6.2.2. Microscopic Theory of the Dielectric Function

To derive the first priciples theory of optical properties of matter we begin with the quantum theory for interaction of photons and electrons. Here, we will retain ourselves in the one-electron picture and several approximations pertinent to our case.

The unperturbed one-electron Hamiltonian introduced in chapter 2, already, is

$$\mathcal{H}_0 = p^2 / 2m + V(\mathbf{r}), \tag{6.22}$$

where $V(\mathbf{r})$ is the crystal potential without photons. The time-dependent solutions to the S-eq. are Bloch functions

$$|\mathbf{k},t\rangle = u_{\mathbf{k}}(\mathbf{r})\, e^{\,i\,(\mathbf{k}\cdot\mathbf{r} - E_{\mathbf{k}}t/\hbar)}.$$

The electromagnetic field or photons can be simply described by the vector potential

$$A(\mathbf{r},t) = A_0 \cos[i(\mathbf{q}\cdot\mathbf{r} - \omega t)]$$

by choosing a suitable gauge.

The difference between classical and quantum approach (QED) is quantization of the field to photons with harmonic oscillator energetics, $(n+1/2)\,\hbar\omega$. Thus, in general, a photon can be represented by the properly normalized solution of the classical Maxwell equations.

In our treatment the explicit quantization of the field is not essential for the results we obtain and we can ignore it. Thus, our theory can be considered to be semi-classical.

The electric and magnetic fields of the scalar potential Φ and the vector potential are

$\mathbf{E} = -\nabla\Phi - \partial\mathbf{A}/\partial t$ and $\mathbf{B} = \nabla\times\mathbf{A}$, respectively.

As indicated above, already, representation of the field is not unique. We chose the standing plane waves and Coulomb gauge, in which for the scalar potential

$$\Phi = 0 \tag{6.23a}$$

and for the vector potential

$$\nabla\cdot\mathbf{A} = 0. \tag{6.23b}$$

In Coulomb gauge

$$\mathbf{E} = -\partial\mathbf{A}/\partial t \tag{6.24a}$$

and

$$\mathbf{B} = \nabla\times\mathbf{A}, \tag{6.24b}$$

and the one-electron Hamiltonian takes the form

$$\mathcal{H} = [\mathbf{p} + e\mathbf{A}]^2 / 2m + V(\mathbf{r}) \tag{6.25}$$

for the motion of negatively charged electron (–e) in the field $\mathbf{A}$.

Now,
$[\mathbf{p} + e\mathbf{A}]^2 =$

Thus,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{eR}\,, \qquad (6.28)$$

where

$$\mathcal{H}_{eR} = e/m\ \mathbf{A}\cdot\mathbf{p} \qquad (6.29)$$

is called *electron–radiation interaction Hamiltonian.* It shoud be noted that the particular form of this Hamiltonian depends on the gauge.

Another common representation is

$$\mathcal{H}_{eR} = -e\ \mathbf{r}\cdot\mathbf{E}, \qquad (6.29)$$

which is the *electric dipole approximation* to the above. These two are equivalent in the limit $\mathbf{q} \to 0$ (or $\mathbf{v} \to 0$). Hamiltonian (6.29) includes the *Lorentz force* $e\ \mathbf{v}\times\mathbf{B}$, but both neglect the higher order term $(e^2/2m\ A^2)$.

To obtain the complex dielectric function from the electronic structure we need to evaluate matrix elements for the "optical transitions" $\langle c|\mathcal{H}_{eR}|v\rangle$ between the valence band states $|v\rangle$ and the conduction band states $|c\rangle$ for the *Fermi Golden Rule* (of time-dependent perturbation theory).

Thus, we proceed with evaluation of

$$|\langle c|\mathcal{H}_{eR}|v\rangle|^2 = (e/m)^2\,|\langle c|\mathbf{A}\cdot\mathbf{p}|v\rangle|^2. \qquad (6.31)$$

However, it is worth of noting that as $\mathbf{A}\cdot\mathbf{p}$ contains momentum $\mathbf{p}$, its matrix elements can also be estimated from the experimental effective mass data using relations (2.41 – (2.44) within the framework of $\mathbf{k}\cdot\mathbf{p}$ method.

Now, for the vector potential

$$A(\mathbf{r},t) = A_0 \cos[i(\mathbf{q}\cdot\mathbf{r} - \omega t)]$$

let us write

Evaluate

$$\mathbf{p}\,(u_{\mathbf{k}}(\mathbf{r})\ e^{\,i\,\mathbf{k}\cdot\mathbf{r}})$$

Substituting $|\mathbf{k},t\rangle = u_{\mathbf{k}}(\mathbf{r})\, e^{\,i\,(\mathbf{k}\cdot\mathbf{r} - E_{\mathbf{k}}t/\hbar)}$ for both $|\mathbf{k}_c,t\rangle$ and $|\mathbf{k}_v,t\rangle$ we obtain

Now, split the integration to two parts by writing:

$$\mathbf{r} \;\rightarrow\; \text{"}\Sigma_j\text{"}\; \mathbf{R}_j + \mathbf{r}',$$

where the lattice vector $\mathbf{R}_j$ runs over all unit cells and $\mathbf{r}'$ is integrated over a single representative unit cell.

Thus,