

Notes on excitation of an atom or molecule by an electromagnetic wave field.

F. Lanni / 11feb'12 / rev9sept'14

Because the wavelength of light (400-700nm) is much greater than the diameter of an atom (0.07-0.35 nm) or even the size of a molecule, it is accurate to treat the electric field of the wave as being uniform over the volume occupied by the electron orbits. The effect of the oscillating electric field of the light wave is to polarize the atom by driving the electrons and nucleus in opposite directions at the frequency of the light. In the visible spectrum, frequencies range from 4.28×10^{14} Hz (700 nm light) to 7.50×10^{14} Hz (400 nm light). Because the nuclear mass is >1800 times the mass of the orbiting electrons, the displacement of the electrons is much greater than the opposite displacement of the nucleus. Therefore, we can picture the effect of the passing light wave as an **oscillating distortion** of the electron density of the atom along an axis parallel to the electric field director of the light wave (**Figure 1**)

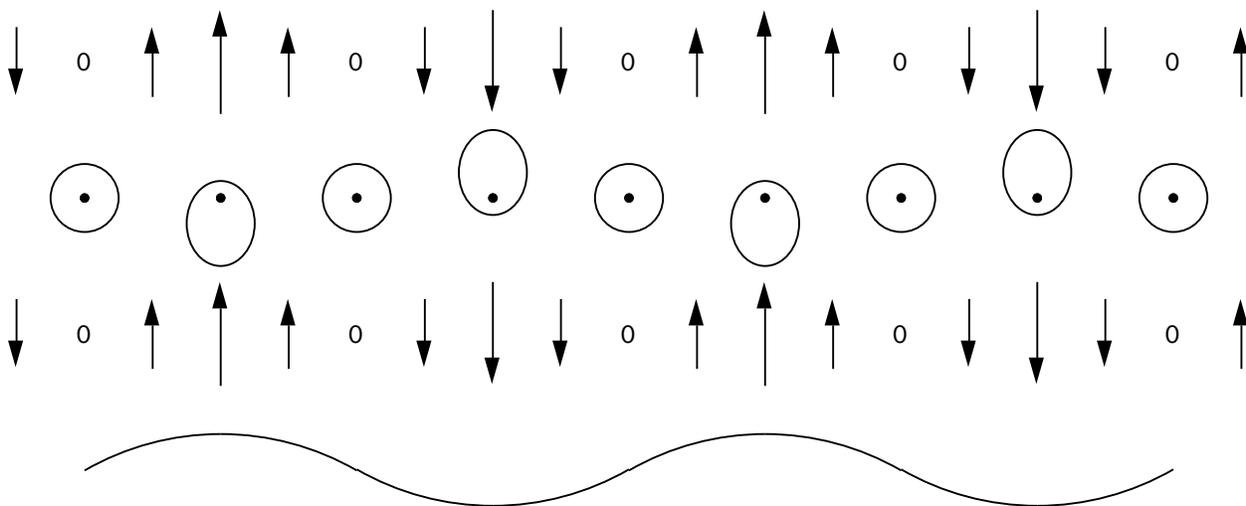


Figure 1. Pictorial representation of the polarization of the electron orbitals of an atom by a passing light wave. The size of the atom is greatly exaggerated relative to the wavelength of the light – the actual wavelength should be >2000 times the diameter of the atom. The light is shown as polarized in the "z" direction, so that the electric field of the light wave (arrows) drives the electrons 'downward' or 'upward', as shown. The electrostatic force on a charged particle, F_{el} , is equal to qE , and is opposite to E for the electron ($q = -e$), and along E for the atomic nucleus ($q = +Ze$). However, the high mass of the nucleus reduces its acceleration, so that the effect of the light wave can be pictured simply as a distortion of the electron density that oscillates up and down at the frequency of the light wave. The upward and downward shift in the **centroid** of the electronic charge "cloud" away from exact centration on the nucleus creates an oscillating **electric dipole**. Under specific conditions, the electric field can do work on the atom, thus transferring energy to the electrons (**electric dipole excitation**) by **light absorption**, or causing light scatter (**dipolar scattering**). In other circumstances, the electrons can radiate energy as a light wave (**electric dipole emission**), or, in quantum terms, as a **photon**. NOTE: The actual *phase* of the polarization relative to the driving field will be dependent on whether the frequency of the light is close to a **resonance frequency** of the bound electrons. In the figure, the

distortion of the atom is shown to be in-phase with \mathbf{E} . This would be the case when the frequency of the light wave is significantly less than an absorption frequency of the electrons. At the bottom of the figure, the light wave is shown schematically as a graph.

