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PHYSICS

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Part I

Classical Nonlinear Optics

(Based on lecture notes by Professor Herbert Winful)

Nonlinear Polarization Response of Materials

In our discussion of nonlinear optics, we will model materials as linear time-shift invariant (LTI) systems, which means the properties of the materials do not change under a shift in time $t \to t - \tau$. LTI systems have the convenient property that they are completely characterized by their impulse response $h(t)$. By taking the convolution of an input signal $f(t)$ with the impulse response $h(t)$, we can find the system's response $y(t)$:

$$y(t) = f(t) * h(t) = \int_{-\infty}^{\infty} h(t - \tau) f(\tau) d\tau \qquad (1.1)$$

For real systems, there are a few restrictions:

1. Causality - Since the response at time t should only depend on the signal prior to time t, we change the upper bound of the response integral:

$$y(t) = \int_{-\infty}^{t} h(t - \tau) f(\tau) d\tau \qquad (1.2)$$

2. Reality - Since $f(t)$ and $y(t)$ are real, $h(t)$ should be real as well.

3. Time-Invariance - Since the system is time-invariant, $h(t)$ should be time-invariant as well (depends not on t or τ, but only on $t - \tau$).

1.1 Time-Domain Linear Response

Before the discovery of nonlinear optical effects, it was believed that the polarization of materials responded to applied fields linearly according to their first-order impulse response[1] $\chi^{(1)}(t)$. It is called *first-order* in anticipation of additional nonlinear orders that we will discuss later. In its most general form, the first-order time-domain susceptibility is a second rank tensor:

[1] Not to be confused with their frequency susceptibility $\chi^{(1)}(\omega)$

$$\bar{\bar{\chi}}^{(1)}(t) = \begin{bmatrix} \chi_{xx}^{(1)}(t) & \chi_{xy}^{(1)}(t) & \chi_{xz}^{(1)}(t) \\ \chi_{yx}^{(1)}(t) & \chi_{yy}^{(1)}(t) & \chi_{yz}^{(1)}(t) \\ \chi_{zx}^{(1)}(t) & \chi_{zy}^{(1)}(t) & \chi_{zz}^{(1)}(t) \end{bmatrix} \qquad (1.3)$$

Therefore, each component of the polarization will depend on the convolution of the components of $\bar{\bar{\chi}}^{(1)}(t)$ with all three components of the applied field:

$$
\begin{aligned}
P_x^{(1)}(t) &= \epsilon_0 \left[\int_{-\infty}^{\infty} \left(\chi_{xx}^{(1)}(t-\tau)E_x(\tau) + \chi_{xy}^{(1)}(t-\tau)E_y(\tau) + \chi_{xz}^{(1)}(t-\tau)E_z(\tau) \right) d\tau \right] \hat{x} \\
P_y^{(1)}(t) &= \epsilon_0 \left[\int_{-\infty}^{\infty} \left(\chi_{yx}^{(1)}(t-\tau)E_x(\tau) + \chi_{yy}^{(1)}(t-\tau)E_y(\tau) + \chi_{yz}^{(1)}(t-\tau)E_z(\tau) \right) d\tau \right] \hat{y} \\
P_z^{(1)}(t) &= \epsilon_0 \left[\int_{-\infty}^{\infty} \left(\chi_{zx}^{(1)}(t-\tau)E_x(\tau) + \chi_{zy}^{(1)}(t-\tau)E_y(\tau) + \chi_{zz}^{(1)}(t-\tau)E_z(\tau) \right) d\tau \right] \hat{z}
\end{aligned}
$$

$$(1.4)$$

This notation is a bit clunky, so we instead express the polarization in Einstein summation convention:

$$
P_i^{(1)}(t) = \epsilon_0 \int_{-\infty}^{\infty} \chi_{ij}^{(1)}(t-\tau)E_j(\tau)d\tau \tag{1.5}
$$

where any repeated index[2] is summed over. It is important that you become fluid in switching back and forth between Einstein summation convention and the explicit sum form. Practice by going from 1.5 to 1.4 and back a few times.

[2] In the context of nonlinear optics, all letter subscripts $(i, j, k, \ell \ldots)$ should be understood as representing the Cartesian coordinates x, y, z.

1.2 Time-Domain Nonlinear Response

It is now known that the polarization of materials does not respond linearly at high intensities. Instead, there are nonlinear terms in the polarization response, which are denoted by $P_i^{(2)}(t)$, $P_i^{(3)}(t)\ldots$, and form the so-called **Volterra series**:

$$
\begin{aligned}
P_i(t) = &\ \underbrace{\epsilon_0 \int_{-\infty}^{\infty} \chi_{ij}^{(1)}(t-\tau_1)E_j(\tau_1)d\tau_1}_{P_i^{(1)}(t)} \\
&+ \underbrace{\epsilon_0 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_{ijk}^{(2)}(t-\tau_1, t-\tau_2)E_j(\tau_1)E_k(\tau_2)d\tau_1 d\tau_2}_{P_i^{(2)}(t)} \\
&+ \underbrace{\epsilon_0 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_{ijk\ell}^{(3)}(t-\tau_1, t-\tau_2, t-\tau_3)E_j(\tau_1)E_k(\tau_2)E_\ell(\tau_3)d\tau_1 d\tau_2}_{P_i^{(3)}(t)} \\
&+ \ldots
\end{aligned}
$$

$$(1.6)$$

In the case in which the material responds instantaneously, the time-domain susceptibility of each order becomes a delta function:

$$\chi_{ij}^{(1)}(t - \tau_1) = \chi_{ij}^{(1)}\delta(t - \tau_1)$$

$$\chi_{ijk}^{(2)}(t - \tau_1, t - \tau_2) = \chi_{ij}^{(2)}\delta(t - \tau_1)\delta(t - \tau_2)$$

$$\chi_{ijk\ell}^{(3)}(t - \tau_1, t - \tau_2, t - \tau_3) = \chi_{ijk\ell}^{(3)}\delta(t - \tau_1)\delta(t - \tau_2)\delta(t - \tau_3)$$

$$\vdots \qquad (1.7)$$

In this case, the Volterra series simplifies to:

$$P_i(t) = \epsilon_0 \left[\chi_{ij}^{(1)} E_j(t) + \chi_{ijk}^{(2)} E_j(t)E_k(t) + \chi_{ijk\ell}^{(3)} E_j(t)E_k(t)E_\ell(t) + \ldots \right] \qquad (1.8)$$

1.3   The Anharmonic Oscillator Model

In the Lorentz model of the atom, the electron and nucleus are treated as being connected by an effective spring. If this spring had a spring constant of $k = m\omega_0^2$ and obeyed Hooke's law, the equation of motion for the electron[3] in one dimension reads:

$$m\ddot{x} = -m\omega_0^2 x - m\gamma\dot{x} - eE(t) \qquad (1.9)$$

[3] Assuming no nuclear motion, which is reasonable since most nuclei are much more massive than the electron.

where $E(t)$ is an applied electric field along the direction of motion and γ is a damping constant that represents the loss of energy. Just like in real springs however, Hooke's law is only an approximation. There are in fact nonlinear components of the spring restoring force, which result in amazingly different behavior. For now, we only include the next order component that depends on x^2:

$$m\ddot{x} = -m\omega_0^2 x - bx^2 - m\gamma\dot{x} - eE(t) \qquad (1.10)$$

One important point is that this second order term that depends on x^2 exists only in non-centrosymmetric[4] materials. To see this we find the potential energy associated with the restoring force of the spring:

[4] Centrosymmetry means invariance under coordinate inversion $\mathbf{r} \to -\mathbf{r}$.

$$U_{spring}(x) = \int -m\omega_0^2 x - bx^2 dx = -\frac{1}{2}m\omega_0^2 x^2 - \frac{1}{3}bx^3 \qquad (1.11)$$

Since the potential energy must be invariant under coordinate inversion in centrosymmetric materials $(x \to -x)$, we try making such a transformation:

$$U_{spring}(-x) = -\frac{1}{2}m\omega_0^2 x^2 + \frac{1}{3}bx^3 \qquad (1.12)$$

We thus find that the second order restoring force must be zero for the centrosymmetric condition to hold:

$$U_{spring}(x) \neq U_{spring}(-x) \quad \text{unless} \quad b = 0 \qquad (1.13)$$

In fact, it is not hard to show that all nonlinear components that de-pend on even powers of x must vanish for centrosymmetric materials.

Assuming that the nonlinear component is very small compared to the linear component ($mbx^2 \ll m\omega_0^2 x$), we can use perturbation the-ory to solve this problem. To do so, we first expand the displacement $x(t)$ as a power series in b (since b is small):

$$x(t) = x_0(t) + bx_1(t) + b^2 x_2(t) + b^3 x_3(t) + \dots \qquad (1.14)$$

Plugging this expansion of $x(t)$ into 1.10 (keeping only the first three terms), we find:

$$-\frac{eE(t)}{m} - bx_0^2 - b^2 2x_0 x_1 = \left(\ddot{x}_0 + \gamma \dot{x}_0 + \omega_0^2 x_0 \right)$$
$$+ b \left(\ddot{x}_1 + \gamma \dot{x}_1 + \omega_0^2 x_1 \right)$$
$$+ b^2 \left(\ddot{x}_2 + \gamma \dot{x}_2 + \omega_0^2 x_2 \right) \qquad (1.15)$$

where we neglected terms that dependended on b^3, b^4, and b^5, since they will only contribute when additional terms in the expansion 1.14 are included. By the uniqueness of power series, we can match the terms on each side according to the power of b in front:

$$b^0 : \quad \ddot{x}_0 + \gamma \dot{x}_0 + \omega_0^2 x_0 = -\frac{eE(t)}{m} \qquad (1.16a)$$

$$b^1 : \quad \ddot{x}_1 + \gamma \dot{x}_1 + \omega_0^2 x_1 = -x_0^2 \qquad (1.16b)$$

$$b^2 : \quad \ddot{x}_2 + \gamma \dot{x}_2 + \omega_0^2 x_2 = -2x_0 x_1 \qquad (1.16c)$$

If we included higher order terms in the expansion 1.14, there would be more equations for $x_3(t)$, $x_4(t)$, and so on. The strategy for solving 1.16a, 1.16b, and 1.16c is the following:

1. Solve for the impulse response function of 1.16a. $x_0(t)$ is then the convolution of the impulse response with $-\frac{eE(t)}{m}$.

2. By inspection, we see that the impulse response of 1.16b is iden-tical to that of 1.16a. $x_1(t)$ is then the convolution of the impulse response with $-x_0^2$, which we know from step 1.

3. Again find $x_2(t)$ by convolving the impulse response with $-2x_0 x_1$, which we know from the results of step 1 and 2.

To find the impulse response $h(t)$ of 1.16a, we input a Dirac delta function for the signal:

$$\ddot{h} + \gamma \dot{h} + \omega_0^2 h = \delta(t) \qquad (1.17)$$

The easiest way to solve for $h(t)$ is to first take the Fourier transform of both sides[5]:

[5] Recall that derivatives turn into factors of $-i\omega$:
$$\mathcal{F}\{\dot{f}(t)\} = -i\omega F(\omega)$$
$$\mathcal{F}\{\ddot{f}(t)\} = -\omega^2 F(\omega)$$

$$-\omega^2 H(\omega) - i\gamma\omega H(\omega) + \omega_0^2 H(\omega) = 1$$

and a little rearranging gives the Fourier transform of $h(t)$:

$$H(\omega) = \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{1.18}$$

A quick look at a Fourier transform table gives the inverse Fourier transform $h(t)$:

$$h(t) = \mathcal{F}^{-1}\{H(\omega)\} = \frac{e^{-\frac{\gamma}{2}t}}{\sqrt{\omega_0^2 - \left(\frac{\gamma}{2}\right)^2}} \sin\left(\sqrt{\omega_0^2 - \left(\frac{\gamma}{2}\right)^2}\, t\right) u(t) \tag{1.19}$$

where $u(t)$ is the Heaviside step function. Dropping the integral limits (which are understood to be $-\infty$ to ∞ unless otherwise noted), the solution for $x_0(t)$ is thus:

$$x_0(t) = h(t) * \left(-\frac{eE(t)}{m}\right)$$

$$= \int h(t - \tau)\left(-\frac{eE(\tau)}{m}\right) d\tau \tag{1.20}$$

We then find $x_1(t)$ by convolving the impulse response with $-x_0^2$:

$$x_1(t) = h(t) * \left[-\int h(t - \tau_1)\left(-\frac{eE(\tau_1)}{m}\right) d\tau_1 \int h(t - \tau_2)\left(-\frac{eE(\tau_2)}{m}\right) d\tau_2\right]$$

$$= -\frac{e^2}{m^2} \iiint h(t - \tau)h(t - \tau_1)h(t - \tau_2)E(\tau_1)E(\tau_2) d\tau d\tau_1 d\tau_2$$

$$= -\frac{e^2}{m^2} \iiint h(t - \tau)h(\tau - \tau_1)h(\tau - \tau_2)E(\tau_1)E(\tau_2) d\tau d\tau_1 d\tau_2$$

$$= -\frac{e^2}{m^2} \iint Z(t - \tau_1, t - \tau_2)E(\tau_1)E(\tau_2) d\tau_1 d\tau_2 \tag{1.21}$$

where we've defined the integral[6]:

$$Z(t - \tau_1, t - \tau_2) = \int_{-\infty}^{\infty} h(t - \tau)h(\tau - \tau_1)h(\tau - \tau_2) d\tau \tag{1.22}$$

By the same process (the details are left as an exercise), we find $x_2(t)$:

$$x_2(t) = -2\frac{e^3}{m^3} \iiint Z^{(2)}(t - \tau_1, t - \tau_2, t - \tau_3)E(\tau_1)E(\tau_2)E(\tau_3) d\tau_1 d\tau_2 d\tau_3 \tag{1.23}$$

where we've defined the additional integral:

$$Z^{(2)}(t - \tau_1, t - \tau_2, t - \tau_3) = -\int Z(t - \tau_3, t - \tau_4)h(\tau_4 - \tau_1)h(\tau_4 - \tau_2) d\tau_4 \tag{1.24}$$

[6] We can see that this integral depends only on the differences $t - \tau_1$ and $t - \tau_2$ by making the substitution $u = t - \tau$ in the integral:

$$-\int h(u)h(t - u - \tau_1)h(t - u - \tau_2) du$$

Integrating over u will give only a $t - \tau_1$ and $t - \tau_2$ dependence.

The total polarization can thus be written as:

$$
\begin{aligned}
P(t) = &- Nex(t) \\
= &- Nex_0(t) - Nebx_1(t) - Neb^2 x_2(t) + \ldots \\
= &\underbrace{\frac{Ne^2}{m} \int h(t-\tau)E(\tau)d\tau}_{P^{(1)}(t)} + \underbrace{\frac{Ne^3}{m^2} \iint Z(t-\tau_1, t-\tau_2)E(\tau_1)E(\tau_2)d\tau_1 d\tau_2}_{P^{(2)}(t)} \\
&+ \underbrace{\frac{2Ne^4}{m^2} \iiint Z^{(2)}(t-\tau_1, t-\tau_2, t-\tau_3)E(\tau_1)E(\tau_2)E(\tau_3)d\tau_1 d\tau_2 d\tau_3}_{P^{(3)}(t)} \\
&+ \ldots
\end{aligned}
\tag{1.25}
$$

Comparing to the Volterra series 1.6, we find the time-domain suscep-tibilities of the first three orders to be:

$$
\chi^{(1)}(t-\tau_1) = \frac{Ne^2}{m\epsilon_0} h(t-\tau)
\tag{1.26}
$$

$$
\chi^{(2)}(t-\tau_1, t-\tau_2) = \frac{Ne^3 b}{m^2 \epsilon_0} Z(t-\tau_1, t-\tau_2)
\tag{1.27}
$$

$$
\chi^{(3)}(t-\tau_1, t-\tau_2, t-\tau_3) = \frac{2Ne^4 b^2}{m^2 \epsilon_0} Z^{(2)}(t-\tau_1, t-\tau_2, t-\tau_3)
\tag{1.28}
$$

1.4 Frequency-Domain Nonlinear Response

The time-domain description of the nonlinear polarization response is useful for certain situations such as when ultra-short pulses are the applied field. In many cases however, it is more convenient to describe nonlinear phenomena by a frequency response.

