Define $q_n \equiv \sum_{i \in n} q_i$ total charge molecule n

$\vec{p}_n \equiv \sum_{i \in n} q_i \vec{r}_{ni}$ dipole moment about center of mass of molec n

$\overleftrightarrow{Q}'_n \equiv \sum_{i \in n} 3 q_i \vec{r}_{ni} \vec{r}_{ni}$ quadrapole moment about center of mass of molec n

(prime on $\overleftrightarrow{Q}'$ since definitio
here is a little different
from that of multipole exp)

$$\langle \rho_n(\vec{r},t) \rangle = q_n f(\vec{r}-\vec{r}_n) - \vec{p}_n \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n) + \frac{1}{6} \sum_{\alpha\beta} (Q'_n)_{\alpha\beta} \frac{\partial^2 f(\vec{r}-\vec{r}_n)}{\partial r_\alpha \partial r_\beta}$$

Now use $\langle \delta(\vec{r}-\vec{r}_n) \rangle = f(\vec{r}-\vec{r}_n)$ by definition of averaging

$$\Rightarrow \langle \rho_n(\vec{r},t) \rangle = \langle q_n \delta(\vec{r}-\vec{r}_n) \rangle$$

$$- \vec{\nabla} \cdot \langle \vec{p}_n \delta(\vec{r}-\vec{r}_n) \rangle$$

$\vec{\nabla} \cdot p\, \delta = \vec{p} \cdot \vec{\nabla} \delta$

$$+ \frac{1}{6} \sum_{\alpha\beta} \frac{\partial^2}{\partial r_\alpha \partial r_\beta} \langle (Q'_n)_{\alpha\beta} \delta(\vec{r}-\vec{r}_n) \rangle$$

Now

$$\langle \rho_{\text{bound}}(\vec{r},t) \rangle = \sum_n \langle \rho_n(\vec{r},t) \rangle$$

$$= \left\langle \sum_n q_n \delta(\vec{r}-\vec{r}_n) \right\rangle - \vec{\nabla} \cdot \left\langle \sum_n \vec{p}_n \delta(\vec{r}-\vec{r}_n) \right\rangle$$

$$+ \frac{1}{6} \sum_{\alpha\beta} \frac{\partial^2}{\partial r_\alpha \partial r_\beta} \left\langle \sum_n (Q_n)'_{\alpha\beta} \delta(\vec{r}-\vec{r}_n) \right\rangle$$

Define $\vec{\mathbb{P}}(\vec{r},t) \equiv \langle \sum_n \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle$ average polarizat density

$\overleftrightarrow{\mathbb{Q}}'(r,t) \equiv \frac{1}{6}\langle \sum_n \overleftrightarrow{Q}'_n \, \delta(\vec{r}-\vec{r}_n) \rangle$ average quadrapole density

$$\langle \rho_{bound} \rangle = \sum_n \langle q_n \, \delta(\vec{r}-\vec{r}_n) \rangle - \vec{\nabla}\cdot\vec{\mathbb{P}} + \sum_{\alpha\beta} \frac{\partial^2}{\partial r_\alpha \partial r_\beta} \overleftrightarrow{\mathbb{Q}}'_{\alpha\beta}$$

~~Denote~~

Define the macroscopic charge density

$$\rho \equiv \langle \sum_{i \text{ free}} q_i \, \delta(\vec{r}-\vec{r}_i) \rangle + \langle \sum_{\substack{n \\ \text{molec}}} q_n \, \delta(\vec{r}-\vec{r}_n) \rangle$$

Then

$$\vec{\nabla}\cdot\vec{E} = 4\pi\langle \rho_0 \rangle = 4\pi\left[\rho - \vec{\nabla}\cdot\vec{\mathbb{P}} + \sum_{\alpha\beta} \frac{\partial^2}{\partial r_\alpha \partial r_\beta} \overleftrightarrow{\mathbb{Q}}'_{\alpha\beta}\right]$$

$$\sum_\alpha \frac{\partial}{\partial r_\alpha}\left[E_\alpha + 4\pi \mathbb{P}_\alpha - 4\pi \sum_\beta \frac{\partial}{\partial r_\beta} \mathbb{Q}'_{\alpha\beta}\right] = 4\pi\rho$$