How may the oscillating distortion of the atom be described in terms of quantum mechanics? Take the simplest case of a **hydrogen atom**, with a single electron. As shown in **Figure 2**, if the electron is initially in a **1s** state (spherically symmetric), the distorted state shown in Figure 1 can be approximated by "adding in" some percentage of an appropriately oriented **2p** state, in this case, a **2p_z** state. The *interference* of the two wavefunctions is constructive on one side, and destructive on the other, so that the spherical s-state becomes asymmetric. If the weighting

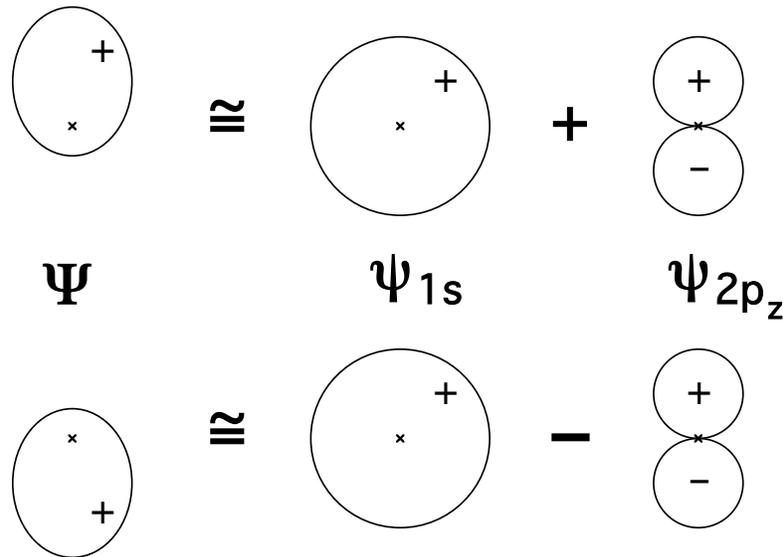


Figure 2. Approximation of the time-dependent polarized wavefunction as a time-dependent linear combination of atomic orbitals (LCAO). Pictorial representation, in which the wavefunctions are shown as polar plots. The relative *phase* within each wavefunction is shown by + and - signs; the two "lobes" of a 2p wavefunction have opposite phase.

coefficient for the **2p** state is positive, the distortion will be 'upward', and will be 'downward' if the weighting coefficient is negative - i.e., if the **2p** wavefunction is subtracted instead of added. Therefore, a rough approximation for the wavefunction Ψ would be $\Psi = \psi_{1s} + \sin(\omega t)\psi_{2p}$. A slightly more general form is:

$$\Psi(\underline{r}, t) = c_1(t) \psi_{1s}(\underline{r}, t) + c_2(t) \psi_{2p}(\underline{r}, t) \quad \text{eq. 1}$$

where we expect that the weighting coefficients $c_1(t)$ and $c_2(t)$ will be oscillatory under some circumstances. This type of approximation is known as "linear combination of atomic orbitals" (LCAO). It is necessary that this trial wavefunction must be a solution to the **time-dependent Schrodinger equation** for the hydrogen atom, in which the **potential energy term** must include the electrostatic potential energy of the electric dipole induced by the light wave. For a classical

electric dipole $\boldsymbol{\mu}$ in an electric field \mathbf{E} , the potential energy is the negative of the inner product of the two vectors:

$$V_{\text{dipole}} = -\boldsymbol{\mu} \cdot \mathbf{E} \quad \text{eq. 2}$$

Therefore, in the time-dependent Schrodinger equation:

$$i \hbar \partial \psi(\underline{r}, t) / \partial t = -(\hbar^2 / 2m) \nabla^2 \psi(\underline{r}, t) + V(\underline{r}, t) \psi(\underline{r}, t)$$

the potential energy term $V(\underline{r}, t) \psi(\underline{r}, t)$ must include **both** the electrostatic "1/r" Coulombic potential between electron and nucleus, and the potential energy of polarization of the atom.