Our goal now is to transform the Volterra series into the frequency domain via Fourier transforms. We will do this according to the polarization components identified using the underbraces in 1.6, and begin by defining the first order frequency domain susceptibility:

$$
\chi_{ij}^{(1)}(\omega) = \mathcal{F}\{\chi_{ij}^{(1)}(t)\} = \int \chi_{ij}^{(1)}(t)e^{i\omega t}dt
\tag{1.29}
$$

Recalling that the Fourier transform of the convolution of two func-tions is the product of the individual Fourier transforms of each function, we find the first order polarization:

$$
\begin{aligned}
P_i^{(1)}(\omega) &= \mathcal{F}\{P_i^{(1)}(t)\} \\
&= \epsilon_0 \mathcal{F}\{\chi_{ij}^{(1)}(t) * E_j(t)\} \\
&= \epsilon_0 \mathcal{F}\{\chi_{ij}^{(1)}(t)\}\mathcal{F}\{E_j(t)\} \\
&= \epsilon_0 \chi_{ij}^{(1)}(\omega)E_j(\omega)
\end{aligned}
\tag{1.30}
$$

The frequency form of the second term will involve both a double Fourier transform and a double convolution, which transforms in the same way as single Fourier transforms and convolutions. First defining the second order susceptibility:

$$\chi_{ijk}^{(2)}(\omega_1, \omega_2) = \mathcal{F}\{\chi_{ijk}^{(2)}(t_1, t_2)\} = \iint \chi_{ijk}^{(2)}(t_1, t_2)e^{i(\omega_1 t_1 + \omega_2 t_2)}dt_1 dt_2$$

(1.31)

We now calculate the frequency domain polarization response by making the substitutions $t_1 = t - \tau_1$ and $t_2 = t - \tau_2$ along the way and a bit of leg work:

$$
\begin{aligned}
P_i^{(2)}(\omega) &= \mathcal{F}\{P_i^{(2)}(t)\} \\
&= \mathcal{F}\left\{\epsilon_0 \iint \chi_{ijk}^{(2)}(t - \tau_1, t - \tau_2)E_j(\tau_1)E_k(\tau_2)d\tau_1 d\tau_2\right\} \\
&= \epsilon_0 \mathcal{F}\left\{\iint \chi_{ijk}^{(2)}(t_1, t_2)E_j(t - t_1)E_k(t - t_2)dt_1 dt_2\right\} \\
&= \epsilon_0 \mathcal{F}\left\{\iint \chi_{ijk}^{(2)}(t_1, t_2)\mathcal{F}^{-1}\{e^{i\omega_1 t_1}E_j(\omega_1)\}\mathcal{F}^{-1}\{e^{i\omega_2 t_2}E_k(\omega_2)\}dt_1 dt_2\right\} \\
&= \frac{\epsilon_0}{(2\pi)^2}\mathcal{F}\left\{\iint \chi_{ijk}^{(2)}(t_1, t_2)\left[\int e^{i\omega_1 t_1}E_j(\omega_1)e^{-i\omega_1 t}d\omega_1 \int e^{i\omega_2 t_2}E_k(\omega_2)e^{-i\omega_2 t}d\omega_2\right]dt_1 dt_2\right\} \\
&= \frac{\epsilon_0}{(2\pi)^2}\mathcal{F}\left\{\iint \left[\iint \chi_{ijk}^{(2)}(t_1, t_2)e^{i(\omega_1 t_1 + \omega_2 t_2)}dt_1 dt_2\right] E_j(\omega_1)E_k(\omega_2)e^{-i(\omega_1 + \omega_2)t}d\omega_1 d\omega_2\right\} \\
&= \frac{\epsilon_0}{(2\pi)^2}\mathcal{F}\left\{\iint \chi_{ijk}^{(2)}(\omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2)e^{-i(\omega_1 + \omega_2)t}d\omega_1 d\omega_2\right\} \\
&= \frac{\epsilon_0}{(2\pi)^2}\iiint \chi_{ijk}^{(2)}(\omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2)e^{-i(\omega_1 + \omega_2 - \omega)t}d\omega_1 d\omega_2 dt \\
&= \frac{\epsilon_0}{(2\pi)^2}\iint \chi_{ijk}^{(2)}(\omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2)\left[\int e^{-i(\omega_1 + \omega_2 - \omega)t}dt\right]d\omega_1 d\omega_2 \\
&= \frac{\epsilon_0}{2\pi}\iint \chi_{ijk}^{(2)}(\omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2)\delta(\omega - \omega_1 - \omega_2)d\omega_1 d\omega_2
\end{aligned}
$$

(1.32)

where in the last line, we used the well-known Fourier transform of unity:

$$\int e^{-i\omega t}dt = 2\pi\delta(\omega) \rightarrow \int e^{-i(\omega_1 + \omega_2 - \omega)t}dt = 2\pi\delta(\omega - \omega_1 - \omega_2)$$

(1.33)

The delta function $\delta(\omega - \omega_1 - \omega_2)$ requires that, for a non-zero polarization response, the polarization frequency must satisfy $\omega = \omega_1 + \omega_2$.

By more tedious algebra (which is left as an exercise), we would obtain the third order polarization:

$$P_i^{(3)}(\omega) = \frac{\epsilon_0}{(2\pi)^2}\iiint \chi_{ijk\ell}^{(3)}(\omega_1, \omega_2, \omega_3)E_j(\omega_1)E_k(\omega_2)E_\ell(\omega_3)\delta(\omega - \omega_1 - \omega_2 - \omega_3)d\omega_1 d\omega_2 d\omega_3$$

(1.34)

where the third order susceptibility is defined as:

$$\chi_{ijk\ell}^{(3)}(\omega_1,\omega_2,\omega_3) = \mathcal{F}\{\chi_{ijk\ell}^{(3)}(t_1,t_2,t_3)\}$$
$$= \iiint \chi_{ijk\ell}^{(3)}(t_1,t_2,t_3)e^{i(\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3)}dt_1 dt_2 dt_3$$

$$(1.35)$$

1.5 Notation of Maker and Terhune

We have now derived the frequency domain descriptions of the first (1.30), second (1.32), and third order (1.34) polarizations. Surprisingly (or not), we find that the nonlinear polarization components only have frequencies in combinations of the input frequencies (which can be negative!). To make this condition explicit, we insert the polarization frequency ω into the susceptibility as an argument:

$$\chi_{ijk}^{(2)}(\omega_1,\omega_2) \rightarrow \chi_{ijk}^{(2)}(\omega;\omega_1,\omega_2) \qquad (1.36)$$

$$\chi_{ijk\ell}^{(3)}(\omega_1,\omega_2,\omega_3) \rightarrow \chi_{ijk\ell}^{(3)}(\omega;\omega_1,\omega_2,\omega_3) \qquad (1.37)$$

This is known as the **notation of Maker and Terhune**, after Paul Maker and Robert Terhune who proposed it while at Ford Research Labs in Dearborn, MI. To avoid confusing the reader, the above notation is equivalent to the following:

$$\chi_{ijk}^{(2)}(\omega_1,\omega_2) \rightarrow \chi_{ijk}^{(2)}(\omega = \omega_1 + \omega_2;\omega_1,\omega_2)$$

$$\chi_{ijk\ell}^{(3)}(\omega_1,\omega_2,\omega_3) \rightarrow \chi_{ijk\ell}^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3;\omega_1,\omega_2,\omega_3)$$

in which the allowed frequency components $\omega = \omega_1 + \omega_2$ and $\omega = \omega_1 + \omega_2 + \omega_3$ are indicated explicitly. What this notation provides is that the first argument separated by the semicolon specifies which frequency component of the polarization the susceptibility results in. We will adopt this notation from here on.

1.6 Susceptibility Symmetry Properties

There is an additional step which will simplify future analysis, which is to determine the symmetry properties of the nonlinear susceptibilities 1.31 and 1.35. There are three main symmetry properties that the susceptibility obeys:

1. **Intrinsic Permutation Symmetry**: All materials obey intrinsic permutation symmetry, in which the susceptibilities of all orders are invariant under simultaneous permutation of indices and their associated frequencies, *except* the first. For the first and second

order susceptibilities, the symmetry in equation form reads:

$$\chi_{ijk}^{(2)}(\omega;\omega_1,\omega_2) = \chi_{ikj}^{(2)}(\omega;\omega_2,\omega_1) \tag{1.38}$$

$$\chi_{ijk\ell}^{(3)}(\omega;\omega_1,\omega_2,\omega_3) = \chi_{ikj\ell}^{(3)}(\omega;\omega_2,\omega_1,\omega_3) = \chi_{ij\ell k}^{(3)}(\omega;\omega_1,\omega_3,\omega_2) \tag{1.39}$$

2. **Full Permutation Symmetry**: If a material is lossless at the frequencies involved[7] in the interaction, the susceptibilities of all orders are invariant under simultaneous permutation of all indices and their associated frequency, *including* the first. This is simply an extension of intrinsic permutation symmetry, so the first and second order-susceptibilities will have the symmetry properties given by 1.38 and 1.39 *plus* the permutations of the first index. For brevity, we give two examples of full permutation symmetry and leave the others as an exercise:

[7] The frequencies "involved" in the interaction refer to ω, ω_1, and ω_2 for second-order interactions and $\omega, \omega_1, \omega_2$, and ω_3 for third-order interactions.

$$\chi_{ijk}^{(2)}(\omega;\omega_1,\omega_2) = \chi_{kji}^{(2)}(\omega_2;\omega_1,\omega) \tag{1.40}$$

$$\chi_{ijk\ell}^{(3)}(\omega;\omega_1,\omega_2,\omega_3) = \chi_{jik\ell}^{(3)}(\omega_1;\omega,\omega_2,\omega_3) \tag{1.41}$$

3. **Kleinman Symmetry**: If the frequencies involved are far from material resonances, which is often the case, the susceptibility will be approximately independent of frequency. This means that the susceptibility is dispersionless, which allows for permutation of all indices *without* permuting the frequencies, known as Kleinman symmetry. Again, we give two examples of Kleinman symmetry[8]:

[8] See page 39 of Boyd's book for a full list of Kleinman symmetries for the second-order susceptibility.

$$\chi_{ijk}^{(2)}(\omega;\omega_1,\omega_2) = \chi_{kji}^{(2)}(\omega;\omega_1,\omega_2) \tag{1.42}$$

$$\chi_{ijk\ell}^{(3)}(\omega;\omega_1,\omega_2,\omega_3) = \chi_{ikj\ell}^{(3)}(\omega;\omega_1,\omega_2,\omega_3) \tag{1.43}$$

1.7 Field Propagation in Nonlinear Media

In general, we can write an arbitrary field composed of sinusoidal components with frequencies ω_n in terms of complex exponentials[9]:

[9] For clarity we have suppressed the dependence of $\mathbf{E}$ on the position $\mathbf{r}$.

$$\begin{aligned}
\mathbf{E}(t) &= \sum_{\omega_n} |\mathbf{E}^{\omega_n}| \cos(\omega_n t + \phi_n) \\
&= \sum_{\omega_n} \frac{|\mathbf{E}^{\omega_n}|}{2} \left(e^{-i\omega_n t} e^{-i\phi_n} + e^{i\omega_n t} e^{i\phi_n} \right) \\
&= \sum_{\omega_n} \frac{1}{2} \left[\left(\mathbf{E}^{\omega_n}\right) e^{-i\omega_n t} + \left(\mathbf{E}^{\omega_n}\right)^* e^{i\omega_n t} \right]
\end{aligned} \tag{1.44}$$

where we've defined the complex field amplitude:

$$\mathbf{E}^{\omega_n} = |\mathbf{E}^{\omega_n}| e^{-i\phi_n} \tag{1.45}$$

We can find the frequency spectrum of 1.44 via Fourier transform:

$$
\begin{aligned}
\mathbf{E}(\omega) &= \mathcal{F}\{\mathbf{E}(t)\} \\
&= \sum_{\omega_n} \left[\frac{1}{2} \int (\mathbf{E}^{\omega_n})\, e^{i(\omega-\omega_n)t} dt + \frac{1}{2} \int (\mathbf{E}^{\omega_n})^*\, e^{i(\omega+\omega_n)t} dt \right] \\
&= \sum_{\omega_n} \pi \left[(\mathbf{E}^{\omega_n})\, \delta(\omega - \omega_n) + (\mathbf{E}^{\omega_n})^*\, \delta(\omega + \omega_n) \right] \qquad (1.46)
\end{aligned}
$$

Similarly, the polarization in a medium induced by an applied field with discrete frequencies can also be written as:

$$
\mathbf{P}(t) = \sum_{\omega_m} \frac{1}{2} \left[(\mathbf{P}^{\omega_m})\, e^{-i\omega_m t} + (\mathbf{P}^{\omega_m})^*\, e^{i\omega_m t} \right] \qquad (1.47)
$$

$$
\mathbf{P}(\omega) = \sum_{\omega_m} \pi \left[(\mathbf{P}^{\omega_m})\, \delta(\omega - \omega_m) + (\mathbf{P}^{\omega_m})^*\, \delta(\omega + \omega_m) \right] \qquad (1.48)
$$

Recalling elementary electromagnetism, Maxwell's equations give the electric field wave equation:

$$
\begin{aligned}
-\mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2} &= \nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \\
&= \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \\
&= -\nabla^2 \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \qquad (1.49)
\end{aligned}
$$

where we've assumed that the field is a plane wave ($\nabla \cdot \mathbf{E} = 0$). Plugging in the time-domain descriptions of the electric field and polarization **??** and **??**, we find:

$$
\sum_{\omega_m} \frac{\mu_0 \omega_m^2}{2} \left[(\mathbf{P}^{\omega_m})\, e^{-i\omega_m t} + (\mathbf{P}^{\omega_m})^*\, e^{i\omega_m t} \right] = -\sum_{\omega_n} \frac{1}{2} \left[\nabla^2 (\mathbf{E}^{\omega_n})\, e^{-i\omega_n t} + \nabla^2 (\mathbf{E}^{\omega_n})^*\, e^{i\omega_n t} \right]
$$

$$
- \sum_{\omega_n} \frac{\omega_n^2}{2c^2} \left[(\mathbf{E}^{\omega_n})\, e^{-i\omega_n t} + (\mathbf{E}^{\omega_n})^*\, e^{i\omega_n t} \right]
$$

Some additional manipulations:

$$
Re \left\{ \sum_{\omega_m} \mu_0 \omega_m^2 \mathbf{P}^{\omega_m} e^{-i\omega_m t} \right\} = -Re \left\{ \sum_{\omega_n} \left[\nabla^2 \mathbf{E}^{\omega_n} + \frac{\omega_n^2}{c^2} \mathbf{E}^{\omega_n} \right] e^{-i\omega_n t} \right\}
$$

$$
\rightarrow \sum_{\omega_m} \mu_0 \omega_m^2 \mathbf{P}^{\omega_m} = -\sum_{\omega_n} \left[\nabla^2 \mathbf{E}^{\omega_n} + \frac{\omega_n^2}{c^2} \mathbf{E}^{\omega_n} \right] e^{-i(\omega_n - \omega_m)t}
$$

For stationary solutions independent of time t, we require $\omega_n = \omega_m$. Equating each term in the power series:

$$
-\mu_0 \omega_n^2 \mathbf{P}^{\omega_n} = \nabla^2 \mathbf{E}^{\omega_n} + \frac{\omega_n^2}{c^2} \mathbf{E}^{\omega_n} \qquad (1.50)
$$

It is convenient to separate the polarization $\mathbf{P}^{\omega_n}$ into its linear and nonlinear components ($\mathbf{P}^{\omega_n L}$ and $\mathbf{P}^{\omega_n NL}$ respectively):

$$\begin{aligned}
\mathbf{P}^{\omega_n} &= \mathbf{P}^{\omega_n L} + \mathbf{P}^{\omega_n NL} \\
&= \epsilon_0 \bar{\bar{\chi}}^{(1)}(\omega_n) \mathbf{E}^{\omega_n} + \mathbf{P}^{\omega_n NL}
\end{aligned} \tag{1.51}$$

where $\bar{\bar{\chi}}^{(1)}(\omega_n)$ is the first-order frequency susceptibility found by taking the Fourier transform of 1.3. The susceptibility tensor's components will depend on our choice of coordinate system, and for a special choice, known as the **principal coordinate system**, it will be diagonal:

$$\bar{\bar{\chi}}^{(1)}(\omega_n) = \begin{bmatrix} \chi_1^{(1)}(\omega_n) & 0 & 0 \\ 0 & \chi_2^{(1)}(\omega_n) & 0 \\ 0 & 0 & \chi_3^{(1)}(\omega_n) \end{bmatrix} \tag{1.52}$$

The first-order susceptibility is also related to the index of refraction tensor[10] and the relative permittivity tensor by:

$$\bar{\bar{\epsilon}}(\omega_n) = \bar{\bar{n}}^2(\omega_n) = 1 + \bar{\bar{\chi}}^{(1)}(\omega_n) \tag{1.53}$$

[10] In the principal coordinate system, the index of refraction tensor will also be diagonal. The diagonal components are called **principal refractive indices**.

