The dielectric response (which is related to refractive index, $n = \sqrt{\varepsilon / \varepsilon_0}$) is an extremely important physical property of materials.

Previously, we calculated optical absorption based on quantum transitions across a semiconducting bandgap. Surprisingly, dielectric response (even for a static electric field) can be calculated from the same knowledge of quantum transitions.
Relationship between $\alpha$ & $\varepsilon$

To understand this relationship, we study an electron on a lightly-damped spring.

$$\omega_0 = \sqrt{\frac{k}{m}}$$

- This is a simple system for which we can derive both $\alpha(w)$ and $\varepsilon(w)$. $\alpha(w)$ has a sharp peak at $\omega_0$.

- $\alpha_{si}(w)$ can be mimicked using many electron-on-spring systems, each with a different $\omega_0$.

The dielectric response of each electron-on-$\alpha$ spring then add together, yielding $\varepsilon_{si}(w)$. 
Solving the eqn of motion for an electron on a spring

\[
\frac{d^2 x}{dt^2} + \gamma \frac{dx}{dt} + \omega_0^2 x = -\frac{e}{m} E
\]

- **damping coefficient**
- **Electric field gives driving force**

Assume \( E = E_0 e^{-i\omega t} \) (electric field from a photon of energy \( \hbar \omega \))

Then \( x = X_0 e^{-i\omega t} \)

\( X_0 \) will be complex if there is a phase difference between \( E \) field and electron position.

\[
X_0 = \left( -\frac{e}{m} \frac{E_0}{\omega_0^2 - \omega^2 - i\omega \delta} \right)
\]
If I fill space with a 3d grid of electrons on springs \(\Rightarrow (N\) electrons, total volume \(L^3\))

\[
\begin{align*}
\uparrow \\
\rightarrow -m\Theta & -m\Theta & -m\Theta \\
\leftarrow -m\Theta & -m\Theta & -m\Theta \\
\downarrow
\end{align*}
\]

Then the polarization of the "material" is

\[
P = \frac{N}{L^3} \left(-e\mathbf{x}\right)
\]

\[\text{\text{dipole moment of a displaced electron.}}\]

\[
= \frac{N}{L^3} \left(\frac{e^2}{m} \frac{E_0}{\omega_0^2 - \omega^2 - i\omega\delta} \right) e^{i\omega t}
\]

The dielectric constant of this material we've created is defined as

\[
\epsilon = \epsilon_0 + \frac{P}{E}
\]
\( \varepsilon(\omega) = \varepsilon_0 + \frac{N}{L^3} \frac{e^2}{m} \frac{1}{\omega_0^2 - \omega^2 - i\omega \gamma} \)

Assuming \( \gamma \ll \omega_0 \)

\[ \varepsilon_{\text{Re}}(\omega) = \varepsilon_0 + \frac{N}{L^3} \frac{e^2}{m} \frac{1}{\omega_0^2 - \omega^2}, \quad \text{for } \omega < \omega_0. \]

\[ \varepsilon_{\text{im}} = \frac{N}{L^3} \frac{e^2}{m} \frac{\omega \gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2} \]

**Key Insight:** A peak in absorption at one freq contributes to \( \varepsilon_{\text{Re}} \) at all frequencies.
We apply this idea by making a crude model for the properties of Si:

Model Si as a diamond lattice with one electron on a spring located at each lattice site. This material has a single absorption peak at \( \hbar \omega = 3.4 \text{ eV} \) (the direct bandgap of Si), i.e. \( \omega_0 = \frac{3.4 \text{ eV}}{\hbar} \)

\[
\frac{N}{L^3} = 5 \times 10^{28} \text{ m}^{-3} \quad (\text{since density is } 2.3 \text{ g/cm}^3 \text{ and atomic mass is } 28 \text{ g/mol})
\]

Therefore

\[
\frac{\varepsilon_{\text{Re}}}{\varepsilon_0} = 1 + \frac{N}{L^3} \frac{\varepsilon^2}{\varepsilon_0 \mu} \frac{1}{\omega_0^2 - \omega^2}
\]

This coefficient is known as \( \omega_p^2 \), the plasma freq squared.

\[
= 1 + \frac{(25 \times 10^{15})^2}{(6 \times 10^{15})^2 - \omega^2}
\]

@ \( \omega = 0 \) \( \frac{\varepsilon_{\text{Re}}}{\varepsilon_0} = 17 \), quite close to the actual answer.
Pop Quiz

Repeat the estimate for SiO₂

Assume the same number of electrons on springs,

\[ \frac{N}{L^3} = 5 \times 10^{28} \text{ m}^{-3}. \]
LIMITATIONS OF BAND THEORY (AS IMPLEMENTED BY WIEN2K)

Many of you have noticed that Wien2K underestimates the bandgap of semiconductors.

"Band theory ignores electron-electron repulsions, this is the reason why many (thousands) of compounds that are expected to be metallic are in fact insulators."

For more discussion see p.226 Sutton.

What Sutton calls "Band theory" is generally known as "the tight binding model." Indeed, the tight binding model makes some big approximations.

- DFT programs like Wien2k do better than tight binding. DFT accounts for the electrostatic potential of the nuclei $V_{\text{Nuclei}}(\mathbf{r})$ and the electrons $V_{\text{Electrons}}(\mathbf{r})$ to compute $V_{\text{eff}}(\mathbf{r})$ in a self-consistent manner.
I
Construct $V_{H}(r) = \int \frac{\rho(r')}{4\pi\varepsilon_0 |r - r'|} \, dr'$

Construct $V_{\text{eff}}(r) = V_{H}(r) + V_{N}(r)$

Solve $-\frac{\hbar^2}{8\pi^2 m} \nabla^2 \Psi_j(r) + V_{\text{eff}}(r) \Psi_j(r) = \varepsilon_j \Psi_j(r)$

Construct output $\rho(r) = \sum_{j \text{ occupied}} \Psi_j(r)^* \Psi_j(r)$

Is output $\rho(r)$ the same as input $\rho(r)$?

**Yes** → STOP

**No** → Guess input $\rho(r)$ e.g. a superposition of atomic charge densities

Fig. 11.1 Flow chart of a self-consistent calculation in the Hartree approximation.

Note: $V_{H}(r)$ is not used by DFT, there are better approximations to find $V_{\text{eff}}(r)$. Wien2k use the "local density approximation" (LDA) when computing $V_{\text{eff}}(r)$.

A more accurate method is the "generalized gradient approximation" (GGA) that accounts for both local electron density and the gradient in electron density.