The total Coulombic potential energy of the electron in the field of the nucleus can be represented by an integral over the electron density, $\rho_{\text{el}} = -e |\Psi|^2$:

$$\begin{aligned} dV_{\text{Coul}} &= (-e \rho_{\text{el}} dv) (+e / 4\pi\epsilon_0 r) \\ V_{\text{Coul, total}} &= +e / (4\pi\epsilon_0) \int (1/r) (-e |\Psi|^2) dv \\ &= \int \Psi^* (-e^2 / 4\pi\epsilon_0 r) \Psi dv \end{aligned} \quad \text{eq. 3}$$

which defines the **Coulombic potential energy operator** that appears in the Schrodinger equation:

$$V_{\text{Coul}} = -e^2 / 4\pi\epsilon_0 r \quad \text{eq. 4}$$

For the linearly polarized light wave in this example, the electric field at the location of the atom can be represented as $\mathbf{E}(t) = \mathbf{E}_0 \sin[\omega t]$, where \mathbf{E}_0 points in the z-direction. The induced **dipole moment** of the polarized atom is proportional to the degree of charge separation between the nucleus and electron density. Since we set the nucleus at the origin of coordinates, the dipole moment is the charge on the electron multiplied by the vector from the origin to the centroid of the electron density. Since $|\Psi|^2 = \Psi\Psi^*$ is the normalized **electron density**, the location of the centroid is simply the first moment of $\Psi\Psi^*$, i.e., the average position of the electron. Therefore:

$$\begin{aligned} \boldsymbol{\mu}(t) &= -e \int \mathbf{r} |\Psi|^2 dv \\ &= \int \Psi^* (-e \mathbf{r}) \Psi dv \end{aligned} \quad \text{eq. 5}$$

so that

$$\begin{aligned} V_{\text{pol, total}} &= -\boldsymbol{\mu} \cdot \mathbf{E} = -\int \Psi^* (-e \mathbf{r} \cdot \mathbf{E}) \Psi dv \\ &= \int \Psi^* (e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t]) \Psi dv \end{aligned} \quad \text{eq. 6}$$

By analogy to the Coulombic potential energy operator, we define the **induced dipole potential energy operator** to be:

$$V_{\text{pol}} = e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t] \quad \text{eq. 7}$$

Therefore, the Schrodinger equation for the illuminated atom has the form:

$$\begin{aligned}
 i \hbar \partial \psi(\underline{r}, t) / \partial t &= -(\hbar^2 / 2m) \nabla^2 \psi(\underline{r}, t) + (V_{\text{Coul}}(\underline{r}) + V_{\text{pol}}(t)) \psi(\underline{r}, t) \\
 &= -(\hbar^2 / 2m) \nabla^2 \psi(\underline{r}, t) + (-e^2 / 4\pi\epsilon_0 r + e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t]) \psi(\underline{r}, t) \\
 &= (\mathbf{H}_0 + e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t]) \psi(\underline{r}, t)
 \end{aligned} \tag{eq. 8}$$

where \mathbf{H}_0 is the unperturbed Hamiltonian operator for the hydrogen atom. It is into this equation that we must substitute eq. 1, the **LCAO approximation** for $\psi(\underline{r}, t)$, to determine the weighting coefficients $c_1(t)$ and $c_2(t)$, and thus the behavior of the atom:

$$\begin{aligned}
 i \hbar (\partial / \partial t) \{c_1(t) \psi_{1s}(\underline{r}, t) + c_2(t) \psi_{2p}(\underline{r}, t)\} \\
 = (\mathbf{H}_0 + e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t]) \{c_1(t) \psi_{1s}(\underline{r}, t) + c_2(t) \psi_{2p}(\underline{r}, t)\}
 \end{aligned} \tag{eq. 9}$$

Since the **1s** and **2p_z** wavefunctions are **eigenstates** of H_0 , they satisfy the eigenvalue equations:

$$\mathbf{H}_0 \psi_{1s}(\underline{r}, t) = E_{1s} \psi_{1s}(\underline{r}, t) \quad \text{and} \quad \mathbf{H}_0 \psi_{2p}(\underline{r}, t) = E_{2p} \psi_{2p}(\underline{r}, t)$$

where E_{1s} and E_{2p} are the usual hydrogen energy levels for the **1s** and **2p** states. This greatly simplifies the TDSE. Additionally, since $\psi_n(\underline{r}, t) = \phi_n(\underline{r}) \exp[-iE_n t / \hbar]$:

$$\begin{aligned}
 \phi_{1s}(\underline{r}) \exp[-iE_{1s} t / \hbar] i \hbar (\partial c_1(t) / \partial t) + c_1(t) \phi_{1s}(\underline{r}) i \hbar (\partial / \partial t) \exp[-iE_{1s} t / \hbar] \\
 + \phi_{2p}(\underline{r}) \exp[-iE_{2p} t / \hbar] i \hbar (\partial c_2(t) / \partial t) + c_2(t) \phi_{2p}(\underline{r}) i \hbar (\partial / \partial t) \exp[-iE_{2p} t / \hbar] \\
 = c_1(t) E_{1s} \phi_{1s}(\underline{r}) \exp[-iE_{1s} t / \hbar] + c_2(t) E_{2p} \phi_{2p}(\underline{r}) \exp[-iE_{2p} t / \hbar] \\
 + e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t] \{c_1(t) \phi_{1s}(\underline{r}) \exp[-iE_{1s} t / \hbar] + c_2(t) \phi_{2p}(\underline{r}) \exp[-iE_{2p} t / \hbar]\}
 \end{aligned}$$

canceling common terms:

$$\begin{aligned}
 \phi_{1s}(\underline{r}) \exp[-iE_{1s} t / \hbar] i \hbar (\partial c_1(t) / \partial t) + \phi_{2p}(\underline{r}) \exp[-iE_{2p} t / \hbar] i \hbar (\partial c_2(t) / \partial t) \\
 = e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t] \{c_1(t) \phi_{1s}(\underline{r}) \exp[-iE_{1s} t / \hbar] + c_2(t) \phi_{2p}(\underline{r}) \exp[-iE_{2p} t / \hbar]\}
 \end{aligned} \tag{eq. 10}$$

Since $\psi_{1s}(\underline{r}, t)$ and $\psi_{2p}(\underline{r}, t)$ are eigenfunctions of H_0 , they are **orthogonal**:

$$\int \psi_{1s}(\underline{r}, t)^* \psi_{2p}(\underline{r}, t) d v = 0 \quad \text{or, in Dirac notation:} \quad \langle 1s | 2p_z \rangle = 0$$

Therefore, the Schrodinger equation for the LCAO wavefunction (eq. 10) may be greatly simplified by projecting it on $\psi_{1s}(\underline{r}, t)$ and $\psi_{2p}(\underline{r}, t)$. In Dirac notation, eq. 10 is:

$$\begin{aligned} i\hbar(\partial c_1(t)/\partial t) |\psi_{1s}\rangle + i\hbar(\partial c_2(t)/\partial t) |\psi_{2pz}\rangle \\ = e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t] \{ c_1(t) |\phi_{1s}\rangle \exp[-iE_{1s}t/\hbar] + c_2(t) |\phi_{2pz}\rangle \exp[-iE_{2p}t/\hbar] \} \end{aligned}$$

Projecting onto $|\psi_{1s}\rangle = |\phi_{1s}\rangle \exp[-iE_{1s}t/\hbar]$: $|\psi_{1s}\rangle^* = \langle \psi_{1s}| = \langle \phi_{1s}| \exp[+iE_{1s}t/\hbar]$

$$\begin{aligned} i\hbar(\partial c_1(t)/\partial t) \langle \psi_{1s} | \psi_{1s} \rangle + i\hbar(\partial c_2(t)/\partial t) \langle \psi_{1s} | \psi_{2pz} \rangle \\ = \langle \psi_{1s} | e \mathbf{r} \cdot \mathbf{E}_0 \sin[\omega t] \{ c_1(t) |\phi_{1s}\rangle \exp[-iE_{1s}t/\hbar] + c_2(t) |\phi_{2pz}\rangle \exp[-iE_{2p}t/\hbar] \} \end{aligned}$$

$$\begin{aligned} i\hbar(\partial c_1(t)/\partial t) \cdot 1 + 0 \\ = c_1(t) \langle \phi_{1s} | e \mathbf{r} \cdot \mathbf{E}_0 | \phi_{1s} \rangle \sin[\omega t] \exp[+ iE_{1s}t/\hbar - iE_{1s}t/\hbar] \\ + c_2(t) \langle \phi_{1s} | e \mathbf{r} \cdot \mathbf{E}_0 | \phi_{2pz} \rangle \sin[\omega t] \exp[+ iE_{1s}t/\hbar - iE_{2p}t/\hbar] \end{aligned}$$

$$\begin{aligned} i\hbar \partial c_1(t)/\partial t = c_1(t) \langle \phi_{1s} | e \mathbf{r} \cdot \mathbf{E}_0 | \phi_{1s} \rangle \sin[\omega t] \\ + c_2(t) \langle \phi_{1s} | e \mathbf{r} \cdot \mathbf{E}_0 | \phi_{2pz} \rangle \sin[\omega t] \exp[iE_{1s}t/\hbar - iE_{2p}t/\hbar] \end{aligned}$$

