Chapter 11: Dielectric Properties of Materials

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Electromagnetic fields are essential probes of material properties

- IR absorption
- Spectroscopy

The interaction of the field and material may be described either classically or Quantum mechanically. We will first do the former.

1 Classical Dielectric Response of Materials

Classically, materials are characterized by their dielectric response of either the bound or free charge. Both are described by Maxwells equations

\[
\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad \nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} \quad (1)
\]

and Ohm’s law

\[
\mathbf{j} = \sigma \mathbf{E}. \quad (2)
\]

Both effects may be combined into an effective dielectric constant \( \tilde{\epsilon} \), which we will now show. For an isotropic medium, we have
Figure 1: If the average excursion of the electron is small compared to the wavelength of the radiation $< x > \ll \lambda$, then we may ignore the wave-vector dependence of the radiation so that $\epsilon(k, \omega) \approx \epsilon(\omega)$.

$$D(\omega) = \epsilon(\omega)E(\omega)$$

where

$$\mathcal{E}(t) = \int d\omega e^{-i\omega t} \mathcal{E}(\omega) \quad H(t) = \int d\omega e^{-i\omega t} H(\omega)$$

$$D(t) = \int d\omega e^{-i\omega t} D(\omega) \quad B(t) = \int d\omega e^{-i\omega t} B(\omega)$$

$$\mathcal{E}(\omega) = \mathcal{E}^*(-\omega) \Rightarrow \mathcal{E}(t) \in \Re$$

Then $\nabla \times H = \frac{4\pi}{c} j + \frac{1}{c} \frac{\partial D}{\partial t}$ implies

$$\nabla \times \int d\omega e^{-i\omega t} H(\omega) = \frac{4\pi}{c} \int d\omega e^{-i\omega t} j(\omega) + \frac{1}{c} \frac{\partial}{\partial t} \int d\omega e^{-i\omega t} D(\omega)$$

(7)
\[
\int d\omega e^{-i\omega t} \left\{ \nabla \times \mathbf{H}(\omega) - \frac{4\pi}{c} \mathbf{j}(\omega) - \frac{1}{c}(-i\omega)\mathbf{D}(\omega) \right\} = 0 \quad (8)
\]

\[
\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j} - i\frac{\omega}{c} \mathbf{D}(\omega)
\]

\[
= \frac{4\pi\sigma}{c} \mathbf{E} - i\frac{\omega}{c} \epsilon \mathbf{E} = \begin{cases} 
- \frac{i\omega}{c} \mathbf{E} \left( \epsilon - \frac{c}{\omega} \frac{4\pi\sigma}{c} \right) &= -\frac{i\omega}{c} \epsilon \tilde{\epsilon} \\
\frac{4\pi}{c} \mathbf{E} \left( \sigma - \frac{c}{4\pi} \frac{i\omega}{c} \epsilon \right) &= \frac{4\pi}{c} \mathbf{E} \tilde{\sigma} 
\end{cases} \quad (9)
\]

Thus we could either define an effective conductivity \(\tilde{\sigma} = \sigma - \frac{i\omega\epsilon}{4\pi}\) which takes into account dielectric effects, or an effective dielectric constant \(\tilde{\epsilon} = \epsilon + \frac{4\pi\sigma}{\omega}\), which accounts for conduction.

### 1.1 Conditions on \(\epsilon\)

From the reality of \(\mathbf{D}(t)\) and \(\mathbf{E}(t)\), one has that \(\mathbf{E}(+\omega) = \mathbf{E}^*(-\omega)\) and \(\mathbf{D}(\omega) = \mathbf{D}^*(-\omega)\), hence for \(\mathbf{D} = \epsilon \mathbf{E}\),

\[
\epsilon(\omega) = \epsilon^*(-\omega) \quad (10)
\]
Additional constraints are obtained from causality

\[
D(t) = \int d\omega \epsilon(\omega) E(\omega) e^{-i\omega t}
\]

\[
= \int d\omega \epsilon(\omega) e^{-i\omega t} \int \frac{dt'}{2\pi} e^{i\omega t'} E(t')
\]

\[
= \frac{1}{2\pi} \int dt d\omega (\epsilon(\omega) - 1 + 1) E(t') e^{-i\omega(t-t')}
\] (11)

then we make the substitution

\[
\chi(\omega) \equiv \frac{\epsilon - 1}{4\pi}
\] (12)

\[
D(t) = 2 \int d\omega \left( \chi(\omega) + \frac{1}{4\pi} \right) E(t') e^{-i\omega(t-t')}
\]

\[
D(t) = E(t) + 2 \int d\omega \chi(\omega) E(t') e^{-\omega(t-t')}
\] (13)