Plugging the polarization **??** into the wave equation **??**, we find:

$$\begin{aligned}
-\mu_0 \omega_n^2 \mathbf{P}^{\omega_n NL} &= \nabla^2 \mathbf{E}^{\omega_n} + \frac{\omega_n^2}{c^2} \left[1 + \bar{\bar{\chi}}(\omega_n) \right] \mathbf{E}^{\omega_n} \\
&= \nabla^2 \mathbf{E}^{\omega_n} + \frac{\omega_n^2}{c^2} \bar{\bar{n}}^2(\omega_n) \mathbf{E}^{\omega_n}
\end{aligned} \tag{1.54}$$

For now we assume that the medium is **isotropic** (we will examine the anisotropic case later). We thus drop the vector dependence of the electric field and polarization to find:

$$\nabla^2 E^{\omega_n} + \frac{\omega_n^2 n^2(\omega_n)}{c^2} E^{\omega_n} = -\mu_0 \omega_n^2 P^{\omega_n NL} \tag{1.55}$$

Assuming that the plane wave field propagates in the $\hat{z}$ direction, we rewrite the field amplitude with the propagation factor pulled out:

$$E^{\omega_n} = A^{\omega_n}(z) e^{i k^{\omega_n} z} \quad \text{where} \quad k^{\omega_n} = \frac{n(\omega_n)\omega_n}{c} \tag{1.56}$$

Plugging this new amplitude form into the wave equation yields[11]:

[11] Notice that $\frac{\omega_n^2 n^2(\omega_n)}{c^2} = (k^{\omega_n})^2$.

$$\begin{aligned}
-\mu_0 \omega_n^2 P^{\omega_n NL} &= \left(\frac{d^2 A^{\omega_n}}{dz^2} + 2i k^{\omega_n} \frac{dA^{\omega_n}}{dz} - (k^{\omega_n})^2 A^{\omega_n} \right) e^{i k^{\omega_n} z} + \frac{\omega_n^2 n^2(\omega_n)}{c^2} A^{\omega_n} e^{i k^{\omega_n} z} \\
&= \left(\frac{d^2 A^{\omega_n}}{dz^2} + 2i k^{\omega_n} \frac{dA^{\omega_n}}{dz} \right) e^{i k^{\omega_n} z}
\end{aligned}$$

Since in real scenarios the amplitude of each frequency component will be slowly varying, we make the **slowly varying envelope approximation (SVEA)**:

$$\frac{d^2 A^{\omega_n}}{dz^2} + 2i k^{\omega_n} \frac{dA^{\omega_n}}{dz} \approx 2i k^{\omega_n} \frac{dA^{\omega_n}}{dz} \tag{1.57}$$

The wave equation in the SVEA finally becomes:

$$2ik^{\omega_n}\frac{dA^{\omega_n}}{dz} = -\mu_0\omega_n^2 P^{\omega_n NL}e^{-ik^{\omega_n}z} \qquad (1.58)$$

We will use this equation as the starting point for analyzing many different nonlinear optics phenomena.

Second-Order Nonlinear Polarization

2.1 Second-Order Susceptibility

The first step to analyzing second-order polarization phenomena is to derive the exact form of the second-order susceptibility. Recall the form of $\chi^{(2)}(t - \tau_1, t - \tau_2)$ given by 1.27 and 1.22:

$$\chi^{(2)}(t - \tau_1, t - \tau_2) = \frac{Ne^3 b}{m^2 \epsilon_0} Z(t - \tau_1, t - \tau_2)$$

$$= \frac{Ne^3 b}{m^2 \epsilon_0} \int h(t - \tau) h(\tau - \tau_1) h(\tau - \tau_2) d\tau \qquad (2.59)$$

We can write the impulse response functions above as integrals:

$$h(t - \tau) = \frac{1}{2\pi} \int H(\omega) e^{-i\omega(t-\tau)} d\omega$$

$$h(\tau - \tau_1) = \frac{1}{2\pi} \int H(\omega_1) e^{-i\omega_1(\tau-\tau_1)} d\omega_1$$

$$h(\tau - \tau_2) = \frac{1}{2\pi} \int H(\omega_2) e^{-i\omega_2(\tau-\tau_2)} d\omega_2$$

Plugging these explicit integral forms into the equation for the time-domain susceptibility:

$$\chi^{(2)}(t - \tau_1, t - \tau_2) = \frac{Ne^3 b}{m^2 \epsilon_0 (2\pi)^3} \iiiint H(\omega) H(\omega_1) H(\omega_2) e^{-i\omega(t-\tau)} e^{-i\omega_1(\tau-\tau_1)} e^{-i\omega_2(\tau-\tau_2)} d\omega d\omega_1 d\omega_2 d\tau$$

$$= \frac{Ne^3 b}{m^2 \epsilon_0 (2\pi)^3} \iiint H(\omega) H(\omega_1) H(\omega_2) \left[\int e^{-i(\omega_1+\omega_2-\omega)\tau} d\tau \right] e^{i(\omega_1\tau_1+\omega_2\tau_2)} e^{-i\omega t} d\omega d\omega_1 d\omega_2$$

$$= \frac{Ne^3 b}{m^2 \epsilon_0 (2\pi)^2} \iiint H(\omega) H(\omega_1) H(\omega_2) \delta(\omega_1 + \omega_2 - \omega) e^{i(\omega_1\tau_1+\omega_2\tau_2)} e^{-i\omega t} d\omega d\omega_1 d\omega_2$$

$$= \frac{Ne^3 b}{m^2 \epsilon_0 (2\pi)^2} \iint H(\omega_1) H(\omega_2) \left[\int H(\omega) \delta(\omega_1 + \omega_2 - \omega) e^{-i\omega t} d\omega \right] e^{i(\omega_1\tau_1+\omega_2\tau_2)} d\omega_1 d\omega_2$$

$$= \frac{Ne^3 b}{m^2 \epsilon_0 (2\pi)^2} \iint H(\omega_1 + \omega_2) H(\omega_1) H(\omega_2) e^{-i(\omega_1+\omega_2)t} e^{i(\omega_1\tau_1+\omega_2\tau_2)} d\omega_1 d\omega_2$$

$$= \frac{Ne^3 b}{m^2 \epsilon_0 (2\pi)^2} \iint H(\omega_1 + \omega_2) H(\omega_1) H(\omega_2) e^{-i[\omega_1(t-\tau_1)+\omega_2(t-\tau_2)]} d\omega_1 d\omega_2$$

$$= \frac{Ne^3 b}{m^2 \epsilon_0 (2\pi)^2} \mathcal{F}^{-1} \left\{ H(\omega_1 + \omega_2) H(\omega_1) H(\omega_2) \right\}$$

$$(2.60)$$

We have now derived a very nice result by recognizing in the last line that the double integral simply represents an inverse Fourier transform. It is now trivial to find the frequency susceptibility:

$$
\begin{aligned}
\chi^{(2)}(\omega;\omega_1,\omega_2) &= \mathcal{F}\{\chi^{(2)}(t-\tau_1,t-\tau_2)\} \\
&= \frac{Ne^3b}{m^2\epsilon_0}\mathcal{F}\left\{\mathcal{F}^{-1}\{H(\omega_1+\omega_2)H(\omega_1)H(\omega_2)\}\right\} \\
&= \frac{Ne^3b}{m^2\epsilon_0}H(\omega_1+\omega_2)H(\omega_1)H(\omega_2) \qquad (2.61)
\end{aligned}
$$

Recalling the Lorentz model frequency response found in 1.18:

$$
H(\omega) = \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}
$$

We plug into 2.61 to find:

$$
\begin{aligned}
\chi^{(2)}(\omega;\omega_1,\omega_2) &= \frac{Ne^3b}{m^2\epsilon_0}H(\omega_1+\omega_2)H(\omega_1)H(\omega_2) \\
&= \frac{Ne^3b}{m^2\epsilon_0}\frac{1}{(\omega_0^2-\omega_1^2-i\gamma\omega_1)(\omega_0^2-\omega_2^2-i\gamma\omega_2)[\omega_0^2-(\omega_1+\omega_2)^2-i\gamma(\omega_1+\omega_2)]}
\end{aligned}
$$
$$(2.62)$$

We thus see that the second order susceptibility becomes large as $\omega_1 \to \omega_0$, $\omega_2 \to \omega_0$, or $\omega_1 + \omega_2 \to \omega_0$.

2.2 Numerical Estimate of $\chi^{(2)}$

It is often the case that the first resonance of a material ω_0 is much higher than the input frequencies ($\omega_0 \gg \omega_1, \omega_2$). We can thus approximate 2.77 as independent of input frequencies ω_1 and ω_2 by:

$$
\chi^{(2)} \approx \frac{Ne^3b}{m^2\epsilon_0\omega_0^6}
$$

We can then estimate the value of the nonlinear coefficient b, by assuming that the second-order restoring force becomes comparable to the linear restoring force when the electron displacement becomes greater than or equal to the material lattice constant d:

$$
m\omega_0^2 d \approx mbd^2 \to b \approx \frac{\omega_0^2}{d} \qquad (2.63)
$$

Also plugging in $N \approx \frac{1}{d^3}$, the second order susceptibility is approximately:

$$
\chi^{(2)} \approx \frac{e^3}{m^2\epsilon_0\omega_0^4 d^4} \qquad (2.64)
$$

Plugging in some standard values $\omega_0 = 10^{16}\frac{rad}{s}$ and $d = 3\text{Å}$:

$$
\chi^{(2)} \approx 6.9 * 10^{-12}\frac{m}{V}
$$

which agrees pretty well with typical measured values for many materials.

2.3 Miller's Rule

In 1964[12], Robert Miller at Bell Labs noticed a relation between the first and second-order susceptibilities. Recalling the first and second order susceptibilities:

$$\chi^{(1)}(\omega) = \frac{Ne^2}{m\epsilon_0}\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\chi^{(2)}(\omega;\omega_1,\omega_2) = \frac{Ne^3 b}{m^2\epsilon_0}\frac{1}{(\omega_0^2 - \omega_1^2 - i\gamma\omega_1)(\omega_0^2 - \omega_2^2 - i\gamma\omega_2)[\omega_0^2 - (\omega_1 + \omega_2)^2 - i\gamma(\omega_1 + \omega_2)]}$$

Notice that we can write $\chi^{(2)}(\omega;\omega_1,\omega_2)$ in terms of $\chi^{(1)}(\omega)$:

$$\chi^{(2)}(\omega;\omega_1,\omega_2) = \frac{Ne^3 b}{m^2\epsilon_0}\left(\frac{m\epsilon_0}{Ne^2}\right)^3 \chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)\chi^{(1)}(\omega_1 + \omega_2)$$

$$(2.65)$$

We can thus rearrange to find a constant quantity:

$$\frac{m\epsilon_0^2 b}{N^2 e^3} = \frac{\chi^{(2)}(\omega;\omega_1,\omega_2)}{\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)\chi^{(1)}(\omega_1 + \omega_2)} = constant \qquad (2.66)$$

Since we have found a constant ratio between $\chi^{(1)}$ and $\chi^{(2)}$, a larger $\chi^{(1)}$ would, in general, mean a larger $\chi^{(2)}$. This relationship has served as a useful guide for identifying materials with larger second-order nonlinearities.

2.4 General Second-Order Polarization

We now consider a material with an applied field consisting of two monochromatic components $\omega = \omega_a$ and $\omega = \omega_b$. Following the complex exponential form of **??**, the frequency spectrum is thus:

$$\mathbf{E}(\omega) = \pi\left[\mathbf{E}^{\omega_a}\delta(\omega - \omega_a) + (\mathbf{E}^{\omega_a})^*\,\delta(\omega + \omega_a) + \mathbf{E}^{\omega_b}\delta(\omega - \omega_b) + (\mathbf{E}^{\omega_b})^*\,\delta(\omega + \omega_b)\right]$$
$$(2.67)$$

Similarly, the polarization spectrum can also be written as:

$$\mathbf{P}(\omega) = \pi\left[\sum_{\omega_n}\mathbf{P}^{\omega_n}\delta(\omega - \omega_n) + (\mathbf{P}^{\omega_n})^*\,\delta(\omega + \omega_n)\right] \qquad (2.68)$$

where the amplitudes of the positive and negative frequency components for the field and polarization are complex conjugates:

$$\mathbf{E}^{-\omega} = (\mathbf{E}^{\omega})^* \quad \text{and} \quad \mathbf{P}^{-\omega} = (\mathbf{P}^{\omega})^* \qquad (2.69)$$

which means that only one of either the positive or negative frequency amplitude is needed to know the other. Plugging 2.68 into 1.32, we find $P_i^{(2)}(\omega)$ due to a dichromatic field:

$$
\begin{aligned}
P_i^{(2)}(\omega) = \frac{\epsilon_0 \pi}{2} \iint & \chi_{ijk}^{(2)}(\omega; \omega_1, \omega_2) \left[E_j^{\omega_a} \delta(\omega_1 - \omega_a) + \left(E_j^{\omega_a} \right)^* \delta(\omega_1 + \omega_a) + E_j^{\omega_b} \delta(\omega_1 - \omega_b) + \left(E_j^{\omega_b} \right)^* \delta(\omega_1 + \omega_b) \right] \\
& \left[E_k^{\omega_a} \delta(\omega_2 - \omega_a) + \left(E_k^{\omega_a} \right)^* \delta(\omega_2 + \omega_a) + E_k^{\omega_b} \delta(\omega_2 - \omega_b) + \left(E_k^{\omega_b} \right)^* \delta(\omega_2 + \omega_b) \right] \delta(\omega - \omega_1 - \omega_2) d\omega_1 d\omega_2
\end{aligned}
$$

$$
= \frac{\epsilon_0 \pi}{2} \left[\underbrace{\chi_{ijk}^{(2)}(2\omega_a; \omega_a, \omega_a) E_j^{\omega_a} E_k^{\omega_a} \delta(\omega - 2\omega_a) + \chi_{ijk}^{(2)}(-2\omega_a; -\omega_a, -\omega_a) \left(E_j^{\omega_a} E_k^{\omega_a} \right)^* \delta(\omega + 2\omega_a)}_{\text{Second Harmonic Generation } (\omega = 2\omega_a)} \right.
$$

$$
+ \underbrace{\chi_{ijk}^{(2)}(2\omega_b; \omega_b, \omega_b) E_j^{\omega_b} E_k^{\omega_b} \delta(\omega - 2\omega_b) + \chi_{ijk}^{(2)}(-2\omega_b; -\omega_b, -\omega_b) \left(E_j^{\omega_b} E_k^{\omega_b} \right)^* \delta(\omega + 2\omega_b)}_{\text{Second Harmonic Generation } (\omega = 2\omega_b)}
$$

$$
\begin{aligned}
&+ \chi_{ijk}^{(2)}(\omega_a + \omega_b; \omega_a, \omega_b) E_j^{\omega_a} E_k^{\omega_b} \delta(\omega - \omega_a - \omega_b) + \chi_{ijk}^{(2)}(-\omega_a - \omega_b; -\omega_a, -\omega_b) \left(E_j^{\omega_a} E_k^{\omega_b} \right)^* \delta(\omega + \omega_a + \omega_b) \\
&+ \underbrace{\chi_{ijk}^{(2)}(\omega_b + \omega_a; \omega_b, \omega_a) E_j^{\omega_b} E_k^{\omega_a} \delta(\omega - \omega_b - \omega_a) + \chi_{ijk}^{(2)}(-\omega_b - \omega_a; -\omega_b, -\omega_a) \left(E_j^{\omega_b} E_k^{\omega_a} \right)^* \delta(\omega + \omega_b + \omega_a)}_{\text{Sum Frequency Generation } (\omega = \omega_a + \omega_b)}
\end{aligned}
$$

$$
\begin{aligned}
&+ \chi_{ijk}^{(2)}(\omega_a - \omega_b; \omega_a, -\omega_b) E_j^{\omega_a} \left(E_k^{\omega_b} \right)^* \delta(\omega - \omega_a + \omega_b) + \chi_{ijk}^{(2)}(\omega_b - \omega_a; -\omega_a, \omega_b) \left(E_j^{\omega_a} \right)^* E_k^{\omega_b} \delta(\omega + \omega_a - \omega_b) \\
&+ \underbrace{\chi_{ijk}^{(2)}(\omega_a - \omega_b; -\omega_b, \omega_a) \left(E_j^{\omega_b} \right)^* E_k^{\omega_a} \delta(\omega + \omega_b - \omega_a) + \chi_{ijk}^{(2)}(\omega_b - \omega_a; \omega_b, -\omega_a) E_j^{\omega_b} \left(E_k^{\omega_a} \right)^* \delta(\omega - \omega_b + \omega_a)}_{\text{Difference Frequency Generation } (\omega = |\omega_a - \omega_b|)}
\end{aligned}
$$

$$
+ \underbrace{\chi_{ijk}^{(2)}(0; \omega_a, -\omega_a) E_j^{\omega_a} \left(E_k^{\omega_a} \right)^* \delta(\omega) + \chi_{ijk}^{(2)}(0; -\omega_a, \omega_a) \left(E_j^{\omega_a} \right)^* E_k^{\omega_a} \delta(\omega)}
$$

$$
\left. + \underbrace{\chi_{ijk}^{(2)}(0; \omega_b, -\omega_b) E_j^{\omega_b} \left(E_k^{\omega_b} \right)^* \delta(\omega) + \chi_{ijk}^{(2)}(0; -\omega_b, \omega_b) \left(E_j^{\omega_b} \right)^* E_k^{\omega_b} \delta(\omega)}_{\text{Optical Rectification } (\omega = 0)} \right]
$$

$$
(2.70)
$$

This form for the polarization that we've found matches quite nicely with the form given by 3.94. By inspection we find the respective polarization amplitudes for each phenomena:

