(i)}$$

$$\langle \mathbf{E}_{site(i)} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{V}\frac{1}{3\varepsilon_0}\langle \mathbf{p} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{3\varepsilon_0}\langle \mathbf{P} \rangle$$

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Field due to collection of induced dipoles -- continued

$$\mathbf{E}(\mathbf{r})_{site(i)} = \mathbf{E}(\mathbf{r})_{tot} - \left(\mathbf{E}_i^0(\mathbf{r})\right)_{site(i)}$$

$$= \mathbf{E}(\mathbf{r})_{tot} - \frac{1}{4\pi\varepsilon_0}\left(\frac{3\mathbf{r}\,(\mathbf{p}_i\cdot\mathbf{r}) - r^2\mathbf{p}_i}{r^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right)$$

$$\left\langle \mathbf{E}_{site(i)}\right\rangle = \left\langle \mathbf{E}_{tot}\right\rangle - \left\langle \frac{1}{4\pi\varepsilon_0}\left(\frac{3\mathbf{r}\,(\mathbf{p}_i\cdot\mathbf{r}) - r^2\mathbf{p}_i}{r^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right)\right\rangle$$

$$\left\langle \mathbf{E}_{site(i)}\right\rangle = \left\langle \mathbf{E}_{tot}\right\rangle + \frac{1}{V}\frac{1}{3\varepsilon_0}\langle \mathbf{p}\rangle = \left\langle \mathbf{E}_{tot}\right\rangle + \frac{1}{3\varepsilon_0}\langle \mathbf{P}\rangle$$

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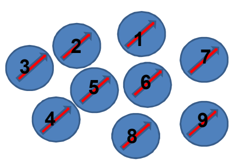
Field due to collection of induced dipoles -- continued



$$\left\langle \mathbf{E}_{site(i)}\right\rangle = \left\langle \mathbf{E}_{tot}\right\rangle + \frac{1}{3\varepsilon_0}\langle \mathbf{P}\rangle$$

$$\langle \mathbf{p}\rangle = \varepsilon_0\gamma_{mol}\left\langle \mathbf{E}_{site}\right\rangle$$

$$\langle \mathbf{P}\rangle = \frac{1}{V}\langle \mathbf{p}\rangle = \frac{\varepsilon_0\gamma_{mol}}{V}\left(\left\langle \mathbf{E}_{tot}\right\rangle + \frac{1}{3\varepsilon_0}\langle \mathbf{P}\rangle\right)$$

$$\langle \mathbf{P}\rangle = \frac{\varepsilon_0\gamma_{mol}}{V}\frac{\left\langle \mathbf{E}_{tot}\right\rangle}{1-\frac{\gamma_{mol}}{3V}} = \varepsilon_0\chi_e\left\langle \mathbf{E}_{tot}\right\rangle$$

Claussius-Mossotti equation

$$\chi_e = \frac{\frac{\gamma_{mol}}{V}}{1-\frac{\gamma_{mol}}{3V}} = \frac{\varepsilon}{\varepsilon_0} - 1 \qquad \gamma_{mol} = 3V\left(\frac{\varepsilon/\varepsilon_0 - 1}{\varepsilon/\varepsilon_0 + 2}\right)$$

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Example of the Clausius-Mossotti equation –

Pentane (C_5H_{12}) at various densities

Density (g/cm3)	Mol/m3	ε/ε0	3V*(ε/ε0-1)/(ε/ε0+2)
0.613	5.12536E+27	1.82	1.25646E-28
0.701	5.86114E+27	1.96	1.24084E-28
0.796	6.65544E+27	2.12	1.22536E-28
0.865	7.23236E+27	2.24	1.2131E-28
0.907	7.58353E+27	2.33	1.2151E-28

$\gamma_{mol} = 1.2 \times 10^{-28}\ m^3 = 0.12\ nm^3$

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Re-examination of electrostatic energy in dielectric media

$$W = \frac{1}{2}\int d^3r \rho_{mono}(\mathbf{r})\Phi(\mathbf{r})$$

In terms of displacement field:

$$\nabla \cdot \mathbf{D} = \rho_{mono}(\mathbf{r})$$

$$W = \frac{1}{2}\int d^3r\ \nabla\cdot\mathbf{D}\ \Phi(\mathbf{r}) = \frac{1}{2}\int d^3r\ \nabla\cdot\left(\mathbf{D}(\mathbf{r})\ \Phi(\mathbf{r})\right) - \frac{1}{2}\int d^3r\ \mathbf{D}(\mathbf{r})\cdot\nabla\Phi(\mathbf{r})$$

$$= \quad 0 \quad + \frac{1}{2}\int d^3r\ \mathbf{D}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})$$

$$W = \frac{1}{2}\int d^3r\ \mathbf{D}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})$$

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Comment on the "Modern Theory of Polarization"

Some references:

- R. D.King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993)
- R. Resta, Rev. Mod. Physics **66**, 699 (1994)
- R. Resta, J. Phys. Condens. Matter 23, 123201 (2010)
- N. A. Spaldin, J. Solid State Chem. **195**, 2 (2012)

Basic equations:

$$\varepsilon_0\nabla\cdot\mathbf{E} = \rho_{tot} = \rho_{bound} + \rho_{mono}$$

$$\nabla\cdot\mathbf{P} = \rho_{bound}$$

$$\nabla\cdot\mathbf{D} = \rho_{mono}$$

$$\varepsilon_0\mathbf{E} = \mathbf{D} + \mathbf{P}$$

Note: In general **P** is highly dependent on the boundary values; often it is more convenient/meaningful to calculate **ΔP**.

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Comment on the "Modern Theory of Polarization" -- continued

$$\nabla\cdot\Delta\mathbf{P} = \Delta\rho_{bound} = \Delta\rho^{nuclear}_{bound} + \Delta\rho^{electronic}_{bound}$$

$$\Delta\mathbf{P}^{electronic} = -\frac{e}{V_{crystal}}\sum_n \langle w_{n0}|\mathbf{r}|w_{n0}\rangle$$

Note: The concept of the polarization of a periodic solid is not unique:

N.A. Spaldin / Journal of Solid State Chemistry 195 (2012) 2–10 3

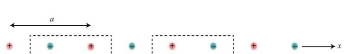

Fig. 1. One-dimensional chain of alternating anions and cations, spaced a distance $a/2$ apart, where a is the lattice constant. The dashed lines indicate two representative unit cells which are used in the text for calculation of the polarization.

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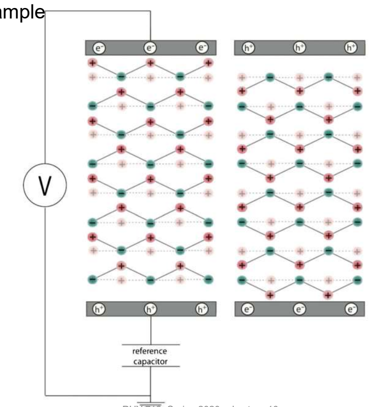
ΔP example



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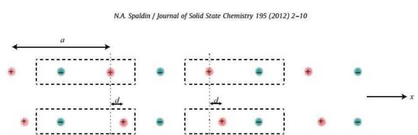
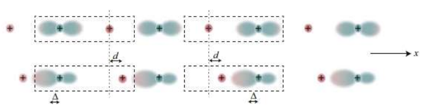
ΔP example -- linear visualization



Effects on the electronic distribution



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