Define electric displacement vector

$$D_\alpha = E_\alpha + 4\pi \mathbb{P}_\alpha - 4\pi \sum_\beta \frac{\partial}{\partial r_\beta} \mathbb{Q}'_{\alpha\beta}$$

then $\boxed{\vec{\nabla}\cdot\vec{D} = 4\pi\rho}$

In most materials, the quadrapole and higher terms are negligible and we can take

$$\vec{D} = \vec{E} + 4\pi\vec{\mathbb{P}}$$

why quadrapole + higher order terms can generally be ignored:

Let a_0 be the length scale that characterizes the size of a molecule in the dielectric
Let l be the typical spacing between molecules
Let L be the length scale of the spatial averaging function $f(\vec{r})$. $L \gg a_0$

dipole moment per a_0

$$\Rightarrow \text{polarization } \mathbb{P} \sim \frac{a_0}{l^3}$$

$$\vec{\nabla} \cdot \vec{\mathbb{P}} \sim \left(\frac{a_0}{L}\right) \frac{1}{l^3}$$

since $\mathbb{P}$ cannot vary on length scale short than the averaging lengt L

quadrapole moment

$$Q \sim a_0^2$$

quadrapole density $\mathbb{Q} \sim \frac{a_0^2}{l^3}$

$$\frac{\partial^2 \mathbb{Q}}{\partial r_\alpha \partial r_\beta} \sim \left(\frac{a_0}{L}\right)^2 \frac{1}{l^3}$$

each higher moment gives extra factor a_0
each higher derivative gives extra factor $\frac{1}{L}$

So quadrapole is smaller than dipole term by factor $\left(\frac{a_0}{L}\right) \ll 1$. Higher terms smaller ~~b~~ by additional factors of $\left(\frac{a_0}{L}\right)$

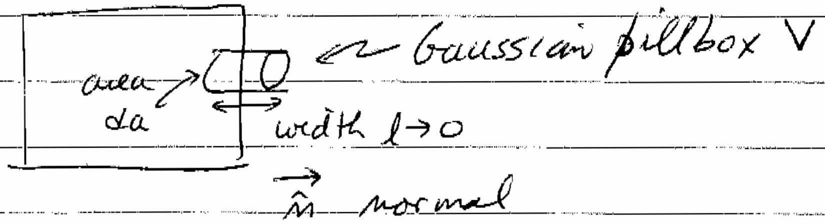
For insulators one generally has $\rho_n = 0$
molecules are neutral.

In this case the macroscopic ρ is just the free charge $\rho = \langle \rho_{free} \rangle$.

And the bound charge is just

$$\boxed{\langle \rho_{bound} \rangle = -\vec{\nabla} \cdot \vec{\mathbb{P}}}$$

At a <u>surface</u> of a dielectric



$$-\int_V d^3r \; \vec{\nabla} \cdot \vec{\mathbb{P}} = -\oint_S da \; \hat{n} \cdot \vec{\mathbb{P}}$$

contrib from sides $\to 0$ as $l \to 0$
contrib from outside surface $= 0$ as $\mathbb{P} = 0$ outside

$$= \hat{n} \cdot \vec{\mathbb{P}} \, da$$

only contrib is from inside surfac
($\hat{n}$ is <u>outward</u> normal

$$= \int_V d^3r \; \rho_{bound}$$

as $l \to 0$, $\int_V d^3r \; \rho_{bound} \to \int da \; \sigma_{bound} = da \, \sigma_{bound}$ surface charge

$$\Rightarrow \boxed{\sigma_{bound} = \hat{n} \cdot \vec{\mathbb{P}}}$$ at surface of dielectric

Magnetic Materials

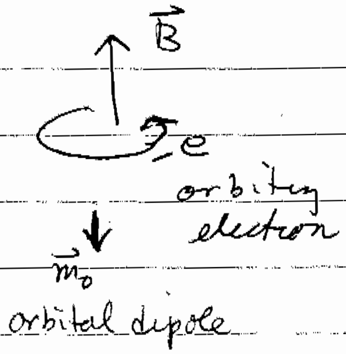
Circulating currents on atomic scale give rise to local magnetic dipole moments, which create local magnetic fields in the material.