- Second Harmonic Generation $(\omega = 2\omega_a)$ and $(\omega = 2\omega_b)$:

$$
P_i^{2\omega_a} = \frac{\epsilon_0}{2} \chi_{ijk}^{(2)}(2\omega_a; \omega_a, \omega_a) E_j^{\omega_a} E_k^{\omega_a} \tag{2.71}
$$

$$
P_i^{2\omega_b} = \frac{\epsilon_0}{2} \chi_{ijk}^{(2)}(2\omega_b; \omega_b, \omega_b) E_j^{\omega_b} E_k^{\omega_b} \tag{2.72}
$$

- Sum Frequency Generation ($\omega = \omega_a + \omega_b$):

$$
\begin{aligned}
P_i^{\omega_a+\omega_b} &= \frac{\epsilon_0}{2}\left[\chi_{ijk}^{(2)}(\omega_a+\omega_b;\omega_a,\omega_b)E_j^{\omega_a}E_k^{\omega_b} + \chi_{ijk}^{(2)}(\omega_b+\omega_a;\omega_b,\omega_a)E_j^{\omega_b}E_k^{\omega_a}\right]\\
&= \frac{\epsilon_0}{2}\left[\chi_{ijk}^{(2)}(\omega_a+\omega_b;\omega_a,\omega_b)E_j^{\omega_a}E_k^{\omega_b} + \chi_{ikj}^{(2)}(\omega_b+\omega_a;\omega_a,\omega_b)E_k^{\omega_a}E_j^{\omega_b}\right]\\
&= 2\frac{\epsilon_0}{2}\chi_{ijk}^{(2)}(\omega_a+\omega_b;\omega_a,\omega_b)E_j^{\omega_a}E_k^{\omega_b} \qquad (2.73)
\end{aligned}
$$

where in the second line we invoked intrinsic permutation symmetry to swap the indices. The second and first terms are thus equal[13]:

- Difference Frequency Generation ($\omega = |\omega_a - \omega_b|$):

$$
\begin{aligned}
P_i^{\omega_a-\omega_b} &= \frac{\epsilon_0}{2}\left[\chi_{ijk}^{(2)}(\omega_a-\omega_b;\omega_a,-\omega_b)E_j^{\omega_a}\left(E_k^{\omega_b}\right)^* + \chi_{ijk}^{(2)}(\omega_a-\omega_b;-\omega_b,\omega_a)\left(E_j^{\omega_b}\right)^*E_k^{\omega_a}\right]\\
&= \frac{\epsilon_0}{2}\left[\chi_{ijk}^{(2)}(\omega_a-\omega_b;\omega_a,-\omega_b)E_j^{\omega_a}\left(E_k^{\omega_b}\right)^* + \chi_{ikj}^{(2)}(\omega_a-\omega_b;\omega_a,-\omega_b)E_j^{\omega_a}\left(E_k^{\omega_b}\right)^*\right]\\
&= 2\frac{\epsilon_0}{2}\chi_{ijk}^{(2)}(\omega_a-\omega_b;\omega_a,-\omega_b)E_j^{\omega_a}\left(E_k^{\omega_b}\right)^* \qquad (2.74)
\end{aligned}
$$

- Optical Rectification ($\omega = 0$):

$$
\begin{aligned}
P_i^{\omega_a-\omega_a} &= \frac{\epsilon_0}{2}\left[\chi_{ijk}^{(2)}(0;\omega_a,-\omega_a)E_j^{\omega_a}\left(E_k^{\omega_a}\right)^* + \chi_{ijk}^{(2)}(0;-\omega_a,\omega_a)\left(E_j^{\omega_a}\right)^*E_k^{\omega_a}\right]\\
&= \frac{\epsilon_0}{2}\left[\chi_{ijk}^{(2)}(0;\omega_a,-\omega_a)E_j^{\omega_a}\left(E_k^{\omega_a}\right)^* + \chi_{ikj}^{(2)}(0;\omega_a,-\omega_a)E_j^{\omega_a}\left(E_k^{\omega_a}\right)^*\right]\\
&= 2\frac{\epsilon_0}{2}\chi_{ijk}^{(2)}(0;\omega_a,-\omega_a)E_j^{\omega_a}\left(E_k^{\omega_a}\right)^* \qquad (2.75)
\end{aligned}
$$

$$
P_i^{\omega_b-\omega_b} = 2\frac{\epsilon_0}{2}\chi_{ijk}^{(2)}(0;\omega_b,-\omega_b)E_j^{\omega_b}\left(E_k^{\omega_b}\right)^* \qquad (2.76)
$$

Notice that there is a factor of 2 for all polarization amplitudes except for second harmonic generation. We can thus write a general expression for the second-order polarization amplitudes as:

$$
P_i^{\omega_1+\omega_2} = D\frac{\epsilon_0}{2}\chi_{ijk}^{(2)}(\omega_1,\omega_2)E_j^{\omega_1}E_k^{\omega_2} \qquad (2.77)
$$

where D is called the **degeneracy factor**, with the values[14]:

$$
D = \begin{cases} 1 & \text{if}\quad \omega_1 = \omega_2 \\ 2 & \text{if}\quad \omega_1 \neq \omega_2 \end{cases} \qquad (2.78)
$$

2.5 The d-Coefficients and Effective Susceptibility

For historical reasons, measured values of the second-order susceptibility are not given in the literature by $\chi^{(2)}$, but instead are given in terms of a so-called d-coefficient:

$$
d_{ijk}(\omega;\omega_1,\omega_2) = \frac{\chi_{ijk}^{(2)}(\omega;\omega_1,\omega_2)}{2} \qquad (2.79)
$$

From here on, all second-order analysis will be performed in terms of the d-coefficients rather than the susceptibility, which differ only by a factor of 2.

We will find in the next chapter that in real nonlinear crystals, only a specific polarization component $\mathbf{P}_{pm}^{\omega_1+\omega_2}$ generated by two specific components of the fundamental beams $\mathbf{E}_{1,pm}^{\omega_1}$ and $\mathbf{E}_{2,pm}^{\omega_2}$ will grow constructively as they propagate. The subscript pm stands for "phase-matched" (we will discuss this in the next chapter), and we also include an extra 1 and 2 to distinguish between different phase-matched components in the SHG case $\omega_1 = \omega_2$. It is therefore convenient to define an **effective susceptibility** $d_{eff}^{\omega_1+\omega_2}$, which directly relates the amplitudes of $\mathbf{P}_{pm}^{\omega_1+\omega_2}$, $\mathbf{E}_{1,pm}^{\omega_1}$, and $\mathbf{E}_{2,pm}^{\omega_2}$:

$$P_{pm}^{\omega_1+\omega_2} = \epsilon_0 d_{eff}^{\omega_1+\omega_2} E_{1,pm}^{\omega_1} E_{2,pm}^{\omega_2} \tag{2.80}$$

This is probably very confusing, so we examine this in an example.

Example (d_{eff} of SHG): Suppose we have a SHG process, in which we find that the two phase-matched components of the fundamental are the components pointing in the direction of the two unit vectors:

$$\hat{\mathbf{u}}_1 = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \qquad \hat{\mathbf{u}}_2 = \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \tag{2.81}$$

and the phase-matched component of the polarization points in the direction of the unit vector:

$$\hat{\mathbf{u}}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{2.82}$$

Explicitly, the two phase-matched components of $\mathbf{E}^\omega$ are:

$$\mathbf{E}_{pm}^\omega = (\mathbf{E}^\omega \cdot \hat{\mathbf{u}}_1)\hat{\mathbf{u}}_1 = E_{pm}^\omega \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} \qquad \mathbf{E}_{pm}^\omega = (\mathbf{E}^\omega \cdot \hat{\mathbf{u}}_2)\hat{\mathbf{u}}_2 = E_{pm}^\omega \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}$$
$$\tag{2.83}$$

We now plug these two components into 2.77 to find the net SHG polarization generated:

$$\begin{aligned}
P_i^{2\omega} &= \frac{\epsilon_0}{2} \chi_{ijk}^{(2)}(\omega,\omega)(E_1^\omega)_j (E_2^\omega)_k \\
&= \frac{\epsilon_0}{2} \left[\chi_{ixx}^{(2)} \frac{E_1^\omega}{\sqrt{2}} \left(-\frac{E_2^\omega}{\sqrt{2}} \right) + \chi_{ixy}^{(2)} \frac{E_1^\omega}{\sqrt{2}} \left(-\frac{E_2^\omega}{\sqrt{2}} \right) + \chi_{iyx}^{(2)} \left(-\frac{E_1^\omega}{\sqrt{2}} \right) \frac{E_2^\omega}{\sqrt{2}} + \chi_{iyy}^{(2)} \left(-\frac{E_1^\omega}{\sqrt{2}} \right) \left(-\frac{E_2^\omega}{\sqrt{2}} \right) \right] \\
&= -\frac{\epsilon_0}{4} \left[\chi_{ixx}^{(2)} + \chi_{ixy}^{(2)} + \chi_{iyx}^{(2)} + \chi_{iyy}^{(2)} \right] E_1^\omega E_2^\omega \tag{2.84}
\end{aligned}$$

The only component of the polarization that grows points in the direction of $\hat{\mathbf{u}}_3$, which is given by:

$$\mathbf{P}_{pm}^{2\omega} = (\mathbf{P}_{pm}^{2\omega} \cdot \hat{\mathbf{u}}_3)\hat{\mathbf{u}}_3 \tag{2.85}$$

The phase-matched polarization amplitude is thus:

$$
\begin{aligned}
P_{pm}^{2\omega} &= \mathbf{P}_{pm}^{2\omega} \cdot \hat{\mathbf{u}}_3 \\
&= P_z^{2\omega} \\
&= -\frac{\epsilon_0}{4} \left[\chi_{zxx}^{(2)} + \chi_{zxy}^{(2)} + \chi_{zyx}^{(2)} + \chi_{zyy}^{(2)} \right] E_1^\omega E_2^\omega
\end{aligned} \tag{2.86}
$$

Comparing to 2.80, we find the effective susceptibility:

$$d_{eff}^{2\omega} = -\frac{1}{4} \left[\chi_{zxx}^{(2)} + \chi_{zxy}^{(2)} + \chi_{zyx}^{(2)} + \chi_{zyy}^{(2)} \right] \tag{2.87}$$

This result can be simplified further by taking into account intrinsic/overall permutation and/or Kleinman symmetry.

In the next chapter, we will find out how the phase-matching components are determined by examining SHG in detail.

Second Harmonic Generation (SHG)

3.1 The d-Matrix

As derived earlier, the SHG polarization amplitude is given by:

$$\begin{aligned}
P_i^{2\omega} &= \frac{\epsilon_0}{2} \chi_{ijk}^{(2)}(2\omega; \omega, \omega) E_j^\omega E_k^\omega \\
&= \epsilon_0 d_{ijk}(2\omega, \omega, \omega) E_j^\omega E_k^\omega
\end{aligned} \tag{3.88}$$

For SHG specifically, the fact that both of the input frequencies are identical allows us to make a simplification. By intrinsic permutation symmetry we can swap the j and k indices of the d-coefficient, but swapping the corresponding frequencies has no effect since they're identical. We thus find that pairs of j and k indices result in identical d-coefficients, which suggests that we represent each pair (j, k) by a third coefficient ℓ:

(j, k)	(x,x)	(y,y)	(z,z)	(y,z),(z,y)	(x,z),(z,x)	(x,y),(y,x)
ℓ	1	2	3	4	5	6

We have now reduced the 27 d_{ijk} coefficients to 18 $d_{i\ell}$ coefficients, which we represent as a so-called d-matrix[15] (with the frequency arguments suppressed for clarity):

$$d = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \tag{3.89}$$

where the first index i is replaced by $(x, y, z) \rightarrow (1, 2, 3)$ to match convention. Each polarization component can now be expressed nicely in matrix form:

$$\begin{pmatrix} P_x^{2\omega} \\ P_y^{2\omega} \\ P_z^{2\omega} \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} (E_x^\omega)^2 \\ \left(E_y^\omega\right)^2 \\ (E_z^\omega)^2 \\ 2E_y^\omega E_z^\omega \\ 2E_x^\omega E_z^\omega \\ 2E_x^\omega E_y^\omega \end{pmatrix} \tag{3.90}$$

3.2   Symmetry Properties of the d-Coefficients

If the material has a certain symmetry represented by a 3x3 transformation tensor (matrix) a_{ij}, the d-coefficients will obey the same symmetry according to:

$$d'_{ijk} = a_{i\ell}a_{jm}a_{kn}d_{\ell mn} \tag{3.91}$$

Example (Monoclinic 2 Class): Crystals that are in the monoclinic 2 class obey the two-fold rotation operation around a certain axis (in this case y) represented by:

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{or} \quad a_{ij} = \begin{cases} -\delta_{ij} & \text{if} \quad i = x,z \\ +\delta_{ij} & \text{if} \quad i = y \end{cases} \tag{3.92}$$

Since the transformation matrix a is diagonal, the condition 3.94 reduces to:

$$d'_{ijk} = a_{ii}a_{jj}a_{kk}d_{ijk} \tag{3.93}$$

Since the transformed tensor d'_{ijk} should be invariant under the transformation a, all of the elements d_{ijk} for which $a_{ii}a_{jj}a_{kk} = -1$ must equal 0. According to 3.95, all indices (ijk) in which the index y appears 0 or 2 times.

Example (Orthorhombic 222): Crystals that are in the orthorhombic 222 class obey the two-fold rotation operation around all three axes x, y, and z. The operator for a two-fold rotation around the y axis is given by 3.95 in the first example. The operators for a two-fold rotation about the x and z axes are similarly:

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{or} \quad a_{ij} = \begin{cases} -\delta_{ij} & \text{if} \quad i = y,z \\ +\delta_{ij} & \text{if} \quad i = x \end{cases} \tag{3.94}$$

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{or} \quad a_{ij} = \begin{cases} -\delta_{ij} & \text{if} \quad i = x,y \\ +\delta_{ij} & \text{if} \quad i = z \end{cases} \tag{3.95}$$

We thus find that all elements d_{ijk} with indices (ijk) in which the index x, y, and z appear 0 or two times must equal 0. The only non-zero elements are thus $d_{123}, d_{213}, d_{231}, d_{312}$, and d_{321}.

