First Order Polarizability

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The dipole moment, $\mathbf{p}$, of an atom or molecule in a weak applied electric field $\mathbf{E}$ can be approximated by

$$\mathbf{p} = \alpha\mathbf{E}, \tag{1}$$

where α is the polarizability tensor. Being a tensor, it allows for the fact that the induced dipole moment is not necessarily in the direction of the applied field. For simplicity, we treat the polarizability as a scalar so that the induced dipole moment and electric field are parallel and choose the coordinate system so that the z-axis is along the field. This reduces the problem to one dimension.

All models of the polarizability begin by calculating the dipole moment as a function of the electric field. The resultant model function for the dipole moment, $p(E)$, is expanded in a power series of the electric field, and the coefficient of the linear term is the polarizability.

Here, we are interested in modeling the polarizability using time dependent perturbation theory, where the electric coupling between the applied field and the electrons is weak compared with the binding energy of the electrons in the molecule. The time-dependent perturbation potential is of the form

$$\begin{aligned} V(t) &= -\mathbf{p} \cdot \mathbf{E}, \\ &= -pE_0 \cos \omega t, \end{aligned} \tag{2}$$

where ω is the applied field's frequency. For convenience, we express $\cos(\omega t)$ as

$$\cos(\omega t) = \frac{e^{i\omega t} + e^{-i\omega t}}{2}, \tag{3}$$

The full Hamiltonian is $H = H_0 + V(t)$, where H_0 is Hamiltonian of the system in the absence of perturbation with

$$H_0 |n\rangle = E_n |n\rangle, \tag{4}$$

where E_n is the eigenvalue and $|n\rangle$ an eigenvector of H_0.

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Using standard perturbation theory, the eigenvectors of the full Hamiltonian, $H = H_0 + V(t)$, are expanded in terms of the unperturbed eigenvectors,

$$|u\rangle \equiv |n; t\rangle = \sum_n c_n(t) e^{-i\Omega_n t} |n\rangle, \qquad (5)$$

where $\Omega_n = E_n/\hbar$ and the time-varying coefficients, $c_n(t)$, are related to the time-dependent perturbation $V(t)$. $c_n(t)$ can be written as series of coefficients,

$$c_n(t) = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \ldots = \sum_{i=0}^{\infty} c_n^i(t), \qquad (6)$$

that are given by[1]

$$c_n^{(N)}(t) = \frac{-i}{\hbar} \sum_l \int_{-\infty}^t V_{nl}(t') c_l^{(N-1)}(t') e^{i\Omega_{nl}t'}, \qquad (7)$$

where $V_{nl}(t') = \langle n| V(t') |l\rangle$ and

$$\omega_{nl} = \omega_n - \omega_l \qquad (8)$$

is internal frequency difference between state n and l.

Substituting Equation (2) into Equation (6) and assuming that the system is in ground state at $t = 0$ (subscript g denotes the ground state), we get

$$c_n^{(0)} = \delta_{ng} \qquad (9)$$

and

$$
\begin{aligned}
c_n^{(1)}(t) &= \frac{-i}{\hbar} \int_{-\infty}^t e^{i\Omega_{ng}t'} V_{ng}(t') dt' \\
&= \frac{qE_0}{2} x_{ng} \left(\frac{e^{i(\Omega_{ng}+\omega)t}}{\Omega_{ng}+\omega} + \frac{e^{i(\Omega_{ng}-\omega)t}}{\Omega_{ng}-\omega} \right),
\end{aligned} \qquad (10)
$$

where $x_{nm} \equiv \langle n| x |m\rangle$. Note that Equation (10) assumes that the perturbation is turned on at a time far in the past so that $c_n^{(1)}(t \to -\infty) \to 0$.

The dipole moment, $p = qx$, is given by the expectation of the dipole operator using the perturbed state

$$\langle p \rangle (t) = \frac{\langle u| p |u\rangle}{\langle u|u\rangle} = q \langle u| x |u\rangle, \qquad (11)$$

where we keep only terms that are first order in the applied field. As such, $\langle u|u\rangle = 1$.

To first order in the external field E, the dipole moment is given by

$$
\begin{aligned}
\langle p \rangle (t) &= q \langle u|x|u \rangle \\
&= q \sum_{m,n} \left\langle n \left(c_n^{(0)} + c_n^{(1)} \right) e^{-i\Omega_n t} \Big| x \Big| e^{-i\Omega_m t} \left(c_m^{(0)} + c_m^{(1)} \right) m \right\rangle \\
&= q \sum_{n,m} e^{-i\Omega_{mn} t} \left[\left(\delta_{n0} + c_n^{(1)^*}(t) \right) \left(\delta_{m0} + c_m^{(1)}(t) \right) \right] x_{nm} \\
&= q \left\{ x_{gg} + \sum_n c_n^{(1)^*}(t) e^{-i\Omega_{gn} t} x_{ng} + \sum_m c_m^{(1)}(t) e^{-i\Omega_{mg} t} x_{gm} \right\}, (12)
\end{aligned}
$$