Sources of circulating atomic currents:

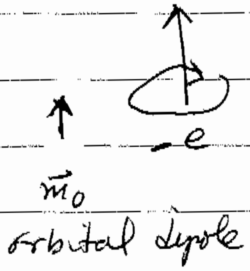
1) intrinsic angular momentum of electrons, ie "electron spin" - can add up and give a net angular momentum to atom
2) orbital angular momentum of electrons - can add up to give net angular momentum of atom.

(1) + (2) ⇒ atoms can have a net magnetic dipole moment. When $\vec{B}=0$, these atomic moments are generally in random orientations and average to zero (exception is a ferromagnet where moments can allign even if $\vec{B}=0$) When apply $\vec{B}\neq 0$, the moments tend to allign parallel to $\vec{B}$ giving a net magnetization density $\vec{M}\propto\vec{B}$. This is a paramagnetic effect.

But there is also a diamagnetic effect from orbital angular momentum (exists even if total angular momentum of electrons is zero, ie exists for atoms with zero net dipole moment)



← applying $\vec B$ to orbiting electron speeds up its orbital velocity. Increased angular momentum of *negatively* charged electron gives change in dipole moment $\Delta\vec m \propto -\vec B$



← applying $\vec B$ to orbiting electron slows down its orbital velocity. Net result is again that $\Delta\vec m \propto -\vec B$

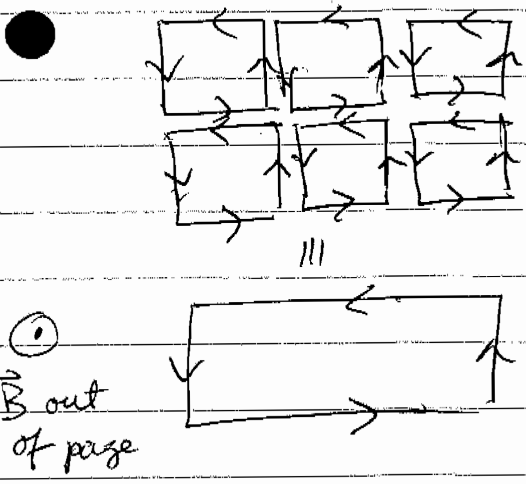
see Griffiths chpt 6 + prob 7.17 2nd ed for details

No matter which way electron orbits with respect to $\vec B$, result is a decrease in magnetic moment, so $\Delta\vec m \propto -\vec B$.
That $\Delta\vec m$ is opposite to $\vec B$ is called *diamagnetism*

Model atomic magnetic moments as small current loops. When loops get oriented, ie there is non zero average magnetization density

$$\vec M(\vec r) = \sum_i \vec m_i \, \delta(\vec r - \vec r_i)$$

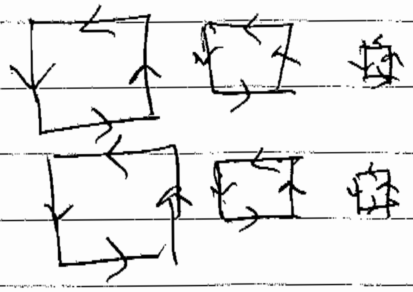
then net effect is to have a current flowing around the system. This current gives rise to magnetic fields alligned atomic moments in a uniform applied $\vec{B}$