If the medium is dispersionless, Kleinman symmetry holds and the number of independent components is reduced even further:

$$\underbrace{d_{xxy}}_{d_{16}} = \underbrace{d_{xyx}}_{d_{16}} = \underbrace{d_{yxx}}_{d_{21}} \rightarrow d_{16} = d_{21}$$

$$\underbrace{d_{xyy}}_{d_{15}} = \underbrace{d_{yxy}}_{d_{26}} = \underbrace{d_{yyx}}_{d_{26}} \rightarrow d_{12} = d_{26}$$

$$\underbrace{d_{xzz}}_{d_{13}} = \underbrace{d_{zxz}}_{d_{35}} = \underbrace{d_{zzx}}_{d_{35}} \rightarrow d_{13} = d_{35}$$

$$\underbrace{d_{xxz}}_{d_{15}} = \underbrace{d_{xzx}}_{d_{15}} = \underbrace{d_{zxx}}_{d_{31}} \rightarrow d_{15} = d_{31}$$

$$\underbrace{d_{yyz}}_{d_{24}} = \underbrace{d_{yzy}}_{d_{24}} = \underbrace{d_{zyy}}_{d_{32}} \rightarrow d_{24} = d_{32}$$

$$\underbrace{d_{yzz}}_{d_{23}} = \underbrace{d_{zyz}}_{d_{34}} = \underbrace{d_{zzy}}_{d_{34}} \rightarrow d_{23} = d_{34}$$

$$\underbrace{d_{xyz}}_{d_{14}} = \underbrace{d_{yxz}}_{d_{25}} = \underbrace{d_{zxy}}_{d_{36}} = \underbrace{d_{zyx}}_{d_{36}} = \underbrace{d_{xzy}}_{d_{14}} = \underbrace{d_{yzx}}_{d_{25}} \rightarrow d_{14} = d_{25} = d_{36}$$

which reduces the number of independent components of the d-matrix from 18 to 10:

$$d = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{pmatrix} \tag{3.96}$$

3.3 SHG Wave Equation

Recall the SHG polarization amplitude from before:

$$P_i^{2\omega} = \epsilon_0 d_{ijk}(2\omega, \omega, \omega) E_j^\omega E_k^\omega$$

Assuming that there is a second harmonic generated at frequency 2ω, this light can then mix with the fundamental light at frequency ω to generate a polarization at the fundamental frequency:

$$P_i^\omega = 2\epsilon_0 d_{ijk}(\omega, 2\omega, -\omega) E_j^{2\omega} (E_k^\omega)^* \tag{3.97}$$

For convenience, we use the effective susceptibility notation developed in the last chapter, and work simply in terms of the amplitudes of the phase-matched fundamental and polarization components:

$$P^{2\omega} = \epsilon_0 d_{eff}^{2\omega} E^\omega E^\omega \qquad P^\omega = \epsilon_0 d_{eff}^\omega E^{2\omega} (E^\omega)^* \tag{3.98}$$

If the nonlinear medium is lossless, overall permutation symmetry applies. This means $d_{eff}^{2\omega} = \frac{1}{2} d_{eff}^\omega = d_{eff}$ and we will make this

assumption here:

$$P^{2\omega} = \epsilon_0 d_{eff} E^\omega E^\omega \qquad P^\omega = 2\epsilon_0 d_{eff} E^{2\omega} \left(E^\omega\right)^* \qquad (3.99)$$

As before, we also assume that the fields propagate as plane waves in the $\hat{z}$ direction, in which case we can pull out the propagation factor:

$$E^{2\omega} = A^{2\omega} e^{ik^{2\omega}z} \qquad E^\omega = A^\omega e^{ik^\omega z} \qquad (3.100)$$

For reference, the SVEA wave equation derived in the first chapter (1.58) is given by:

$$2ik^{\omega_n} \frac{dA^{\omega_n}}{dz} = -\mu_0 \omega_n^2 P^{\omega_n NL} e^{-ik^{\omega_n}z}$$

Plugging in the fundamental and second harmonic amplitudes and polarizations, we find:

$$\frac{dA^{2\omega}}{dz} = i \frac{\mu_0 (2\omega)^2}{2k^{2\omega}} \epsilon_0 d_{eff} \left(A^\omega e^{ik^\omega z}\right)^2 e^{-ik^{2\omega}z} \qquad (3.101)$$

$$\frac{dA^\omega}{dz} = i \frac{\mu_0 \omega^2}{2k^\omega} 2\epsilon_0 d_{eff} A^{2\omega} e^{ik^{2\omega}z} \left(A^\omega e^{ik^\omega z}\right)^* e^{-ik^\omega z} \qquad (3.102)$$

We can now simplify the above by defining the **wave impedance** in terms of η_0, the impedance of free space:

$$\eta^{\omega_n} = \frac{\eta_0}{n(\omega_n)} \quad \text{where} \quad \eta_0 = \sqrt{\frac{\mu_0}{\epsilon_0}} \qquad (3.103)$$

The wave equations for $A^{2\omega}$ and A^ω can thus be written as:

$$\frac{dA^{2\omega}}{dz} = i\omega \eta^{2\omega} \epsilon_0 d_{eff} \left(A^\omega\right)^2 e^{i\Delta kz} \qquad (3.104)$$

$$\frac{dA^\omega}{dz} = i\omega \eta^\omega \epsilon_0 d_{eff} A^{2\omega} \left(A^\omega\right)^* e^{-i\Delta kz} \qquad (3.105)$$

where we've defined the **wave-vector mismatch** between the fundamental and second harmonic:

$$\Delta k = 2k^\omega - k^{2\omega} \qquad (3.106)$$

This wave-vector mismatch defines the **phase-matching condition** of SHG. For zero mismatch ($\Delta k = 0$) there is so-called "perfect phase-matching", which results in the greatest generated second harmonic field. For finite mismatch ($\Delta k \neq 0$), the greater the mismatch the less second harmonic is generated.

3.4 *SHG In The Non-Depleted Pump Approximation*

In real situations, the fundamental (referred to as the "pump") intensity is often sufficient for the change in pump amplitude (from either material loss or conversion to SHG light) to be neglected:

$$\frac{dA^\omega}{dz} \approx 0 \qquad \text{(non-depleted pump approximation)} \qquad (3.107)$$

The pump amplitude is thus always equal to its initial value $A^\omega(z) = A^\omega(0)$, which simplifies the second harmonic amplitude equation:

$$\frac{dA^{2\omega}}{dz} = i\omega\eta^{2\omega}\epsilon_0 d_{eff}[A^\omega(0)]^2 e^{i\Delta kz}$$
$$= Ce^{i\Delta kz} \quad \text{where} \quad C = i\omega\eta^{2\omega}\epsilon_0 d_{eff}[A^\omega(0)]^2 \qquad (3.108)$$

The second harmonic amplitude at a distance z is thus given by:

$$A^{2\omega}(z) = \int_0^z Ce^{i\Delta kz'}dz'$$
$$= C\frac{e^{i\Delta kz} - 1}{i\Delta k}$$
$$= 2Ce^{i\frac{\Delta k}{2}z}\left(\frac{e^{i\frac{\Delta k}{2}z} - e^{-i\frac{\Delta k}{2}z}}{2i\Delta k}\right)$$
$$= zCe^{i\frac{\Delta k}{2}z}\left[\frac{sin\left(\frac{\Delta k}{2}z\right)}{\frac{\Delta k}{2}z}\right]$$
$$= zCe^{i\frac{\Delta k}{2}z}sinc\left(\frac{\Delta k}{2}z\right) \qquad (3.109)$$

The intensity is then proportional to the amplitude squared:

$$I^{2\omega}(z) = \frac{|A^{2\omega}(z)|^2}{2\eta^{2\omega}} = z^2\frac{|C|^2}{2\eta^{2\omega}}sinc^2\left(\frac{\Delta k}{2}z\right) \qquad (3.110)$$

We see that for $\Delta k \neq 0$, the second harmonic intensity will oscillate with distance, with the first maximum occuring at a distance L_c called the **coherence length**:

$$L_c = \frac{\pi}{\Delta k} \qquad (3.111)$$

Figure 3.1: Second harmonic intensity as a function of distance for different wave-vector mismatches.

Plotted in figure 3.1, as the wavevector mismatch decreases, the amplitude of the oscillations grows and approaches quadratic growth as $\Delta k \rightarrow 0$. Of course, indefinite quadratic growth is unphysical since it violates conservation of energy, and is a result of the non-depleted pump approximation. We should therefore define the limits under which we can make the approximation. Before we do, let us define the SHG conversion efficiency:

$$\eta_{SHG}(z) = \frac{P^{2\omega}(z)}{P^\omega(0)}$$
$$\approx \frac{I^{2\omega}(z)}{I^\omega(0)}$$
$$= \frac{2\eta^\omega z^2\left(\omega\eta^{2\omega}\epsilon_0 d_{eff}[A^\omega(0)]^2\right)^2}{2\eta^{2\omega}[A^\omega(0)]^2}sinc^2\left(\frac{\Delta k}{2}z\right)$$
$$= 2\eta^{2\omega}\left(\eta^\omega z\omega\epsilon_0 d_{eff}\right)^2 I^\omega(0)sinc^2\left(\frac{\Delta k}{2}z\right) \qquad (3.112)$$

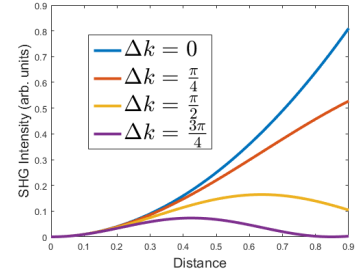where we've assumed that the area of the fundamental and second harmonic beams are approximately equal.

A rough guideline is that the non-depleted pump approximation is valid for conversion efficiencies less than or equal to 25%. For higher conversion efficiencies, pump depletion must be accounted for, which will be treated in the next section.

3.5 SHG With Pump Depletion

In most cases we can apply the non-depleted pump approximation and use the results derived in the previous section to find the second harmonic intensity propagating through a nonlinear crystal. When the conversion efficiency is very high however, we must take into account the energy in the pump field decreasing with distance. The most obvious case of such high efficiency is in the case of perfect phase-matching ($\Delta k = 0$), which we examine first.

Pump-Depleted SHG $(\Delta k = 0)$

For perfect phase-matching, we find the wave equations:

$$\frac{dA^{2\omega}}{dz} = i\omega\eta^{2\omega}\epsilon_0 d_{eff} \left(A^\omega\right)^2 \tag{3.113}$$

$$\frac{dA^\omega}{dz} = i\omega\eta^\omega\epsilon_0 d_{eff} A^{2\omega} \left(A^\omega\right)^* \tag{3.114}$$

We can write out the phase-matching condition:

$$\begin{aligned}
0 &= \Delta k \\
&= 2k^\omega - k^{2\omega} \\
&= 2\frac{\omega n(\omega)}{c} - \frac{2\omega n(2\omega)}{c}
\end{aligned}$$

We can thus see that for perfect phase-matching, the index at frequencies ω and 2ω must be identical:

$$n(\omega) = n(2\omega) \quad \text{for } \Delta k = 0 \tag{3.115}$$

We shall see how to achieve such a situation later. This also makes the wave impedances for the fundamental and second harmonic identical ($\eta^\omega = \eta^{2\omega}$), which gives:

$$\frac{dA^{2\omega}}{dz} = i\omega\eta^{2\omega}\epsilon_0 d_{eff} \left(A^\omega\right)^2 \tag{3.116}$$

$$\frac{dA^\omega}{dz} = i\omega\eta^\omega\epsilon_0 d_{eff} A^{2\omega} \left(A^\omega\right)^* \tag{3.117}$$

Part II

Semi-Classical Quantum Theory

(Based on "Introduction to Quantum Optics" - Grynberg, Aspect, and Fabre)

Perturbation Theory

We now consider the general problem, in which the Hamiltonian is too complicated to solve exactly. Although an analytical solution would be nice, we can solve these problems approximately through a technique known as **perturbation theory**. In most practical problems, we can separate the Hamiltonian into two parts, $\hat{H}_0$ and $\hat{H}_1(t)$:

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t) \tag{1.118}$$

in which $\hat{H}_0$ is a time-independent Hamiltonian with corresponding eigenstates and eigenenergies $|n\rangle$ and E_n:

$$\hat{H}_0 |n\rangle = E_n |n\rangle \tag{1.119}$$

and $\hat{H}_1(t)$ is a time-dependent adjustment to the total Hamiltonian, called a **perturbation**, that must be small in magnitude compared to $\hat{H}_0$ for perturbation theory to be practically applied[16].

    To apply perturbation theory, we write the perturbation in a slightly different form:

$$\hat{H}_1(t) = \lambda \hat{H}_1'(t) \tag{1.120}$$

where λ is a parameter that we'll use only for the purpose of bookkeeping. In the end, we set $\lambda = 1$ to make $\hat{H}_1(t) = \hat{H}_1'(t)$ and our solution exact. The time-dependent Schrodinger equation is given by:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \left(\hat{H}_0 + \lambda \hat{H}_1'(t) \right) |\psi(t)\rangle \tag{1.121}$$

We now project onto an arbitrary eigenstate $|k\rangle$ by adding $\langle k|$ to the left of each term on both sides [17]:

$$i\hbar \frac{d}{dt} \langle k \,|\, \psi(t)\rangle = \langle k \,|\, \hat{H}_0 \,|\, \psi(t)\rangle + \lambda \langle k \,|\, \hat{H}_1' \,|\, \psi(t)\rangle$$

$$= E_k \langle k \,|\, \psi(t)\rangle + \lambda \sum_n \langle k \,|\, \hat{H}_1'(t) \,|\, n\rangle \langle n \,|\, \psi(t)\rangle \tag{1.122}$$

Recall that the eigenstates $|n\rangle$ form an orthonormal basis, so we can express any arbitrary function as a superposition of all $|n\rangle$:

$$|\psi(t)\rangle = \sum_n \gamma_n(t) e^{-i\frac{E_n}{\hbar}t} |n\rangle \tag{1.123}$$

[16] Specifically, the off-diagonal matrix elements of $\hat{H}_1(t)$ must be very small compared to the corresponding energy differences: $|\langle n \,|\, \hat{H}_1(t) \,|\, m\rangle| \ll |E_n - E_m|$

[17] In the second line, we use the closure relation: $\sum_n |n\rangle \langle n| = 1$

Notice that the coefficients $\gamma_n(t)$ are time-dependent to allow for $\psi(t)$ to have a time-dependence. Plugging 1.123 into 1.122, we obtain[18]:

$$\left[E_k \gamma_k(t) + i\hbar \frac{d}{dt} \gamma_k(t) \right] e^{-i\frac{E_k}{\hbar}t} = E_k \gamma_k(t) e^{-i\frac{E_k}{\hbar}t} + \lambda \sum_n \langle k \, | \, \hat{H}_1'(t) \, | \, n \rangle \, \gamma_n(t) e^{-i\frac{E_n}{\hbar}t}$$

(1.124)

A slight rearrangement gives:

$$i\hbar \frac{d}{dt} \gamma_k(t) = \lambda \sum_n \langle k \, | \, \hat{H}_1'(t) \, | \, n \rangle \, e^{i\frac{E_k - E_n}{\hbar}t} \gamma_n(t)$$

(1.125)

At this point, it seems like we've done nothing but made the problem more complicated. However, if we expand $\gamma_k(t)$ as a power series in λ:

$$\gamma_k(t) = \gamma_k^{(0)}(t) + \lambda \gamma_k^{(1)}(t) + \lambda^2 \gamma_k^{(2)}(t) + \ldots$$

(1.126)

We can plug 1.126 into 1.125 to find:

$$0 = \left[i\hbar \frac{d}{dt} \gamma_k^{(0)}(t) - 0 \right]$$

$$+ \lambda \left[i\hbar \frac{d}{dt} \gamma_k^{(1)}(t) - \sum_n \langle k \, | \, \hat{H}_1'(t) \, | \, n \rangle \, e^{i\frac{E_k - E_n}{\hbar}t} \gamma_n^{(0)}(t) \right]$$

$$+ \lambda^2 \left[i\hbar \frac{d}{dt} \gamma_k^{(2)}(t) - \sum_n \langle k \, | \, \hat{H}_1'(t) \, | \, n \rangle \, e^{i\frac{E_k - E_n}{\hbar}t} \gamma_n^{(1)}(t) \right]$$

$$\vdots$$

(1.127)

By the uniqueness of power series, each term in the brackets must vanish individually. We thus obtain an infinite set of equations, each of which we refer to by the power of λ they correspond to:

Zeroth Order: $\quad i\hbar \dfrac{d}{dt} \gamma_k^{(0)}(t) = 0$ (1.128a)

First Order: $\quad i\hbar \dfrac{d}{dt} \gamma_k^{(1)}(t) = \sum_n \langle k \, | \, \hat{H}_1'(t) \, | \, n \rangle \, e^{i\frac{E_k - E_n}{\hbar}t} \gamma_n^{(0)}(t)$

(1.128b)

Second Order: $\quad i\hbar \dfrac{d}{dt} \gamma_k^{(2)}(t) = \sum_n \langle k \, | \, \hat{H}_1'(t) \, | \, n \rangle \, e^{i\frac{E_k - E_n}{\hbar}t} \gamma_n^{(1)}(t)$

(1.128c)

rth Order: $\quad i\hbar \dfrac{d}{dt} \gamma_k^{(r)}(t) = \sum_n \langle k \, | \, \hat{H}_1'(t) \, | \, n \rangle \, e^{i\frac{E_k - E_n}{\hbar}t} \gamma_n^{(r-1)}(t)$

(1.128d)

At this point, we can set $\lambda = 1$ to make the problem we just solved exactly equivalent the original problem:

$$\hat{H}_1(t) = \hat{H}_1'(t) \quad \text{and} \quad \gamma_k(t) = \gamma_k^{(0)}(t) + \gamma_k^{(1)}(t) + \gamma_k^{(2)}(t) + \ldots \quad (1.129)$$

where the power series coefficients $\gamma_k^{(r)}(t)$ are still governed by the set of equations 1.128. In principle if we calculated every single $\gamma_k^{(r)}(t)$ for $r = 0$ to $r = \infty$ and summed them, we would find the exact coefficient $\gamma_k(t)$ for each eigenstate[19] in the superposition 1.123. However, the relevant physics of a problem is usually contained in just the first three terms $\gamma_k^{(0)}(t), \gamma_k^{(1)}(t)$, and $\gamma_k^{(2)}(t)$ - up to second order.