Define \( G(t) \equiv 2 \int d\omega \chi(\omega) e^{-i\omega t} \), then

\[
D(t) = E(t) + \int_{-\infty}^{\infty} dt' G(t - t') E(t')
\] (14)

Thus, the electric displacement at time \( t \) depends upon the field at other times; however, it cannot depend upon times \( t' > t \) by causality. Hence

\[
G(\tau) \equiv 0 \quad \tau < 0
\] (15)
Figure 2: If $\chi(\omega)$ is analytic in the upper half plane, then causality is assured.

This can be enforced if $\chi(\omega)$ is analytic in the upper half plane, then we may close

$$G(\tau) = 2 \int_{-\infty}^{\infty} d\omega \chi(\omega) e^{-i\omega \tau}$$

$$= 2 \int_{-\infty}^{\infty} d\omega \chi(\omega) e^{-i\omega \tau} \equiv 0 \quad (16)$$

contour in the upper half plane and obtain zero for the integral since $\chi$ is analytic within and on the contour.

1.2 Kramer’s Kronig Relations

One may also derive an important relation between the real and imaginary parts of the dielectric function $\epsilon(\omega)$ using this analytic property. From the Cauchy integral formula, if $\chi$ is
analytic inside and on the contour $C$, then

$$\chi(z) = \frac{1}{2\pi i} \oint_{C} \frac{\chi(\omega')}{z - \omega'} d\omega'$$  \hspace{1cm} (17)$$

Then taking the contour shown in Fig. 3 and assuming that

$$\chi(\omega) \lesssim \frac{1}{\omega} \text{ for large } \omega \text{ (in fact } \text{Re} \chi \lesssim \frac{1}{\omega} \text{ and } \text{Im} \chi \lesssim \frac{1}{\omega^2} \text{)}$$

we may ignore the large semicircle. Let $z = \omega + i0^+$, so that

$$\chi(\omega + i0^+) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\chi(\omega') d\omega'}{\omega - \omega' - i0^+}$$  \hspace{1cm} (18)$$

$$2\pi i \chi(\omega + i0^+) = P \int_{-\infty}^{\infty} \frac{\chi(\omega') d\omega'}{\omega - \omega'} + i\pi \chi(\omega)$$  \hspace{1cm} (19)$$

$$\chi(\omega) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\chi(\omega')}{\omega - \omega'}$$  \hspace{1cm} (20)$$

Then let $4\pi \chi(\omega) = \epsilon(\omega) - 1 = \epsilon_1 + i\epsilon_2 - 1$ and we get

$$\epsilon_1(\omega) + i\epsilon_2(\omega) - 1 = \frac{2}{\pi} P \int_{-\infty}^{\infty} \frac{-i\epsilon_1(\omega') + \epsilon_2(\omega') + 1}{\omega - \omega'} d\omega'$$  \hspace{1cm} (21)$$
or

\[ \epsilon_1(\omega) - 1 = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')}{\omega - \omega'} d\omega' \]  \hspace{1cm} (22) \\

\[ \epsilon_2(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon_1(\omega') - 1}{\omega - \omega'} d\omega' \]  \hspace{1cm} (23)

which are known as the Kramer’s Kronig relations. Many experiments measure \( \epsilon_2 \) and from Eq. 22 we can calculate \( \epsilon_1 \)!