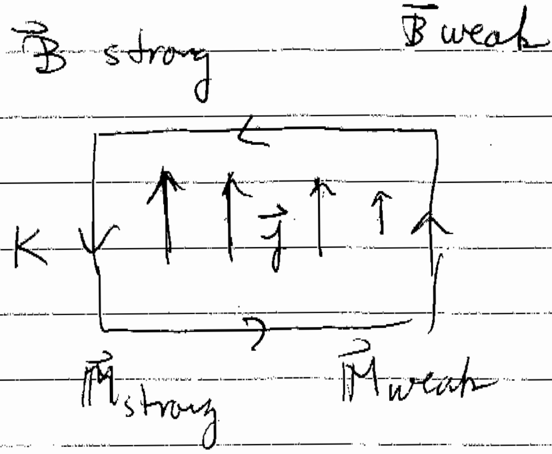
in interior, currents in opposite directions cancell ad so $\vec{J} = 0$ inside

but is net circulation of current around boundary of material $\Rightarrow$ surface current $\vec{K}_{bound}$

If $\vec{B}$ is not uniform, then $\vec{M}$ is not uniform Can create finite current density $\vec{J}$ in interior, as well as surface currents



Now currents in interior do not cancell. Net current $\vec{J}_{bound}$ in interior



$\vec{B}$ out of page $\Rightarrow$ $\vec{M}$ out of page
~~M varies along page~~
$\vec{M}$ varies in direction $\perp$ direction of $\vec{M}$
$\Rightarrow$ $\vec{\nabla}\times\vec{M} \neq 0$ gives $\vec{J}_{bound}$

Average current

$$\langle \vec{j}_0 \rangle = \Big\langle \sum_{i \in \text{free}} q_i \, \vec{v}_i \, \delta(\vec{r}-\vec{r}_i) \Big\rangle + \sum_{\substack{n \\ \text{molec}}} \langle \vec{j}_n \rangle$$

$\uparrow$ current from free charges

$\uparrow$ current from molecule n of the dielectric

$$\langle \vec{j}_n(\vec{r},t) \rangle = \sum_{i \in n} q_i (\vec{v}_n + \vec{v}_{ni}) \langle \delta(\vec{r} - \vec{r}_n(t) - \vec{r}_{ni}(t)) \rangle$$

$$= \sum_{i \in n} q_i (\vec{v}_n + \vec{v}_{ni}) \, f(\vec{r} - \vec{r}_n(t) - \vec{r}_{ni}(t))$$

$\uparrow$ $\vec{v}_n = \dfrac{d\vec{r}_n}{dt}$ $\quad\uparrow$ $\vec{v}_{ni} = \dfrac{d\vec{r}_{ni}}{dt}$ $\quad\uparrow$ position of CM of molec n $\quad\uparrow$ position of charge i wrt CM

as with $\langle \rho_0 \rangle$, we can expand in $\vec{r}_{ni}$

$$\langle \vec{j}_n \rangle = \sum_{i \in n} q_i (\vec{v}_n + \vec{v}_{ni}) \Big\{ f(\vec{r}-\vec{r}_n) - \vec{r}_{ni} \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n) + \frac{1}{2} \sum_{\alpha\beta} (r_{ni})_\alpha (r_{ni})_\beta \frac{\partial^2 f(\vec{r}-\vec{r}_n)}{\partial r_\alpha \partial r_\beta} + \cdots \Big\}$$

we will keep only the first two terms in the expansion

The various terms we have to consider are

① $\sum_{i\in n} q_i \vec{v}_n f(\vec{r}-\vec{r}_n)$

② $\sum_{i\in n} q_i \vec{v}_{ni}\, \delta(\vec{r}-\vec{r}_n)$

③ $-\sum_{i\in n} q_i \vec{v}_n \left[\vec{r}_{ni} \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n)\right]$

④ $-\sum_{i\in n} q_i \vec{v}_{ni} \left[\vec{r}_{ni} \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n)\right]$

$$① = \vec{v}_n f(\vec{r}-\vec{r}_n) \sum_{i\in n} q_i = q_n \vec{v}_n f(r-r_n)$$
$$= \langle q_n \vec{v}_n \delta(\vec{r}-\vec{r}_n)\rangle$$

this is just current of molecule as if it were a point charge q_n. For a neutral molecule $q_n = 0$ and this term vanishes