1.6 First-Order Theory

In some cases we can get away with calculating just the first two terms $\gamma_k^{(0)}(t)$ and $\gamma_k^{(1)}(t)$. From here on out we assume that at an initial time $t = t_0$ the system is in an eigenstate of $\hat{H}_0$ labeled $|i\rangle$, which means $|\gamma_i(t_0)|^2 = \gamma_i(t_0) = 1$. Since 1.128a tells us that the zeroth order coefficient $\gamma_k^{(0)}(t)$ will not change in time, it will equal unity for $k = i$ and zero for $k \neq i$:

$$\gamma_k^{(0)}(t) = \delta_{ik} \tag{1.130}$$

Plugging this result into 1.128b, the Kronecker delta collapses the sum to the $n = i$ term only:

$$i\hbar \frac{d}{dt}\gamma_k^{(1)}(t) = \langle k \,|\, \hat{H}_1'(t) \,|\, i \rangle \, e^{i\frac{E_k - E_i}{\hbar}t}\gamma_i^{(0)}(t) \tag{1.131}$$

We can then integrate 1.131 to find[20]:

$$\boxed{\gamma_k^{(1)}(t) = \tfrac{1}{i\hbar} \int_{t_0}^{t} \langle k \,|\, \hat{H}_1'(t') \,|\, i \rangle \, e^{i\frac{E_k - E_i}{\hbar}t'}\,dt'} \tag{1.132}$$

We are often interested in finding the probability of the quantum system transitioning from an initial state $|i\rangle$ to a different state $|k\rangle$ at time t, where $k \neq i$. This is simply the probability of the system simply *being* in the state $|k\rangle$ at time t, which gives:

$$P_{i \to k} = |\gamma_k(t)|^2 = \left| \gamma_k^{(0)}(t) + \gamma_k^{(1)}(t) \right|^2$$

$$= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} \langle k \,|\, \hat{H}_1'(t') \,|\, i \rangle \, e^{i\frac{E_k - E_i}{\hbar}t'} \right|^2 dt' \tag{1.133}$$

We have thus found that the first-order effect of a perturbation is to induce transitions into other states with probability $P_{i \to k}$. A few examples will now provide physical intuition for this result.

Example (Collision Process): Suppose the stationary Hamiltonian H_0 above is an atomic Hamiltonian, in which the atom is susceptible to collisions. We model a collision process as a perturbation:

$$\hat{H}_1(t) = \hat{W}f(t) \tag{1.134}$$

in which $\hat{W}$ is a constant operator that acts on the atomic system and $f(t)$ is a function for which $f(\pm\infty) \to 0$ and the maximum value occurs at $t = 0$. For convenience we define "before" the collision as $t = -\infty$ and "after" the collision as $t = \infty$, so the probability of the atom initially $(t = -\infty)$ in a state $|i\rangle$ transitioning to a state $|k\rangle$ after the collision $(t = \infty)$ is:

$$P_{i \to k} = \frac{|W_{ki}|^2}{\hbar^2} \left| \int_{-\infty}^{\infty} f(t) e^{i\frac{E_k - E_i}{\hbar}t} dt \right|^2 \quad \text{where} \quad W_{ki} = \langle k \,|\, \hat{W} \,|\, i \rangle \tag{1.135}$$

We now introduce the Fourier transform of $f(t)$ with respect to energy:

$$F(E) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} f(t) e^{i\frac{E}{\hbar}t} dt \tag{1.136}$$

By inspection, we can write 1.135 in terms of $f(t)$'s Fourier transform:

$$\boxed{P_{i \to k} = \frac{2\pi}{\hbar} |W_{ki}|^2 |F(E_k - E_i)|^2} \tag{1.137}$$

By writing the probability in this way, we can gain a key piece of physical insight. A property of Fourier transforms is that the FWHM widths of $f(t)$ and $F(E)$, which we denote Δt and ΔE, are related by an uncertainty principle:

$$\Delta E \Delta t \approx \hbar \tag{1.138}$$

Since this gives the width of $F(E)$ as $\Delta E \approx \frac{\hbar}{\Delta t}$, only states for which $|E_k - E_i| < \frac{\hbar}{2\Delta t}$ lie within the FWHM range. These will be the states which will have a signficant probability of occupation.

Example (Sudden Perturbation): Suppose we again have a system in an initial state $|i\rangle$ at time $t = 0$, and a perturbation $\hat{W}$ is applied at $t = 0$ with a constant value that lasts forever. The transition

probability will thus be:

$$
\begin{aligned}
P_{i \to k}(t) &= \frac{|W_{ki}|^2}{\hbar^2} \left| \int_0^t e^{i \frac{E_k - E_i}{\hbar} t'} dt' \right|^2 \\
&= \frac{|W_{ki}|^2}{\hbar^2} \frac{\hbar^2}{|E_k - E_i|^2} \left| e^{i \frac{E_k - E_i}{\hbar} t} - 1 \right|^2 \\
&= \frac{|W_{ki}|^2}{\hbar^2} \frac{\hbar^2}{|E_k - E_i|^2} \left[2 - 2cos \left(\frac{E_k - E_i}{\hbar} t \right) \right] \\
&= \frac{|W_{ki}|^2}{\hbar^2} \frac{4\hbar^2}{|E_k - E_i|^2} sin^2 \left(\frac{E_k - E_i}{2\hbar} t \right) \\
&= \frac{|W_{ki}|^2}{\hbar^2} sinc^2 \left(\frac{E_k - E_i}{2\hbar} t \right) t^2 \quad (1.139)
\end{aligned}
$$

This is an interesting result that we've just derived. Some key points:

- If we take $t \to \infty$, the probability will go to zero **unless** $E_k = E_i$.

- Its width is approximately[21] $\Delta E \approx \frac{2\pi\hbar}{t}$, implying that only states of energy $E_i - \frac{\pi\hbar}{t} < E_k < E_i + \frac{\pi\hbar}{t}$ have a significant probability of occupation.

- The area A of the probability at a time t will be the product of its maximum value (at $E_k = E_i$) and its first zero (at $E_k - E_i = \pi\frac{2\hbar}{t}$) which gives[22]:

$$
A = \int_{-\infty}^{\infty} \frac{|W_{ki}|^2}{\hbar^2} sinc^2 \left(\frac{E}{2\hbar} t \right) t^2 dE = \frac{|W_{ki}|^2 t^2}{\hbar^2} \left(\pi \frac{2\hbar}{t} \right) = \frac{2\pi |W_{ki}|^2 t}{\hbar}
$$
$$(1.140)$$

Why did we write these parameters down? Notice that for large t, the transition probability goes to zero outside a small range of $E_k - E_i = 0$ and the width approaches zero. This is very reminiscent of a Dirac delta function, which prompts us to write:

$$
\boxed{\lim_{t \to \infty} P_{i \to k}(t) \approx \frac{2\pi |W_{ki}|^2 t}{\hbar} \delta(E_k - E_i)} \quad (1.141)
$$

which, because of the Dirac delta, is a function that only makes sense under an integral[23].

Example (Sinusoidal Perturbation): We consider yet again a system in an initial state $|i\rangle$ at time $t = 0$, except this time the perturbation has a sinusoidal time dependence:

$$
\hat{H}_1(t) = \hat{W} cos(\omega t + \varphi) = \frac{\hat{W}}{2} \left[e^{i(\omega t + \varphi)} + e^{-i(\omega t + \varphi)} \right] \quad (1.142)
$$

The transition probability will thus be[24]:

[21] We use the value $E_k - E_i = \pm \frac{2\hbar}{t} \frac{\pi}{2}$ as a rough estimate of the half-max locations

[22] We made the convenient variable substitution $E = E_k - E_i$

[23] A bit of second-order theory foreshadowing

[24] We substitute in the transition frequency $\omega_{ki} = \frac{E_k - E_i}{\hbar}$

$$P_{i \to k} = \frac{|W_{ki}|^2}{4\hbar^2} \left| \int_0^t \left(e^{i(\omega_{ki}+\omega)t'+i\varphi} + e^{i(\omega_{ki}-\omega)t'-i\varphi} \right) dt' \right|^2$$

$$= \frac{|W_{ki}|^2}{4\hbar^2} \left| \frac{e^{i(\omega_{ki}+\omega)t+i\varphi} - e^{i\varphi}}{i(\omega_{ki}+\omega)} + \frac{e^{i(\omega_{ki}-\omega)t-i\varphi} - e^{-i\varphi}}{i(\omega_{ki}-\omega)} \right|^2 \qquad (1.143)$$

At this point we could chug through the algebra and obtain a messy expression, but the result would be unilluminating. A better way would be to note that the transition probability is extremely small unless $|\omega_{ki} - \omega| \gg \omega$, a condition that is called **quasi-resonant excitation**. Under this condition, the denominator of the first bracket term remains large, but that of the second term becomes small[25]. We thus neglect the first term, an approximation known as the **rotating-wave approximation (RWA)**[26]. The probability thus becomes:

$$P_{i \to k} \approx \frac{|W_{ki}|^2}{4\hbar^2} \left| \frac{e^{i(\omega_{ki}-\omega)t-i\varphi} - e^{-i\varphi}}{i(\omega_{ki}-\omega)} \right|^2$$

$$= \frac{|W_{ki}|^2}{4\hbar^2} \left(\frac{2 - 2cos\left[(\omega_{ki}-\omega)t\right]}{(\omega_{ki}-\omega)^2} \right)$$

$$= \frac{|W_{ki}|^2}{4\hbar^2} sinc^2 \left(\frac{\omega_{ki}-\omega}{2}t \right) t^2$$

$$= \frac{|W_{ki}|^2}{4\hbar^2} sinc^2 \left(\frac{E_k - E_i - \hbar\omega}{2\hbar}t \right) t^2 \qquad (1.144)$$

Following the analysis of the previous example, we again find the parameters of this function:

- Only states with energy $E_i + \hbar\omega - \frac{\hbar\pi}{t} < E_k < E_i + \hbar\omega + \frac{\hbar\pi}{t}$ will have an appreciable population.

- The transition probability has an area:

$$A = \frac{2\hbar\pi}{t} \left(\frac{|W_{ki}|^2}{4\hbar^2}t^2 \right) = \frac{\pi|W_{ki}|^2 t}{2\hbar} \qquad (1.145)$$

For long interaction time t, the probability becomes a Dirac delta:

$$\boxed{\lim_{t \to \infty} P_{i \to k} \approx \frac{\pi|W_{ki}|^2 t}{2\hbar} \delta(E_k - E_i - \hbar\omega)} \qquad (1.146)$$

This is an unexpectedly elegant result. We see that the Dirac delta allows transitions only for which the energy level separation $E_k - E_i = \hbar\omega$, which implies that any change in the system's energy will occur by emission or absorption of an energy $\hbar\omega$[27].

[25] This is assuming $\omega_{ki} > 0$. For $\omega_{ki} < 0$, we would repeat the same following analysis except the second term would be neglected instead of the first.

[26] The name of the RWA originates from NMR, for which much of semi-classical theory was originally developed.

[27] After quantizing the fields, we will formally recognize this as a photon energy. Until then, you're not supposed to know what a photon is!

1.7 When is Second-Order Theory Necessary?

The most obvious situation in which we must go beyond first-order theory is when there is no **direct coupling** between the initial state $|i\rangle$ and another state $|k\rangle$, which means $W_{ki} = \langle k \,|\, \hat{H}_1(t) \,|\, i\rangle = 0$. In this situation, 1.133 tells us that there is zero probability of transitioning to state $|k\rangle$. However if there is a third state $|j\rangle$ which is coupled to $|k\rangle$, meaning $W_{jk} \neq 0$, the system should be able to transition to $|j\rangle$ and then to $|k\rangle$. This is behavior that first-order theory does not predict, so onward to second-order theory!

1.8 Second-Order Theory

Suppose we have the situation described above, in which $\langle k \,|\, \hat{H}_1(t) \,|\, i\rangle = 0$. The first-order coefficient therefore vanishes:

$$\gamma_k^{(1)}(t) = 0 \qquad (1.147)$$

Those for the other states $|j\rangle$ where $j \neq k$ are given by:

$$\gamma_j^{(1)}(t) = \frac{1}{i\hbar} \int_0^t \langle j \,|\, \hat{H}_1(t') \,|\, i\rangle \, e^{i\frac{E_j - E_i}{\hbar} t'} dt' \qquad (1.148)$$

We then plug 1.147 and 1.148 into the second-order equation 1.128c to solve for $\gamma_k^{(2)}(t)$:

$$\gamma_k^{(2)}(t) = \frac{1}{(i\hbar)^2} \int_0^t \sum_{j \neq i,k} \langle k \,|\, \hat{H}_1(t') \,|\, j\rangle \, e^{i\frac{E_k - E_j}{\hbar} t'} \int_0^{t'} \langle j \,|\, \hat{H}_1(t'') \,|\, i\rangle \, e^{i\frac{E_j - E_i}{\hbar} t''} dt'' dt'$$

$$(1.149)$$

where the limit of the summation means that we sum over all values of j not equal to k and i. We exclude k since[28] $\gamma_k^{(1)}(t) = 0$, and we exclude i since the first Bra-ket would become $\langle k \,|\, \hat{H}_1(t') \,|\, i\rangle = 0$.

[28] Physically, the term $j = i$ is equivalent to the state transitioning from $|i\rangle$ to $|i\rangle$, then to $|k\rangle$. This is obviously verboden, so we exclude it.

Example (Ramp Process): We again model the perturbation as $\hat{H}_1(t) = \hat{W} f(t)$, which we examined in an earlier example. However, this time we consider $f(t)$ as a ramp function which increases from 0 to 1 over a time period θ. For convenience, we assign $t = 0$ according to $f(0) = \frac{1}{2}$. To make the calculation simple, we also assume the following[29]:

$$t \gg \theta \gg \frac{1}{|\omega_{ij}|} \qquad (1.150)$$

[29] Remember $\frac{1}{\omega_{ij}} = \frac{\hbar}{E_i - E_j}$, and can be thought of loosely as the characteristic transition time between levels $|i\rangle$ and $|j\rangle$

The physical interpretation of this condition is that we consider times long after the perturbation occurred, and that the transition time $\frac{1}{|\omega_{ij}|}$ is much shorter than all the other time-scales in the problem.

Plugging this perturbation $\hat{H}_1(t) = \hat{W}f(t)$ into 1.149, and integrate starting from a time $t = t_0$ which is before the ramp occurs[30]:

$$\gamma_k^{(2)}(t) = \frac{1}{(i\hbar)^2} \sum_{j \neq i,k} W_{kj} W_{ji} \int_{t_0}^{t} f(t') e^{i\frac{E_k - E_j}{\hbar}t'} \int_{t_0}^{t'} f(t'') e^{i\frac{E_j - E_i}{\hbar}t''} dt'' dt'$$

(1.151)

We first do the inside integral over t'' by parts[31]:

$$\int_{t_0}^{t'} f(t'') e^{i\frac{E_j - E_i}{\hbar}t''} dt'' = \frac{\hbar}{i(E_j - E_i)} \left[e^{i\frac{E_j - E_i}{\hbar}t'} f(t') - \int_{t_0}^{t'} e^{i\frac{E_j - E_i}{\hbar}t''} f'(t'') dt'' \right]$$

(1.152)

Since the second term in the brackets is much smaller than the first[32], we keep only the first term to find:

$$\gamma_k^{(2)}(t) = -\frac{1}{i\hbar} \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \int_{t_0}^{t} e^{i\frac{E_k - E_i}{\hbar}t'} \left(f(t') \right)^2 dt'$$

$$\approx -\frac{1}{i\hbar} \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \int_{0}^{t} e^{i\frac{E_k - E_i}{\hbar}t'} dt'$$

$$= -\frac{1}{i\hbar} \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \frac{\hbar}{i(E_k - E_i)} \left(e^{i\frac{E_k - E_i}{\hbar}t} - 1 \right)$$

(1.153)

where the approximations $(f(t'))^2 \approx 1$ and $t_0 \approx 0$ in the second line are made since we are considering times t long after the ramp occurs (see 1.150), so the bulk contribution of the integral occurs for $t > 0$. The transition probability is thus:

$$P_{i \to k} = |\gamma_k^{(2)}(t)|^2$$

$$= \frac{1}{\hbar^2} \left| \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \right|^2 \left(\frac{\hbar}{E_k - E_i} \right)^2 \left[2 - 2\cos\left(\frac{E_k - E_i}{\hbar}t \right) \right]$$

$$= \frac{1}{\hbar^2} \left| \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \right|^2 \left(\frac{\hbar}{E_k - E_i} \right)^2 4\sin^2\left(\frac{E_k - E_i}{2\hbar}t \right)$$

$$= \frac{1}{\hbar^2} \left| \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \right|^2 \text{sinc}^2\left(\frac{E_k - E_i}{2\hbar}t \right) t^2$$

$$\approx \left| \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \right|^2 \frac{2\pi}{\hbar} \delta(E_k - E_i) t$$

(1.154)

where the delta function approximation occurred naturally since we considered times long after the ramp from the beginning (see 1.150). This is suspiciously similar to the sudden perturbation result 1.141 derived from first-order theory[33]. We can cast it in the same form by defining an effective perturbation W_{ki}^{eff}:

$$\boxed{P_{i \to k} \approx \frac{2\pi W_{ki}^{eff} t}{\hbar} \delta(E_k - E_i)} \quad \text{where} \quad W_{ki}^{eff} = \left| \sum_{j \neq i,k} \frac{W_{kj} W_{ji}}{E_j - E_i} \right|^2$$

(1.155)

[30] We switch the order of the summation and integration, which is generally kosher in physics. If this bothers you, you should be a mathematician.