2 Absorption of E and M radiation

2.1 Transmission

\[ \xi = \xi_0 e^{-i\omega(t-nx/c)} \]

\[ \tilde{n} = 1 \]

\[ \tilde{n} = n + i\kappa = \sqrt{\epsilon(\omega)} \]

\[ \tilde{n} = n^2 + 2in\kappa - \kappa^2 = \epsilon_1 + i\epsilon_2 \]

\[ \epsilon_1 = n^2 - \kappa^2 \]

\[ \epsilon_2 = 2n\kappa \]

Figure 4: In transmission experiments a laser beam is focused on a thin slab of some material we wish to study.

Imagine that a laser beam of known frequency is normally
incident upon a thin slab of some material (see Fig. 4), and we are able to measure its transmitted intensity.

Upon passing through a boundary, part of the beam is reflected and part is transmitted (see Fig. 5). In the case of normal incidence, it is easy to calculate the related coefficients from the conditions of continuity of $\mathbf{E}_\perp$ and $\mathbf{H}_\perp = \mathbf{B}_\perp(\mu = 1)$. 

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad i\mathbf{k} \times \mathbf{E} = \frac{i\omega}{c} \mathbf{B}$$

$$|n\mathbf{E}_\perp| = |\mathbf{B}_\perp|$$

$$\begin{cases}
\mathbf{E}_0 + \mathbf{E}'' = \mathbf{E}' \\
(n\mathbf{E}_0 - \mathbf{E}''') = n\mathbf{E}'
\end{cases} \quad t = \frac{2}{n + 1}$$

In this way the other coefficients may be calculated (see Fig. 6). Accounting for multiple reflections the total transmitted field is
Figure 6: Multiple events contribute to the radiation transmitted through and reflected from a thin slab.

\[ \mathcal{E} = \mathcal{E}_0 t_1 t_2 e^{i k d} + \mathcal{E}_0 t_1 r_2 t_2 e^{3 i k d} + \cdots, \quad \text{where} \quad k = \frac{\tilde{n} \omega}{c} \]

\[ \mathcal{E} = \frac{\mathcal{E}_0 t_1 t_2 e^{i d \tilde{n} \omega / c}}{1 - r_2^2 e^{2 i d \tilde{n} \omega / c}} \]  

(27)  

(28)  

If \( \tilde{n} \sim 1 \) and \( d \) is small, then

\[ \mathcal{E} \simeq \mathcal{E}_0 e^{i d \tilde{n} \omega / c} \]  

(29)  

\[ I \simeq I_0 e^{i d (\tilde{n} - \tilde{n}^*) / c} = I_0 e^{-d \omega 2 \kappa / c} \]  

(30)  

\[ \kappa = \frac{\epsilon_2}{2 \sqrt{\epsilon_1}} \]  

(31)  

\[ I \simeq I_0 e^{-(\epsilon_2 \omega / c) d} \simeq I_0 \left( 1 - \frac{\epsilon_2 \omega}{c} d \right) \]  

(32)  

If the thickness \( d \) is known, then the quantity

\[ \frac{\omega \epsilon_2(\omega)}{c} = \frac{4 \pi \sigma_1(\omega)}{c} \]  

(33)
may be measured (the absorption coefficient). The real part of the dielectric response, \( \epsilon_1(\omega) \) may be calculated with the Kramers Kronig relation

\[
\epsilon_1(\omega) = 1 + \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')}{\omega' - \omega} d\omega'
\]  

(34)

According to Young Kim, this analysis works for sufficiently thin samples in the optical regime, but typically fails in the IR where \( \epsilon_2 \) becomes large.

### 2.2 Reflectivity

Of course, we could also have performed the experiment on a very thick slab of the material, and measured the reflectivity \( R \) However, this is a much more complicated experiment since \( \frac{R}{I} \) depends upon both \( \epsilon_1 \) and \( \epsilon_2(\omega) \), and is hence much more difficult to analyze [See Frederick Wooten, *Optical Properties of Solids*, (Academic Press, San Diego, 1972)].