② Note: $\frac{\partial}{\partial t}\langle \vec{p}_n \delta(\vec{r}-\vec{r}_n)\rangle = \frac{\partial}{\partial t}\Big(\sum_{i\in n} q_i \vec{r}_{ni} f(\vec{r}-\vec{r}_n$

$$= \sum_{i\in n} q_i \vec{v}_{ni} f(\vec{r}-\vec{r}_n)$$
$$+ \sum_{i\in n} q_i \vec{r}_{ni} \left[-\vec{\nabla} f(\vec{r}-\vec{r}_n) \cdot \vec{v}_n\right]$$

So for ②, $\sum_{i\in n} q_i \vec{v}_{ni} f(\vec{r}-\vec{r}_n)$

$$= \frac{\partial}{\partial t}\langle \vec{p}_n \delta(\vec{r}-\vec{r}_n)\rangle$$
$$+ \left[\vec{v}_n \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n)\right] \vec{p}_n$$

So

$$② = \sum_{i\in n} q_i \vec{v}_{ni}\, f(\vec{r}-\vec{r}_n) = \frac{\partial}{\partial t}\langle \vec{p}_n\,\delta(\vec{r}-\vec{r}_n)\rangle + (\vec{v}_n\cdot\vec{\nabla})\langle \vec{p}_n\,\delta(r-r_n)\rangle$$

2nd term is $\sum_\alpha v_{n\alpha}\frac{\partial}{\partial r_\alpha}\langle \vec{p}_n\,\delta(\vec{r}-\vec{r}_n)\rangle$

$$③ = -\vec{v}_n\Big(\sum_{i\in n} q_i \vec{r}_{ni}\Big)\cdot\vec{\nabla} f(\vec{r}-\vec{r}_n) = -\vec{v}_n\left(\vec{p}_n\cdot\vec{\nabla} f(\vec{r}-\vec{r}_n)\right)$$

$$= -\vec{v}_n\,\vec{\nabla}\cdot\langle \vec{p}_n\,\delta(\vec{r}-\vec{r}_n)\rangle = \sum_\alpha \vec{v}_n\frac{\partial}{\partial r_\alpha}\langle p_{n\alpha}\,\delta(\vec{r}-\vec{r}_n)\rangle$$

$$④ = -\vec{\nabla} f(\vec{r}-\vec{r}_n)\cdot\sum_{i\in n} q_i \vec{r}_{ni}\vec{v}_{ni}$$

We have seen the tensor $\sum_i q_i \vec{r}_{ni}\vec{v}_{ni}$ before when we considered the magnetic dipole moment

$$\sum_{i\in n} q_i \vec{r}_{ni}\vec{v}_{ni} = \int d^3r\, \vec{r}\vec{j}$$

where $\vec{j}(\vec{r}) \equiv \sum_{i\in n} q_i \vec{v}_{ni}\,\delta(\vec{r}-\vec{r}_{ni}$
is current density with respect to center of mass of molecule

We had $\int d^3r\,\vec{r}\vec{j} = -\int d^3r\,\vec{j}\vec{r} - \int d^3r\,(\vec{\nabla}\cdot\vec{j})\,\vec{r}\vec{r}$

$\uparrow$
in statics, $\vec{\nabla}\cdot\vec{j} = 0$
in general $\vec{\nabla}\cdot\vec{j} = -\frac{\partial\rho}{\partial t}$

$$\int d^3r\,\vec{r}\vec{j} = -\int d^3r\,\vec{j}\vec{r} + \int d^3r\,\frac{\partial\rho}{\partial t}\,\vec{r}\vec{r}$$

$$= -\int d^3r\,\vec{j}\vec{r} + \frac{\partial}{\partial t}\left[\int d^3r\,\rho\,\vec{r}\vec{r}\right]$$

$\uparrow$
although this is not zero, it is a quadrapole term $\sim O\left(\frac{a_0}{L}\right)^2$ of the same order as the term we dropped when we truncate expansion to linear order