[31] Remember $f(t_0) = 0$, since its before the ramp occurred.

[32] If you want to prove this, integrate the second term by parts as well. You will obtain one term which is smaller than the first bracket term by a factor of $\frac{\hbar f'(t'')}{i(E_j - E_i)}$, and another integral proportional to $f''(t'')$, which will be close to zero for all time.

[33] Unsurprising, since the ramp function looks like a step function for time t long after the ramp.

This effective perturbation[34] W_{ki}^{eff} captures the physical reasoning we stated in the previous section - it sums over all other paths to state $|k\rangle$ that use a third level $|j\rangle$ as an intermediate state. Of course, there are other paths that involve two, three, or even more intermediate states which can be accounted for in higher order terms $\gamma_k^{(3)}(t), \gamma_k^{(4)}(t)$, and so on[35].

[34] We will also show later that a perturbation $\hat{H}_1(t)$ will shift the energy levels E_i of a system according to the effective perturbation: $\Delta E_i = W_{ii}^{eff} = \left| \sum_{j \neq i} \frac{W_{ij} W_{ji}}{E_j - E_i} \right|^2$

[35] These tend to have a small effect on the system dynamics though, so second-order is generally enough.

Coupling To A Continuum

At this point, it seems like the machinery we've developed allows us to calculate any perturbation effect. By knowing the eigenstates of the stationary Hamiltonian $\hat{H}_0$, we simply calculate the matrix elements of $\hat{H}_1(t)$ in the eigenstate basis and plug into 1.128b for the first order correction (and if needed use 1.128c to also find the second order corrections) to find that the perturbation induces transitions between different eigenstates of the system. However, if real systems behaved this way - by simply transitioning back and forth between eigenstates/eigenenergies - physics would be quite boring. For a start, chemical reactions would be impossible since this model implies that electrons are forbidden from leaving their parent nucleus.

To account for such irreversible processes, we introduce the idea of a **continuum**, which is, as the name implies, a set of states with a continuous range of energies. Since such states cannot be normalized, it is easier to begin with a so-called **quasi-continuum**, which is a set of discrete set of states with very closely spaced energies. After solving the quasi-continuum problem, it will be straightforward to adjust the results for a true continuum.

How would we represent a quasi-continuum mathematically? The best example is the canonical particle of mass m in an in an infinite square well of width L, in which the energies of each eigenstate $|n\rangle$ are given by:

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \quad \text{where} \quad n = 0, 1, \ldots \tag{2.1}$$

The separation between energy levels E_n and E_{n+1} are given by:

$$\Delta E = \frac{\hbar^2 \pi^2}{mL^2} n \tag{2.2}$$

We see that the energy spacing depends inversely on the well width L, so as the width goes to infinity the energy spacing goes to zero and we obtain a continuum. There are strict limitations on solving problems this way however, which we will discuss after the calculation.

2.1 1 Discrete Level and Continuum (perturbative soln.)

Suppose we have a Hamiltonian $\hat{H}_0$ whos eigenstates are a single discrete state $|i\rangle$ with energy $E_i = 0$ that the system starts out in, and a quasi-continuum of states $|k\rangle$ due to a infinite square well. For simplicity, we assume that the well is modified in some way[36] so that the energies are equally spaced and defined by:

$$E_k = \epsilon k \quad \text{and} \quad \Delta E = \epsilon, \quad \text{where} \quad k = -\infty \ldots \infty \qquad (2.3)$$

where we relate the energy spacing and well width according to 2.2:

$$\epsilon \propto \frac{1}{L^2} \qquad (2.4)$$

This dependence on L will be critical when connecting our result for a quasi-continuum to that of a real continuum. We then assume a constant perturbation $\hat{H}_1(t) = \hat{W}$, with coupling matrix elements:

$$W_{ki} = \langle k\,|\,\hat{W}\,|\,i\rangle = w \quad \text{and} \quad \langle k\,|\,\hat{W}\,|\,k'\rangle = \langle i\,|\,\hat{W}\,|\,i\rangle = 0 \qquad (2.5)$$

This means that the system can transition from the discrete state $|i\rangle$ to any quasi-continuum state $|k\rangle$, but may not transition between different quasi-continuum states $|k\rangle$ and $|k'\rangle$. We also assume w is real, which means $\langle i\,|\,\hat{W}\,|\,k\rangle = w$ as well. Recall the transition probability for a constant perturbation found in 1.139 (for $E_i = 0$ and $W_{ki} = w$):

$$P_{i \to k}(t) = \frac{w^2}{\hbar^2} sinc^2\left(\frac{E_k}{2\hbar}t\right) t^2 \qquad (2.6)$$

We would now like to find the probability that the system will be in $|i\rangle$ at a time t. This will be given by 100% minus the probability of the system transitioning from $|i\rangle$, which will be the sum of $P_{i \to k}$ for every individual $|k\rangle$:

$$P_i(t) = 1 - \sum_{k=-\infty}^{\infty} P_{i \to k}(t)$$

$$= 1 - \sum_{k=-\infty}^{\infty} \frac{w^2}{\hbar^2} sinc^2\left(\frac{E_k}{2\hbar}t\right) t^2 \qquad (2.7)$$

If we take[37] the energy separation ϵ to be small compared to the *sinc* function width $\frac{2\pi\hbar}{t}$, the *sinc* function will vary slowly with respect to k. This allows us to convert the summation into an integral[38], which we've already solved (see 1.140):

$$P_i(t) = 1 - \int \frac{w^2}{\hbar^2} sinc^2\left(\frac{E_k}{2\hbar}t\right) t^2 dk$$

$$= 1 - \frac{1}{\epsilon} \int \frac{w^2}{\hbar^2} sinc^2\left(\frac{E_k}{2\hbar}t\right) t^2 dE_k$$

$$= 1 - \frac{2\pi w^2}{\hbar\epsilon}t \qquad (2.8)$$

[36] Notice that the walls of the well are still at infinite potential though, so the wavefunction amplitudes inside the well must still obey the normalization condition $\psi \propto \frac{1}{\sqrt{L}}$

[37] Recall that $\epsilon \propto \frac{1}{L}$, so we can make the well width L, which is arbitrary at this point, to be as large as we need.

[38] We use $E_k = \epsilon k \to dk = \frac{1}{\epsilon}dE_k$.

We can write this in terms of a departure probability per unit time Γ:

$$\boxed{P_i(t) = 1 - \Gamma t} \quad \text{where} \quad \Gamma = \frac{2\pi w^2}{\hbar \epsilon} \tag{2.9}$$

Where does the well-width show up in Γ? The matrix element w is proportional[39] to $\frac{1}{L}$, and the energy spacing ϵ is proportional to $\frac{1}{L^2}$. We thus find that Γ is independent of L, so we can take $L \to \infty$ and our result doesn't change. By solving the quasi-continuum problem, we have therefore inadvertently solved the true continuum problem as well! Unfortunately the result we have derived tells us that, for $t > \frac{1}{\Gamma}$, we will obtain a negative occupation probability for $|i\rangle$. This unphysical result means that our result is valid for only short times t, specifically:

$$\text{Condition 1:} \quad t \ll \frac{1}{\Gamma} \tag{2.10}$$

There is also a second condition for our result to be valid, which allowed us to convert the sum to an integral:

$$\text{Condition 2:} \quad \epsilon \ll \frac{2\pi\hbar}{t} \to t \ll \frac{2\pi\hbar}{\epsilon} \tag{2.11}$$

Another important point is that real continuums will not extend over an infinite range of energies, as E_k does, but instead over a finite range Δ. This energy range must be much wider than the *sinc* function width $\frac{2\pi\hbar}{t}$ in 2.8, or else the integral will be "clipped" and the departure probability will be less than Γ. This condition can be written as:

$$\text{Condition 3:} \quad \Delta \gg \frac{2\pi\hbar}{t} \tag{2.12}$$

We will examine this situation in a later example.

2.2 1 Discrete Level and Continuum (non-perturbative soln.)

There are, of course, situations in which we would like to examine the system after long periods of time $t > \frac{1}{\Gamma}$. In 1930, Victor Weisskopf and Eugene Wigner developed a non-perturbative method to do just that[40], of which we use a simplified version.

We write the wave function in terms of their associated coefficients:

$$|\psi(t)\rangle = \gamma_i(t)\,|i\rangle + \sum_{k=-\infty}^{\infty} \gamma_k(t) e^{-i\frac{\epsilon k}{\hbar}t}\,|k\rangle \tag{2.13}$$

Recalling the matrix elements $W_{ki} = W_{ik} = w$ and $W_{kk'} = W_{ii} = 0$, we use 1.125 to write two equations:

$$i\hbar \frac{d}{dt}\gamma_k(t) = w e^{i\frac{E_k}{\hbar}t}\gamma_i(t) \tag{2.14}$$

$$i\hbar \frac{d}{dt}\gamma_i(t) = \sum_{k=-\infty}^{\infty} w e^{-i\frac{E_k}{\hbar}t}\gamma_k(t) \tag{2.15}$$

[39] The Bra-ket makes w proportional to the wavefunction squared. The wavefunctions themselves are proportional to $\frac{1}{\sqrt{L}}$.

[40] See *Berechnung der natÃijrlichen Linienbreite auf Grund der Diracschen Lichttheorie*. Zeitschrift für Physik **63**, 1, (1930). Hopefully you read German!

We can solve the first equation by simple integration[41]:

$$\gamma_k(t) = \frac{w}{i\hbar} \int_0^t \gamma_i(t') e^{i\frac{E_k}{\hbar}t'} dt' \tag{2.16}$$

[41] Remember $\gamma_k(0) = 0$ since the system is initially in state $|i\rangle$

Plugging 2.16 into 2.15, and converting the summation to an integral[42]:

[42] Assuming the energy spacing ϵ is small compared to $\frac{\hbar}{t}$.

$$
\begin{aligned}
\frac{d}{dt}\gamma_i(t) &= -\frac{w^2}{\hbar^2} \sum_{k=-\infty}^{\infty} e^{-i\frac{E_k}{\hbar}t} \int_0^t \gamma_i(t') e^{i\frac{E_k}{\hbar}t'} dt' \\
&= -\frac{\Gamma}{2\pi\hbar} \int_0^t \gamma_i(t') \left[\sum_{k=-\infty}^{\infty} \epsilon e^{i\frac{E_k}{\hbar}(t'-t)} \right] dt' \\
&= -\frac{\Gamma}{2\pi\hbar} \int_0^t \gamma_i(t') \left[\int_{-\infty}^{\infty} \epsilon e^{i\frac{E_k}{\hbar}(t'-t)} dk \right] dt' \\
&= -\frac{\Gamma}{2\pi\hbar} \int_0^t \gamma_i(t') \left[\int_{-\infty}^{\infty} e^{i\frac{E_k}{\hbar}(t'-t)} dE_k \right] dt' \\
&= -\frac{\Gamma}{2\pi\hbar} \int_0^t \gamma_i(t') 2\pi\hbar\delta(t'-t) dt' \\
&= -\Gamma \int_{-t}^0 \gamma_i(t+\tau)\delta(\tau) d\tau \\
&= -\frac{\Gamma}{2}\gamma_i(t) \tag{2.17}
\end{aligned}
$$

where in the last two lines we made the substitution $\tau = t' - t$) and used the result[43] $\int_{-a}^0 \delta(t)dt = \frac{1}{2}\int_{-a}^a \delta(t)dt = \frac{1}{2}$. 2.17 is as straightforward a differential equation as it gets, so we find:

$$\gamma_i(t) = e^{-\frac{\Gamma}{2}t} \tag{2.18}$$

which gives the occupation probability of $|i\rangle$:

$$\boxed{P_i(t) = |\gamma_i(t)|^2 = e^{-\Gamma t}} \tag{2.19}$$

[43] Usually, when the delta function is constructed (such as by a $sinc^2$ function in previous examples) it is defined as an even function centered around zero. If the total integral is equal to unity, then it makes sense intuitively that integrating only up to zero would equal $\frac{1}{2}$. This is not a mathematically rigorous explanation however, so one must look elsewhere for a more kosher derivation.

Also, if we expand 2.18 as a Taylor series:

$$P_i(t) = 1 + (-\Gamma t) + \frac{(-\Gamma t)^2}{2!} + \frac{(-\Gamma t)^3}{3!} + \dots \tag{2.20}$$

the first two terms give us $P_i(t) \approx 1 - \Gamma t$, which is exactly the short-time occupation probability found in 2.9.

We can then substitute 2.18 into 2.14 to find the coefficients for $|k\rangle$:

$$
\begin{aligned}
\gamma_k(t) &= \frac{w}{i\hbar} \frac{e^{\left(i\frac{E_k}{\hbar} - \frac{\Gamma}{2}\right)t} - 1}{i\frac{E_k}{\hbar} - \frac{\Gamma}{2}} \\
&= w \frac{1 - e^{\left(i\frac{E_k}{\hbar} - \frac{\Gamma}{2}\right)t}}{E_k + i\frac{\hbar\Gamma}{2}} \tag{2.21}
\end{aligned}
$$

Which gives the occupation probability for each state $|k\rangle$:

$$P_k(t) = |\gamma_k(t)|^2 = \frac{w^2}{E_k^2 + \left(\frac{\hbar\Gamma}{2}\right)^2}\left[1 + e^{-\Gamma t}\left(1 - 2cos\left(\frac{E_k}{\hbar}\right)\right)\right] \quad (2.22)$$

It's interesting to look at the long-time behavior as well:

$$\lim_{t\to\infty} P_k(t) = \frac{w^2}{E_k^2 + \left(\frac{\hbar\Gamma}{2}\right)^2} \quad (2.23)$$

We thus see that for $t \to \infty$, the occupation probability for $|i\rangle$ goes to zero while the probability distribution for $|k\rangle$ is a Lorentzian distribution with $FWHM = \hbar\Gamma$.

2.3   1 Discrete Level and Continuum With Varied Coupling

Consider the same situation described in the previous 2 sections, with a discrete level coupled to a continuum of states $|k\rangle$ with equally separated energies $E_k = \epsilon k$. This time however, the matrix elements are given by:

$$W_{ki} = w_k = \frac{w}{\sqrt{1 + \left(\frac{E_k}{\Delta}\right)^2}} \quad \text{and} \quad W_{kk'} = W_{ii} = 0 \quad (2.24)$$

The coupling between $|i\rangle$ and the continuum $|k\rangle$ is thus a Lorentzian, so the continuum has[44] an "effective width" Δ.

We begin with the same equations used in the constant coupling solution, 2.14 and 2.15, with the only difference in the problems being $w \to w_k$:

$$i\hbar\frac{d}{dt}\gamma_k(t) = w_k e^{i\frac{E_k}{\hbar}t}\gamma_i(t) \quad (2.25)$$

$$i\hbar\frac{d}{dt}\gamma_i(t) = \sum_{k=-\infty}^{\infty} w_k e^{-i\frac{E_k}{\hbar}t}\gamma_k(t) \quad (2.26)$$

Integrating the first equation:

$$\gamma_k(t) = \int_0^t \frac{w_k}{i\hbar}e^{i\frac{E_k}{\hbar}t'}\gamma_i(t')dt' \quad (2.27)$$

We plug 2.27 into 2.26 to find:

$$\frac{d}{dt}\gamma_i(t) = -\int_0^t \gamma_i(t')\left[\sum_{k=-\infty}^{\infty} \frac{w_k^2}{\hbar}e^{i\frac{E_k}{\hbar}(t'-t)}\right]dt' \quad (2.28)$$

Again assuming the energy spacing ϵ is small compared to $\frac{\hbar}{t}$, we can convert the summation inside the brackets to an integral and evaluate[45]:

[44] By effective width, we mean that states $|k\rangle$ outside the FWHM width Δ are weakly coupled to $|i\rangle$ and thus have a decreasing probability of transition. Roughly, the states inside the FWHM width are those that result in the non-negligible transitions.