To analyze these experiments, one must first measure the reflectivity, \( R(\omega) \) over the entire frequency range. We then write

\[
R(\omega) = r(\omega)r^*(\omega) = \frac{(n - 1)^2 + \kappa^2}{(n + 1)^2 + \kappa^2}
\]  

(35)
\[ \tilde{n} = n + ik \quad \text{and} \quad r(\omega) = \rho(\omega)e^{i\theta} \quad (36) \]

so that \( R(\omega) = \rho(\omega)^2 \). If \( \rho(\omega) \rightarrow 1 \) and \( \theta \rightarrow 0 \) fast enough as the frequency increases, then we may employ the Kramers Kronig relations replacing \( \chi \) with \( \ln r(\omega) = \ln \rho(\omega) + i\theta(\omega) \), so that

\[ \theta(\omega') = -\frac{2\omega'}{\pi} \text{P} \int_0^\infty \frac{\ln \sqrt{R(\omega)}}{\omega^2 - \omega'^2} d\omega \quad (37) \]

Thus, if \( R(\omega) \) is measured over the entire frequency range where it is finite, then we can calculate \( \theta(\omega) \). This complete knowledge of \( R \) is generally not available, and various extrapolation and fitting schemes are used on \( R(\omega) \) so that the integral above may be completed.
We may then use Eq. 35 above to relate $R$ and $\theta$ to the real and imaginary parts of the refractive index,

$$n(\omega) = \frac{1 - R(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)} \cos \theta(\omega)}$$

(38)

and

$$\kappa(\omega) = \frac{2\sqrt{R(\omega)} \sin \theta(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)} \cos \theta(\omega)},$$

(39)

and therefore the dielectric response $\epsilon(\omega) = (n(\omega) + \kappa(\omega))^2$ and the optical conductivity $\sigma(\omega) = \frac{-i\omega\epsilon}{4\pi}$.

2.3 Model Dielectric Response

We have seen that EM radiation is a sensitive probe of the dielectric properties of materials. Absorption and reflectivity experiments allow us to measure some combination of $\epsilon_1$ or $\epsilon_2$, with the remainder reconstructed by the Kramers-Kronig relations.

In order to learn more from such measurements, we need to have detailed models of the materials and their corresponding dielectric properties. For example, the electric field will interact with the moving charges associated with lattice vibrations. At the simplest level, we can model this as the interaction of iso-
lated dipoles composed of bound damped charge $e^*$ and length $s$

$$p = e^* s$$  \hspace{1cm} (40)

The equation of motion for this system is

$$\mu \ddot{s} = -\mu \gamma \dot{s} - \mu \omega_0^2 s + e^* \mathcal{E}$$  \hspace{1cm} (41)

where the first term on the right-hand side is the damping force, the second term is the restoring force, and the third term is the external field. Furthermore, the polarization $P$ is

$$P = \frac{N}{V} e^* s + \frac{N}{V} \alpha \mathcal{E}$$  \hspace{1cm} (42)

where $\alpha$ is the polarizability of the different molecules which make up the material. It is to represent the polarizability of rigid bodies. For example, (see Fig. 8) a metallic sphere has

\[ \alpha = a^3 \]  \hspace{1cm} (43)

Figure 8: We may model our material as a system harmonically bound charge and of metallic spheres with polarizability $\alpha = a^3$. 
If we F.T. these two equations, we get

\[-\mu \omega^2 s = i \omega \mu rs - \mu \omega_0^2 s + e^* \mathcal{E}(\omega) \]

\[\Rightarrow s(\omega) \{\omega_0^2 - \omega^2 - i \omega \gamma\} = \frac{e^* \mathcal{E}(\omega)}{\mu} \]

and

\[P(\omega) = n e^* s(\omega) + n \alpha \mathcal{E}(\omega) \]

or

\[P(\omega) = \mathcal{E}(\omega) \left\{ \frac{n e^*}{\mu} \frac{s^2/\mu}{\omega_0^2 - \omega^2 - i \omega \gamma} + n \alpha \right\} \]

The term in brackets is the complex electric susceptibility of the system \( \chi = \mathcal{E}/P \).

\[\chi(\omega) = n \alpha + \frac{n e^*}{\mu} \frac{s^2}{\omega_0^2 - \omega^2 - i \omega \gamma} = \frac{1}{4\pi} (\epsilon(\omega) - 1) \]

\[\epsilon(\omega) = 1 + 4\pi n \alpha + \frac{4\pi n e^*}{\mu} \frac{s^2}{\omega_0^2 - \omega^2 - i \gamma \omega}, \quad \text{where } \omega_p^2 = \frac{4\pi n e^*}{\mu} \]

