1. Basis Wavefunctions for the Two-Level System

- The Schrödinger Wave Equation (SWE) is given by

\[ i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} = H_{op} \Psi(\vec{r},t) \]

where the Hamiltonian operator is the sum of a time-independent term \( H_0 \) which gives the energy levels in the absence of an external field, and a time-dependent interaction term \( V(t) \) which accounts for the electric dipole interaction of the electron with the external laser field.

\[ H_{op} = H_0 + V(t) \]

- The wavefunction for the system is expressed as the linear superposition of basis wavefunctions \( \psi_1(\vec{r}) \) and \( \psi_2(\vec{r}) \),

\[ \Psi(\vec{r},t) = c_1(t) \psi_1(\vec{r}) + c_2(t) \psi_2(\vec{r}) \]

- The basis wavefunctions \( \psi_1(\vec{r}) \) and \( \psi_2(\vec{r}) \) are eigenfunction solutions of the time-independent SWE in the absence of an external field. Operating with \( H_0 \) on the normalized wavefunctions \( \Psi_1(\vec{r},t) \) and \( \Psi_2(\vec{r},t) \) gives the level energy,

\[ H_0 \Psi_1(\vec{r},t) = \epsilon_1 \Psi_1(\vec{r},t) \quad \Psi_1(\vec{r},t) = \psi_1(\vec{r}) \exp(-i\epsilon_1 t/\hbar) \]

\[ H_0 \Psi_2(\vec{r},t) = \epsilon_2 \Psi_2(\vec{r},t) \quad \Psi_2(\vec{r},t) = \psi_2(\vec{r}) \exp(-i\epsilon_2 t/\hbar) \]

Note that the coefficients \( c_1(t) \) and \( c_2(t) \) will include the oscillatory terms as well as any time-dependence induced by the laser fields; they are defined a little differently than in Problem #3 on Homework #2.
• The eigenfunctions $\psi_1(\vec{r})$ and $\psi_2(\vec{r})$ are orthonormal,

$$\int_{-\infty}^{+\infty} \psi_1^*(\vec{r}) \psi_1(\vec{r}) \, d\mathcal{V} = \int_{-\infty}^{+\infty} \psi_2^*(\vec{r}) \psi_2(\vec{r}) \, d\mathcal{V} = 1$$

$$\int_{-\infty}^{+\infty} \psi_2^*(\vec{r}) \psi_1(\vec{r}) \, d\mathcal{V} = \int_{-\infty}^{+\infty} \psi_1^*(\vec{r}) \psi_2(\vec{r}) \, d\mathcal{V} = 0$$

• The probability that the two-level system will be found in a particular level $m$ is given by

$$P_m = c_m^* c_m$$

• This can be seen to follow naturally from the condition that the wavefunction $\Psi(\vec{r},t)$ must be normalized so that the probability of finding the system in one of the two basis states is 1,

$$\int_{-\infty}^{+\infty} \Psi^* (\vec{r},t) \, \Psi (\vec{r},t) \, d\mathcal{V} = \int_{-\infty}^{+\infty} \left[ c_1^* \psi_1(\vec{r}) + c_2^* \psi_2(\vec{r}) \right] \left[ c_1 \psi_1(\vec{r}) + c_2 \psi_2(\vec{r}) \right] \, d\mathcal{V} = c_1^* c_1 + c_2^* c_2 = 1$$

2. The Electric-Dipole Operator

• The electric-dipole interaction operator $V(t)$ is given by

$$V(t) = -\vec{\mu} \cdot \vec{E}(\vec{r},t)$$

• Typically, there will be only one electron involved in the optical transition and for an atom, the electric dipole is given by

$$\vec{\mu} = -e \vec{r}$$

• The wavelength of light is typically much larger than atomic dimensions so that we can neglect the variation of the electric field over the atomic dimension. Selecting the origin of coordinates at the atomic nucleus we obtain
3. The SWE with the Wavefunction Expressed as the Sum of Basis Wavefunctions

- Substituting the expression \( \Psi(\vec{r}, t) = c_1(t) \psi_1(\vec{r}) + c_2(t) \psi_2(\vec{r}) \) into the SWE we obtain,

\[
\frac{i \hbar \partial \Psi(\vec{r}, t)}{\partial t} = i \hbar \psi_1(\vec{r}) \frac{\partial c_1(t)}{\partial t} + i \hbar \psi_2(\vec{r}) \frac{\partial c_2(t)}{\partial t}
\]

\[
= H_{op} \Psi(\vec{r}, t)
\]

\[
= [H_0 + V(t)][c_1(t) \psi_1(\vec{r}) + c_2(t) \psi_2(\vec{r})]
\]

\[
= c_1(t) \left[ H_0 \psi_1(\vec{r}) \right] + c_2(t) \left[ H_0 \psi_2(\vec{r}) \right] + V(t) c_1(t) \psi_1(\vec{r}) + V(t) c_2(t) \psi_2(\vec{r})
\]

\[
= \varepsilon_1 c_1(t) \psi_1(\vec{r}) + \varepsilon_2 c_2(t) \psi_2(\vec{r}) + V(t) c_1(t) \psi_1(\vec{r}) + V(t) c_2(t) \psi_2(\vec{r})
\]