[45] Remember how to contour integrate?

$$\sum_{k=-\infty}^{\infty} \frac{w_k^2}{\hbar} e^{i\frac{E_k}{\hbar}(t'-t)} = \int_{-\infty}^{\infty} \frac{w^2}{\epsilon\hbar^2} \frac{e^{i\frac{E_k}{\hbar}(t-t')}}{1+\left(\frac{E}{\Delta}\right)^2} dE$$

$$= \frac{\pi w^2 \Delta}{\epsilon\hbar^2} e^{-\frac{\Delta}{\hbar}|t'-t|} \tag{2.29}$$

Substituting 2.29 into 2.28, we find:

$$\frac{d}{dt}\gamma_i(t) = -\frac{\Gamma\Delta}{2\hbar} \int_0^t \gamma_i(t') e^{\frac{\Delta}{\hbar}(t'-t)} dt' \tag{2.30}$$

Recalling the rule for differentiation under the integral sign[46]:

$$\frac{d}{dx}\int_{a(x)}^{b(x)} f(x,t)dt = f(x,b(x))b'(x) - f(x,a(x))a'(x) + \int_{a(x)}^{b(x)} \frac{\partial}{\partial x} f(x,t)dt \tag{2.31}$$

2.30 may be recast elegantly by taking the derivative of both sides:

$$\frac{d^2}{dt^2}\gamma_i(t) = -\frac{\Gamma\Delta}{2\hbar} \frac{d}{dt} \int_0^t \gamma_i(t') e^{\frac{\Delta}{\hbar}(t'-t)} dt'$$

$$= -\frac{\Gamma\Delta}{2\hbar}\left[\gamma_i(t) - \frac{\Delta}{\hbar}\int_0^t \gamma_i(t') e^{\frac{\Delta}{\hbar}(t'-t)} dt'\right]$$

$$= -\frac{\Gamma\Delta}{2\hbar}\left[\gamma_i(t) + \frac{2}{\Gamma}\frac{d}{dt}\gamma_i(t)\right] \tag{2.32}$$

This is now an ordinary differential equation for $\gamma_i(t)$, which we can solve straightforwardly:

$$\gamma_i(t) = e^{\frac{\Delta}{2\Gamma}t}\left(c_1 e^{rt} + c_2 e^{-rt}\right) \quad \text{where} \quad r = \sqrt{\left(\frac{\Delta}{2\Gamma}\right)^2 - \frac{\Gamma\Delta}{2\hbar}} \tag{2.33}$$

[46] For more details, see Wikipedia.

Two-Level Systems

3.1 Coupling to a Stochastic Bath

Consider a two-level system with a Hamiltonian split into a stationary part $\hat{H}_0$ and a time-dependent perturbation $\hat{H}_1(t)$:

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t) \tag{3.1}$$

where the stationary Hamiltonian is the standard two levels with energies $E = 0$ and $E = E_0$:

$$\hat{H}_0 = E_0 \left|1\right\rangle \left\langle1\right| \tag{3.2}$$

and we assume a bilinear coupling of the form:

$$\begin{aligned}
\hat{H}_1(t) &= H_{11}(t) \left|1\right\rangle \left\langle1\right| + H_{01}(t) \left|0\right\rangle \left\langle1\right| + H_{10}(t) \left|1\right\rangle \left\langle0\right| \\
&= \hbar\Delta(t) \left|1\right\rangle \left\langle1\right| + \hbar\Lambda(t) \left|1\right\rangle \left\langle0\right| + \hbar\Lambda^*(t) \left|0\right\rangle \left\langle1\right|
\end{aligned} \tag{3.3}$$

where we've defined the stochastic processes:

$$\Delta(t) = \frac{1}{\hbar} H_{11}(t) \tag{3.4}$$

$$\Lambda(t) = \frac{1}{\hbar} H_{10}(t) \tag{3.5}$$

$$\Lambda^*(t) = \frac{1}{\hbar} H_{01}(t) \tag{3.6}$$

Field-Particle Perturbation

We now discuss arguably the most important perturbation: that from an applied field. The simplest system one could consider is a single particle, which can be perturbed by electric and magnetic fields $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$.

4.1   Potentials

As a review, from electromagnetics we know that these fields can be represented through vector and scalar potentials $\mathbf{A}(\mathbf{r}, t)$ and $\varphi(\mathbf{r}, t)$ respectively by:

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \tag{4.1}$$

$$\mathbf{E}(\mathbf{r}, t) = -\frac{\partial}{\partial t}\mathbf{A}(\mathbf{r}, t) - \nabla \varphi(\mathbf{r}, t) \tag{4.2}$$

These potentials $\mathbf{A}(\mathbf{r}, t)$ and $\varphi(\mathbf{r}, t)$ come in pairs[47], which are related by an arbitrary scalar function $F(\mathbf{r}, t)$:

$$\mathbf{A}'(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \nabla F(\mathbf{r}, t) \tag{4.3}$$

$$\varphi'(\mathbf{r}, t) = \varphi(\mathbf{r}, t) - \frac{\partial}{\partial t}F(\mathbf{r}, t) \tag{4.4}$$

[47] There is an infinite number of these pairs, since there is an infinite number of functions $F(\mathbf{r}, t)$ they could be related by. Each of these pairs will give the same identical field.

These relations between pairs $\{\mathbf{A}(\mathbf{r}, t), \varphi(\mathbf{r}, t)\}, \{\mathbf{A}'(\mathbf{r}, t), \varphi'(\mathbf{r}, t)\} \dots$ are called **gauge transformations**. Some pairs will be more convenient than others in certain problems, so to specify which pair to use we impose an artificial constraint called a **gauge condition**. There are two gauge conditions that are commonly used in atomic physics - the Coulomb gauge and Göppert Mayer gauge. We will discuss them in the following sections.

4.2   Field-Particle Hamiltonian

We present from the outset, the atom-field Hamiltonian for a single particle of mass m and charge q:

$$\hat{H} = \frac{1}{2m}\left(\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}}, t)\right)^2 + q\varphi(\hat{\mathbf{r}}, t) \tag{4.5}$$

There are two ways to justify this Hamiltonian:

1. A practical approach, where it is simply shown that this Hamiltonian recovers the correct equation of motion that we would expect from the classical Lorentz force.

2. A more rigorous approach, where the Hamiltonian is constructed from the particle-field Lagrangian.

We shall take the first approach for now, and take the second after quantizing the field in a later chapter.

4.3 Justification of the Field-Particle Hamiltonian

We first recall the generalized Ehrenfest's theorem[48] for an arbitrary operator $\hat{A}$:

$$\frac{d}{dt}\langle \hat{A}\rangle = \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle + \left\langle\frac{\partial}{\partial t}\hat{A}\right\rangle \tag{4.6}$$

For convenience, we will calculate the commutator of $\hat{x}$ and $\hat{H}$ (we drop the $\hat{\mathbf{r}}$ and t dependences of $\mathbf{A}(\hat{\mathbf{r}},t)$ and $\varphi(\hat{\mathbf{r}},t)$ for brevity):

$$\begin{aligned}
[\hat{x},\hat{H}] &= \hat{x}\left(\frac{(\hat{\mathbf{p}}-q\mathbf{A})^2}{2m}+q\varphi\right)-\left(\frac{(\hat{\mathbf{p}}-q\mathbf{A})^2}{2m}+q\varphi\right)\hat{x} \\
&= \hat{x}\frac{(\hat{\mathbf{p}}-q\mathbf{A})^2}{2m}-\frac{(\hat{\mathbf{p}}-q\mathbf{A})^2}{2m}\hat{x} \\
&= \frac{1}{2m}\left\{\hat{x}\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\left(\hat{\mathbf{p}}-q\mathbf{A}\right)-\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\hat{x}\right\} \\
&= \frac{1}{2m}\left\{\left(\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\hat{x}-[\hat{\mathbf{p}}-q\mathbf{A},\hat{x}]\right)\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\right. \\
&\quad \left.-\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\left(\hat{x}\left(\hat{\mathbf{p}}-q\mathbf{A}\right)+[\hat{\mathbf{p}}-q\mathbf{A},\hat{x}]\right)\right\} \\
&= \frac{1}{2m}\left\{2i\hbar\left(\hat{\mathbf{p}}-q\mathbf{A}\right)+\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\hat{x}\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\right. \\
&\quad \left.-\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\hat{x}\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\right\} \\
&= \frac{i\hbar}{m}\left(\hat{\mathbf{p}}-q\mathbf{A}\right) \tag{4.7}
\end{aligned}$$

In this lengthy derivation, the following relations were used:

- The scalar potential $\varphi(\mathbf{r},t)$ is only a function of position[49], so it commutes with $\hat{x}$.

- Since $\mathbf{A}(\hat{\mathbf{r}},t)$ is also only a function of position, it drops out of the following commutator: $[\hat{\mathbf{p}}-q\mathbf{A},\hat{x}]=[\hat{\mathbf{p}},\hat{x}]=[p_x,\hat{x}]=-i\hbar$

The time derivative of the x position operator, the x component velocity, can thus be found by 4.6 and 4.7:

$$\begin{aligned}
\frac{d}{dt}\langle\hat{x}\rangle = \hat{v}_x &= \frac{1}{i\hbar}\langle[\hat{x},\hat{H}]\rangle+\left\langle\frac{\partial}{\partial t}\hat{x}\right\rangle \\
&= \frac{\hat{\mathbf{p}}-q\mathbf{A}}{m} \tag{4.8}
\end{aligned}$$

[48] Paul Ehrenfest derived the specific relation between the position/momentum operators and their derivatives. Werner Heisenberg was actually the one who derived the general general relation for any operator's time derivative.

[49] We leave out time, since there is no associated operator for t.

The same procedure can be used to find $\hat{v}_y$ and $\hat{v}_z$, so we can generalize 4.8 for the vector $\hat{\mathbf{v}}$:

$$\hat{\mathbf{v}} = \frac{\hat{\mathbf{p}} - q\mathbf{A}}{m} \tag{4.9}$$

The Hamiltonian can thus be written in terms of $\hat{\mathbf{v}}$:

$$\hat{H} = \frac{1}{2}m\hat{\mathbf{v}}^2 + q\varphi \tag{4.10}$$

which is exactly what we would expect from our classical intuition.

Although the clues are all there, we now go further and derive the Lorentz force equation of motion in operator form. To do so, we first need the commutation relations between the velocity components[50]:

[50] Note that the different components of $\mathbf{A}$ commute, since they are all functions of only position.

$$\begin{aligned}
[\hat{v}_x, \hat{v}_y] &= \frac{1}{m^2}\left[(p_x - qA_x)(p_y - qA_y) - (p_y - qA_y)(p_x - qA_x)\right] \\
&= \frac{q}{m^2}\left([A_y, p_x] + [A_x, p_y]\right) \\
&= i\hbar\frac{q}{m^2}\left(\frac{\partial A_y}{\partial x} + \frac{\partial A_x}{\partial y}\right) \\
&= i\hbar\frac{q}{m^2}B_z(\hat{\mathbf{r}}, t) \tag{4.11}
\end{aligned}$$

and by the same reasoning:

$$[\hat{v}_y, \hat{v}_z] = i\hbar\frac{q}{m^2}B_x(\hat{\mathbf{r}}, t) \tag{4.12}$$

$$[\hat{v}_z, \hat{v}_x] = i\hbar\frac{q}{m^2}B_y(\hat{\mathbf{r}}, t) \tag{4.13}$$

Our next step is to write the equation of motion for $\hat{\mathbf{v}}$ using Ehrenfest's theorem. In anticipation of this calculation, we have a few quantities to calculate beforehand:

$$\frac{\partial}{\partial t}\hat{v}_x = -\frac{q}{m}\frac{\partial A_x}{\partial t} \tag{4.14}$$

$$[\hat{v}_x, \varphi] = \frac{1}{m}[p_x, \varphi] = -\frac{i\hbar}{m}\frac{\partial\varphi}{\partial x} \tag{4.15}$$

$$\begin{aligned}
[\hat{v}_x, \hat{H}] &= \left[\hat{v}_x, \frac{1}{2}m\hat{\mathbf{v}}^2 + q\varphi\right] \\
&= \frac{m}{2}\left(\left[\hat{v}_x, \hat{v}_y^2\right] + \left[\hat{v}_x, \hat{v}_z^2\right]\right) + q[\hat{v}_x, \varphi] \\
&= \frac{m}{2}\left\{\left([\hat{v}_x, \hat{v}_y] + \hat{v}_y\hat{v}_x\right)\hat{v}_y - \hat{v}_y\left(\hat{v}_x\hat{v}_y - [\hat{v}_x, \hat{v}_y]\right)\right. \\
&\quad \left. + \left([\hat{v}_x, \hat{v}_z] + \hat{v}_z\hat{v}_x\right)\hat{v}_z - \hat{v}_z\left(\hat{v}_x\hat{v}_z - [\hat{v}_x, \hat{v}_z]\right)\right\} - \frac{i\hbar q}{m}\frac{\partial\varphi}{\partial x} \\
&= \frac{m}{2}\left([\hat{v}_x, \hat{v}_y]\hat{v}_y + \hat{v}_y[\hat{v}_x, \hat{v}_y] + [\hat{v}_x, \hat{v}_z]\hat{v}_z + \hat{v}_z[\hat{v}_x, \hat{v}_z]\right) - \frac{i\hbar q}{m}\frac{\partial\varphi}{\partial x} \\
&= \frac{i\hbar q}{2m}\left(B_z\hat{v}_y + \hat{v}_yB_z - B_y\hat{v}_z - \hat{v}_zB_y\right) - \frac{i\hbar q}{m}\frac{\partial\varphi}{\partial x} \tag{4.16}
\end{aligned}$$

We now use 4.6, 4.14, and 4.15 to find:

$$\frac{d}{dt}\langle \hat{v}_x \rangle = \frac{1}{i\hbar}\left\langle [\hat{v}_x, \hat{H}] \right\rangle + \left\langle \frac{\partial}{\partial t}\hat{v}_x \right\rangle$$

$$= \frac{q}{2m}\left\langle B_z\hat{v}_y + \hat{v}_yB_z - B_y\hat{v}_z - \hat{v}_zB_y \right\rangle - \frac{q}{m}\left\langle \frac{\partial \varphi}{\partial x} + \frac{\partial A_x}{\partial t} \right\rangle \quad (4.17)$$

By the same reasoning:

$$\frac{d}{dt}\langle \hat{v}_y \rangle = \frac{q}{2m}\left\langle B_x\hat{v}_z + \hat{v}_zB_x - B_z\hat{v}_x - \hat{v}_xB_z \right\rangle - \frac{q}{m}\left\langle \frac{\partial \varphi}{\partial y} + \frac{\partial A_y}{\partial t} \right\rangle \quad (4.18)$$

$$\frac{d}{dt}\langle \hat{v}_z \rangle = \frac{q}{2m}\left\langle \hat{v}_xB_y + B_y\hat{v}_x - \hat{v}_yB_x - B_x\hat{v}_y \right\rangle - \frac{q}{m}\left\langle \frac{\partial \varphi}{\partial z} + \frac{\partial A_z}{\partial t} \right\rangle \quad (4.19)$$

By inspection, we can combine 4.17, 4.18, and 4.19 into a single vector equation:

$$m\frac{d}{dt}\langle \hat{\mathbf{v}} \rangle = q\left\langle \frac{\hat{\mathbf{v}}\times\mathbf{B}(\hat{\mathbf{r}},t) - \mathbf{B}(\hat{\mathbf{r}},t)\times\hat{\mathbf{v}}}{2} \right\rangle + q\left\langle \mathbf{E}(\hat{\mathbf{r}},t) \right\rangle$$

$$= q\left\langle \hat{\mathbf{v}}\times\mathbf{B}(\hat{\mathbf{r}},t) \right\rangle + q\left\langle \mathbf{E}(\hat{\mathbf{r}},t) \right\rangle \quad (4.20)$$

We have thus derived from the Field-Particle Hamiltonian the operator form of the Lorentz force equation of motion. Though not a rigorous proof of the validity of 4.5, it is hopefully compelling enough to make the results obtained by using this Hamiltonian seem plausible.