Or, introducing the high and zero frequency limits

\[\epsilon_\infty = 1 + 4\pi n \alpha \]

\[\epsilon_0 = 1 + 4\pi n \alpha + \frac{\omega_p^2}{\omega_0^2} = \epsilon_\infty + \frac{\omega_p^2}{\omega_0^2} \]

\[\epsilon(\omega) = \epsilon_\infty + \frac{\omega_0^2 (\epsilon_0 - \epsilon_\infty)}{\omega_0^2 - \omega^2 - i \gamma \omega} \]
For our causality arguments we must have no poles in the upper complex half plane. This is satisfied since $\gamma > 0$. In addition, we need

$$\chi = \frac{1}{4\pi}(\epsilon(\omega) - 1) \to 0, \quad \text{as } \omega \to \infty \quad (53)$$

This means that $\epsilon_\infty = 1 + 4\pi n\alpha = 1$. Of course $\alpha$ is finite. The problem is that in making $\alpha = \text{constant}$, we neglected the electron mass. I.e., for our example of a metallic sphere, $\alpha < a^3$ for very high $\omega$! (See Fig. 9) due to the finite electronic mass.

![Diagram](image)

$
\uparrow \xi(\omega)
$

Figure 9: For very high $\omega$, $\alpha < a^3$ since the electrons have a finite mass and hence cannot respond instantaneously to changes in the field.

To analyze experiments $\epsilon$ is separated into real $\epsilon_1$ and imaginary parts $\epsilon_2$

$$\epsilon_1(\omega) = -\frac{4\pi}{\omega} \sigma_2 = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)\omega_0^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (54)$$
\[ \epsilon_2(\omega) = \frac{4\pi}{\omega} \sigma_1 = \frac{(\epsilon_0 - \epsilon_\infty)\omega_0^2 \gamma \omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad (55) \]

Thus a phonon mode will give a roughly Lorentzian-like line shape in the optical conductivity \( \sigma_1 \) centered roughly at the phonon frequency. In addition, this form may be used to construct a model reflectivity \( R = |\tilde{n} - 1|^2/|\tilde{n} + 1|^2 \), with \( \tilde{n} = \sqrt{\epsilon} \) which is often appended to the high end of the reflectivity data, so that the Kramers-Kronig integrals may be completed.

Figure 10: Sketch of the real and imaginary parts of the dielectric response of the harmonically bound charge model.
3 The Free-electron gas

Metals have a distinct feature in their optical conductivity $\sigma_1(\omega)$ which may be emulated by the free-electron gas. The equation of motion of the free-electron gas is

$$nm\ddot{s} = -\gamma \dot{s} - neE$$  \hspace{1cm} (56)

In steady state $\gamma \dot{s} = -neE$; however

$$-ne\dot{s} = j = \sigma E = \frac{ne^2\tau}{m}E$$  \hspace{1cm} (57)

in the relaxation time approximation, so

$$\dot{s} = -\frac{e\tau}{m}E = -\frac{ne}{\gamma}E \quad \text{or} \quad \gamma = \frac{nm}{\tau}.$$  \hspace{1cm} (58)

Thus, the equation of motion is

$$nm\ddot{s} = -\frac{nm}{\tau}\dot{s} - neE$$  \hspace{1cm} (59)

If we work in a Fourier representation, then

$$-m\omega^2s(\omega) = \frac{i\omega m}{\tau}s(\omega) - eE(\omega)$$  \hspace{1cm} (60)