So $\int d^3r\, \vec{r}\,\vec{j} \simeq -\int d^3r\, \vec{j}\,\vec{r}$ ignoring the quadrapole term

$$= \frac{1}{2}\int d^3r \left[\vec{r}\,\vec{j} - \vec{j}\,\vec{r}\right]$$

$$\sum_{i\in n} q_i \vec{r}_{ni}\,\vec{v}_{ni} = \frac{1}{2}\sum_{i\in n} q_i \left[\vec{r}_{ni}\,\vec{v}_{ni} - \vec{v}_{ni}\,\vec{r}_{ni}\right]$$

$$-\vec{\nabla} f(r-r_n)\cdot \sum_{i\in n} q_i \vec{r}_{ni}\,\vec{v}_{ni} = -\vec{\nabla} f(\vec{r}-\vec{r}_n)\cdot \frac{1}{2}\sum_{i} \left[\vec{r}_{ni}\,\vec{v}_{ni} - \vec{v}_{ni}\,\vec{r}_{ni}\right.$$

$$= \frac{-1}{2}\sum_{i\in n} q_i \left[(\vec{\nabla} f\cdot\vec{r}_{ni})\,\vec{v}_{ni} - (\vec{\nabla} f\cdot\vec{v}_{ni})\,\vec{r}_{ni}\right]$$

$$= -\frac{1}{2}\sum_{i\in n} q_i\, \vec{\nabla} f \times (\vec{v}_{ni}\times\vec{r}_{ni})$$ triple product rule

$$= \vec{\nabla} f(\vec{r}-\vec{r}_n) \times \frac{1}{2}\sum_{i\in n} \vec{r}_{ni}\times\vec{v}_{ni}\, q_i$$

$$= \vec{\nabla} f(\vec{r}-\vec{r}_n) \times \frac{1}{2}\int d^3r\, \vec{r}\times\vec{j}$$

$$= \vec{\nabla} f(\vec{r}-\vec{r}_n) \times c\,\vec{m}_n$$ where $\vec{m}_n = \frac{1}{2c}\sum_{i\in n} \vec{r}_{ni}\times\vec{v}_{ni}\, q_i$

is magnetic dipole moment of molecule n

$$= \vec{\nabla}\times f(\vec{r}-\vec{r}_n)\, c\,\vec{m}_n$$

$$= \vec{\nabla}\times \left\langle c\,\vec{m}_n\,\delta(\vec{r}-\vec{r}_n)\right\rangle$$

Adding all the pieces

$$\langle \vec{j}_n \rangle = \underset{\textcircled{1}}{\langle q_n \vec{v}_n \, \delta(\vec{r}-\vec{r}_n) \rangle} + c\, \vec{\nabla} \times \underset{\textcircled{4}}{\langle \vec{m}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}$$

$$+ \underset{\textcircled{2}}{\frac{\partial}{\partial t} \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle} + \underset{\textcircled{2}}{(\vec{v}_n \cdot \vec{\nabla}) \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}$$

$$- \underset{\textcircled{3}}{\vec{v}_n \, \vec{\nabla} \cdot \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}$$

Define $\vec{\mathbb{M}}(\vec{r}) \equiv \sum_n \langle \vec{m}_n \, \delta(\vec{r}-\vec{r}_n) \rangle$ average magnetization density

$\vec{\mathbb{P}}(\vec{r}) \equiv \sum_n \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle$ polarization density, as before

$$\sum_n \langle \vec{j}_n \rangle = \sum_n \langle q_n \vec{v}_n \, \delta(\vec{r}-\vec{r}_n) \rangle + c\, \vec{\nabla} \times \vec{\mathbb{M}} + \frac{\partial \vec{\mathbb{P}}}{\partial t}$$

$$+ \sum_n \left[(\vec{v}_n \cdot \vec{\nabla}) \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle - \vec{v}_n \, \vec{\nabla} \cdot \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle \right]$$

see Jackson (6.96) for additional electric quadrapole terms

The last term on the right hand side is usually small and ignored. This is because the molecular velocities $\vec{v}_n$ are usually small, and randomly oriented, so that they average to zero. (See Jackson (6.100) for case of net translation of dielectric, $\vec{v}_n$ = const all n)