- Multiplying through by \( \psi_2^*(\vec{r}) \) and integrating over all space gives us

\[
\frac{i \hbar}{\partial t} \int_{-\infty}^{\infty} \psi_2^*(\vec{r}) \psi_1(\vec{r}) d\mathcal{A} + i \hbar \int_{-\infty}^{\infty} \psi_2^*(\vec{r}) \psi_2(\vec{r}) d\mathcal{A} = i \hbar \int_{-\infty}^{\infty} \psi_2^*(\vec{r}) V(t) \psi_1(\vec{r}) d\mathcal{A} + c_2 \int_{-\infty}^{\infty} \psi_2^*(\vec{r}) V(t) \psi_2(\vec{r}) d\mathcal{A}
\]

- Let's take a closer look at the integrals on the RHS,

\[
c_1 \int_{-\infty}^{\infty} \psi_2^*(\vec{r}) V(t) \psi_1(\vec{r}) d\mathcal{A} = c_1 \left[ \int_{-\infty}^{\infty} \psi_2^*(\vec{r}) (-e \vec{r}) \psi_1(\vec{r}) d\mathcal{A} \right] \cdot E(t) = c_1 \vec{\mu}_{21} \cdot \vec{E}(t) = c_1 V_{21}(t)
\]

- The quantity \( \vec{\mu}_{21} \) is the electric dipole matrix element. The magnitude of the electric dipole matrix element is related to the Einstein coefficient for spontaneous emission by

\[
A_{21} = \frac{8 \pi^2 \varepsilon_0 \hbar}{\varepsilon_0} |\vec{\mu}_{21}|^2
\]
• The electric dipole matrix elements $\mu_{11}$ and $\mu_{22}$ are equal to zero if the atom or molecule has no permanent dipole moment. Setting these equal to zero, the equation reduces to

$$i \hbar \frac{\partial c_2}{\partial t} = \varepsilon_2 c_2 + c_1 V_{12}(t) \quad \Rightarrow \quad \frac{\partial c_2}{\partial t} = -\frac{i}{\hbar} \left[ \varepsilon_2 c_2 + c_1 V_{21}(t) \right]$$

• Similarly we obtain

$$i \hbar \frac{\partial c_1}{\partial t} = \varepsilon_1 c_1 + c_2 V_{12}(t) \quad \Rightarrow \quad \frac{\partial c_1}{\partial t} = -\frac{i}{\hbar} \left[ \varepsilon_1 c_1 + c_2 V_{12}(t) \right]$$

• Now introduce the density matrix

$$\rho_{11}' = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} = \begin{bmatrix} c_1^* & c_1^* \\ c_2^* & c_2^* \end{bmatrix}$$

• The density matrix equation for $\rho_{11}$ becomes

$$\frac{\partial \rho_{11}(t)}{\partial t} = c_1^* \frac{\partial c_1}{\partial t} + c_1 \frac{\partial c_1^*}{\partial t}$$

$$= -\frac{i}{\hbar} \left[ \varepsilon_1 c_1^* c_1 - \varepsilon_1 c_1^* c_1 + c_2 c_1^* V_{12}(t) - c_1 c_2^* V_{21}(t) \right]$$

$$= -\frac{i}{\hbar} \left[ V_{12}(t) \rho_{21}(t) - \rho_{12}(t)V_{21}(t) \right]$$

Similarly we obtain

$$\frac{\partial \rho_{22}(t)}{\partial t} = \frac{i}{\hbar} \left[ V_{12}(t) \rho_{21}(t) - \rho_{12}(t)V_{21}(t) \right]$$

and

$$\frac{\partial \rho_{21}(t)}{\partial t} = -i \omega_{21} \rho_{21}(t) - \frac{i}{\hbar} V_{21}(t) \left[ \rho_{21}(t) - \rho_{22}(t) \right]$$
• With the inclusion of the dephasing rate, \( \gamma_{21} \), and the population transfer rate from level 2 to level 1, \( \Gamma_{21} \), these equations become,

\[
\frac{\partial \rho_{11}(t)}{\partial t} = -\frac{i}{\hbar} \left[ V_{12}(t) \rho_{21}(t) - \rho_{12}(t)V_{21}(t) \right] + \Gamma_{21} \rho_{22}(t)
\]

\[
\frac{\partial \rho_{22}(t)}{\partial t} = +\frac{i}{\hbar} \left[ V_{12}(t) \rho_{21}(t) - \rho_{12}(t)V_{21}(t) \right] - \Gamma_{21} \rho_{22}(t)
\]

\[
\frac{\partial \rho_{21}(t)}{\partial t} = -\rho_{21}(t) \left[ i \omega_{21} - \gamma_{21} \right] - \frac{i}{\hbar} V_{21}(t) \left[ \rho_{11}(t) - \rho_{22}(t) \right]
\]

• The expectation value of the dipole moment for the two level system is given by

\[
\langle \tilde{\mu} \rangle(t) = \rho_{12}(t) \tilde{\mu}_{21} + \rho_{21}(t) \tilde{\mu}_{12}
\]