However, since $P = -ens$

$$\left(m\omega^2 + \frac{i\omega m}{\tau}\right)P = -ne^2E(\omega)$$  \hspace{1cm} (61)
or
\[
P = -\frac{ne^2/m}{\omega^2 + i\omega/\tau} \mathcal{E} = \chi \mathcal{E} = \frac{1}{4\pi}(\epsilon - 1)\mathcal{E} \tag{62}
\]
\[
\epsilon = 1 - \frac{4\pi n^2 e^2}{m\omega} \frac{1}{\omega + i/\tau} = 1 - \frac{\omega_p^2}{\omega} \left\{ \frac{\omega - i/\tau}{\omega^2 + 1/\tau^2} \right\} \tag{63}
\]
\[
\epsilon_1 = 1 - \frac{\omega_p^2}{\omega} \left\{ \frac{\omega}{\omega^2 + 1/\tau^2} \right\}, \quad \epsilon_2 = \frac{\omega_p^2}{\tau \omega^2 + 1/\tau^2} \tag{64}
\]
However, recall that \(\epsilon_1 = -\frac{4\pi \sigma_2}{\omega}\) and \(\epsilon_2 = \frac{4\pi \sigma_1}{\omega}\), so that
\[
\sigma_1(\omega) = \frac{\omega_p^2}{4} \frac{1/\tau \pi}{\omega^2 + 1/\tau^2}. \tag{65}
\]

Figure 11: A sketch of the optical conductivity of a metal at finite temperatures. The low-frequency Drude peak is due to the coherent transport of electrons. The higher frequency peak is due to incoherent scattering of electrons from phonons or electron-electron interactions.
4 Excitons

One of the most dramatic effects of the dielectric properties of semiconductors are excitons. Put simply, an exciton is a hydrogenic bound state made up of a hole and an electron. The Hamiltonian for such a system is

\[
H = \frac{1}{2} m^* v_h^2 + \frac{1}{2} m^* v_e^2 - \frac{e^2}{\epsilon r}
\]  

(66)

As usual, we will work in the center of mass, so

\[
\frac{1}{2} m^* v_h^2 + \frac{1}{2} m^* v_e^2 = \frac{1}{2} (m^*_h + m^*_e) \dot{R}^2 + \mu \dot{r}^2
\]  

(67)

Figure 12: Excitons are hydrogenic bound states of an electron and a hole. In semiconductors with an indirect gap, such as Si, they can be very long lived, since a phonon or defect must be involved in the recombination process to conserve momentum. For example, in ultra-pure Si (\(\approx 10^{12}\) impurities per cc) the lifetime can exceed \(\tau_{Si} \approx 10^{-5}\) s; whereas in direct-gap GaAs, the lifetime is much shorter \(\tau_{GaAs} \approx 10^{-9}\) s and is generally limited by surface states. On the right, the coordinates of the exciton in the center of mass are shown.
\[ \begin{align*}
\bar{R} &= \frac{m_e^* \bar{x}_e + m_h^* \bar{x}_h}{m_h^* + m_e^*}, \quad r = \bar{x}_e - \bar{x}_h
\end{align*} \] (68)

The eigenenergies may be obtained from the Bohr atom solution
\[ E_n = -\mu(Ze^2)^2/(2\hbar^2 n^2) \]
by making the substitutions
\[ \begin{align*}
Ze^2 &\rightarrow \frac{e^2}{\epsilon} \\
\mu &\rightarrow \mu^* = \frac{m_h^* m_e^*}{m_h^* + m_e^*} \quad (70)
\end{align*} \]

In addition there is a cm kinetic energy, let \( \hbar k = P \), then
\[ E_{nK} = \frac{\hbar^2 K^2}{2(m_h^* + m_e^*)} - \frac{\mu^* e^4}{\epsilon^2 2\hbar^2 n^2} + E_g \] (71)

The binding energy is strongly reduced by the dielectric effects, since \( \epsilon \approx 10 \). (it is also reduced by the effective masses, since typically \( m^* < m \)). Thus, typically the binding energy is a small fraction of a Ryber. Similarly, the size of the exciton is much larger than the hydrogen atom
\[ a \approx \frac{\epsilon \mu}{m_e} a_0 \] (72)

This in fact is the justification for the hydrogenic approximation. Since the orbit contains many sites the lattice may be approximated as a continuum and thus the exciton is well approximated as a hydrogenic atom.
Figure 13: An exciton may be approximated as a hydrogenic atom if its radius is large compared to the lattice spacing. In Si, the radius is large due to the reduced hole and electron masses and the enhanced dielectric constant $\epsilon \approx 10$. 