eq. 11

Because the dipole moment operator has **odd parity**, the parity of the integrand in the first integral is (even) x (odd) x (even) = odd, therefore the integral is identically zero. This is not the case for the second integral, where it is (even) x (odd) x (odd) = even. Therefore, only the second term on the right-hand side is non-zero:

$$\begin{aligned} i\hbar \partial c_1(t)/\partial t = c_2(t) \langle \phi_{1s} | e \mathbf{r} \cdot \mathbf{E}_0 | \phi_{2pz} \rangle \sin[\omega t] \exp[- (i/\hbar)(E_{2p} - E_{1s}) t] \\ = c_2(t) \langle \phi_{1s} | e \mathbf{r} | \phi_{2pz} \rangle \cdot \mathbf{E}_0 \sin[\omega t] \exp[- (i/\hbar)(E_{2p} - E_{1s}) t] \end{aligned}$$

eq. 12a

By projecting the TDSE onto $|\psi_{2p}\rangle = |\phi_{2p}\rangle \exp[-iE_{2p}t/\hbar]$, a nearly identical differential equation is obtained for the time-derivative of $c_2(t)$:

$$i\hbar \partial c_2(t)/\partial t = c_1(t) \langle \phi_{2pz} | e \mathbf{r} | \phi_{1s} \rangle \cdot \mathbf{E}_0 \sin[\omega t] \exp[- (i/\hbar)(E_{1s} - E_{2p}) t]$$

eq. 12b

Equations 12a and 12b are a pair of coupled differential equations for $c_1(t)$ and $c_2(t)$. The detailed solution may be found in treatises on quantum mechanics. However, several points can

be made about the dynamics of the electron's wavefunction simply by inspection of the equations:

1. The strength of the coupling between the initial state (1s) and the presumed final state (2p_z) due to the polarization of the atom is determined by the integral $\langle \phi_{2pz} | e \mathbf{r} | \phi_{1s} \rangle$, which is the projection of the polarized 1s state, $e \mathbf{r} | \phi_{1s} \rangle$, onto the 2p_z state, $\langle \phi_{2pz} |$. This is known as the **transition moment integral**:

$$\langle \phi_{2pz} | e \mathbf{r} | \phi_{1s} \rangle = \int \phi_{2pz}^* (e \mathbf{r}) \phi_{1s} dv \quad \text{eq. 13}$$

2. Because the interaction energy between the induced dipole and the electric field of the light wave is a vector inner product, the polarization state of the light relative to the orientation of the molecule will matter, in general. Only for a spherically-symmetric atom is the polarizability independent of orientation. In the foregoing example, the light was "vertically" polarized (\mathbf{E}_0 parallel to the z-axis), and we therefore chose to use a 2p_z orbital in the LCAO wavefunction. If we had chosen instead a 2p_x or 2p_y orbital, the vector value of the transition moment integral (eq. 13) would have been orthogonal to \mathbf{E}_0 .

3. The frequency of the light wave matters greatly. In eqs 12a and 12b, the factor $\sin[\omega t]$ oscillates at the frequency of the light wave, whereas the factor $\exp[-(i/\hbar)(E_{1s} - E_{2p}) t]$ oscillates at the difference frequency for the wavefunctions involved. The two factors fall into and out of phase with each other, and the electron is not driven steadily. However, when the two frequencies are the same, the dynamics embodied in eqs. 12a and 12b change dramatically. This is the resonant condition:

$$\omega = -(E_{1s} - E_{2p})/\hbar \quad \text{eq. 14}$$

which is simply: $\hbar\omega = E_{2p} - E_{1s}$ eq. 15

In other words, in this condition the photon energy equals the energy difference between the initial and final state.

The actual solution of eqs. 12a and 12b is tricky, so only the result is given here; When the frequency band of the light is centered on $(E_{2p} - E_{1s})/\hbar$,

$$\text{absorption rate} = (1/2\hbar^2) \left| \langle \phi_{2pz} | e \mathbf{r} | \phi_{1s} \rangle \cdot \mathbf{E}_0 \right|^2 \quad \text{eq. 16}$$

For simple 1D problems such as Particle-in-a-Box:

$$\text{absorption rate} = (E_0^2/2\hbar^2) \left| \int \phi_{\text{final}}^*(x) e x \phi_{\text{initial}}(x) dx \right|^2 \quad \text{eq. 17}$$

From which we see that the square of the transition moment integral determines the extinction coefficient, and also, as expected, the absorption rate is proportional to the intensity of the light.