Substituting Equation (10) into (12), we find

$$
\begin{aligned}
\langle p \rangle (t) &= p_0 + q\frac{qE_0}{2\hbar} \sum_n |x_{gn}|^2 \left[\left(\frac{e^{i\omega t}}{\Omega_{ng} + \omega} + \frac{e^{-i\omega t}}{\Omega_{ng} - \omega} \right) \right. \\
&\quad + \left. \left(\frac{e^{-i\omega t}}{\Omega_{ng} + \omega} + \frac{e^{i\omega t}}{\Omega_{ng} - \omega} \right) \right]. \quad (13)
\end{aligned}
$$

Decay in excited state population is taken account by including a damping term that leads to a complex internal frequency of the form

$$
\Omega_n = \omega_n - i\Gamma_n/2, \quad (14)
$$

where ω_n and Γ are real. The negative sign in Equation (14) arises from the requirement that the time evolution of the wavefunction, given by $\exp\left(-i\Omega_n t\right)$, must yields a loss in excited state population for $\Gamma_n > 0$. Furthermore, since the ground state is stable (spontaneous transitions from the ground state do not occur in vacuum), we assume that the ground state energy is real.[2] Thus

$$
\Gamma_g = 0. \quad (15)
$$

With this generalization to include loss, Equation (13) becomes

$$
\begin{aligned}
\langle p \rangle (t) &= p_0 + \frac{q^2 E_0}{2\hbar} \sum_n |x_{gn}|^2 \\
&\quad \left[\left(\frac{e^{i\omega t}}{\Omega_{ng} + \omega} + \frac{e^{-i\omega t}}{\Omega_{ng} - \omega} \right) + \left(\frac{e^{-i\omega t}}{\Omega_{ng}^* + \omega} + \frac{e^{i\omega t}}{\Omega_{ng}^* - \omega} \right) \right]. \quad (16)
\end{aligned}
$$

Note that since the induced dipole moment is real, the term in the second set of parentheses must be the complex conjugate of the term in the first set of parenthesis. This requirement determines which frequencies require complex conjugation. By combining terms, Equation (16) can be expressed as

$$
\begin{aligned}
\langle p \rangle (t) &= p_0 + 2\frac{q^2 E_0}{\hbar} \sum_n |x_{gn}|^2 \omega_{ng} \\
&\quad \times \frac{\left(\omega_{ng}^2 - \omega^2 + \frac{\Gamma_{ng}^2}{4} \right) \cos \omega t + \omega \Gamma_{ng} \sin \omega t}{\left(\omega_{ng}^2 - \omega^2 + \frac{\Gamma_{ng}^2}{4} \right)^2 + \omega^2 \Gamma_{ng}^2}, \quad (17)
\end{aligned}
$$

where we have used $\exp(i\phi) = \cos\phi + i\sin\phi$.

According to Equation (17), the induced dipole is not in phase with the applied electric unless $\Gamma_{ng} = 0$. The induced dipole moment can be expressed as

$$\langle p \rangle (t) = \alpha_0(-\omega; \omega) \cos\omega t + \alpha_{\pi/2}(-\omega; \omega) \sin\omega t, \tag{18}$$

which can be inverted by fourier transform to get the polarizabilities,

$$\alpha_0(-\omega; \omega) = 2\frac{q^2}{\hbar} \sum_n |x_{gn}|^2 \frac{\omega_{ng}\left(\omega_{ng}^2 - \omega^2 + \frac{\Gamma_{ng}^2}{4}\right)}{\left(\omega_{ng}^2 - \omega^2 + \frac{\Gamma_{ng}^2}{4}\right)^2 + \omega^2\Gamma_{ng}^2}, \tag{19}$$

$$\alpha_{\pi/2}(-\omega; \omega) = 2\frac{q^2}{\hbar} \sum_n |x_{gn}|^2 \frac{(\omega\omega_{ng}\Gamma_{ng})}{\left(\omega_{ng}^2 - \omega^2 + \frac{\Gamma_{ng}^2}{4}\right)^2 + \omega^2\Gamma_{ng}^2}. \tag{20}$$

Noting that $\cos(\omega t - \phi) = \cos\omega t \cos\phi + \sin\omega t \sin\phi$, the phase of the polarizability is given by

$$\phi = \tan^{-1}\left(\frac{\alpha_{\pi/2}}{\alpha_0}\right). \tag{21}$$

If only the excited state n contributes, as is approximately the case when the photon energy is in resonance with the nth state, the phase is given by,

$$\phi = \tan^{-1}\left(\frac{\alpha_{\pi/2}}{\alpha_0}\right) = \tan^{-1}\left(\frac{2\omega\Gamma_{ng}}{\omega_{ng}^2 - \omega^2 + \frac{\Gamma_{ng}^2}{2}}\right). \tag{22}$$

A more elegant approach to the problem of calculating the polarizability is to use complex basis $\exp(\pm i\omega t)$ rather than the real basis $(\sin\omega t, \cos\omega t)$. In that case, the induced dipole moment in Equation (16) can be written in the form

$$\begin{aligned} \langle p \rangle (t) &= \frac{1}{2}p(\omega)e^{-i\omega t} + c.c. \\ &= \frac{q^2 E_0 e^{-i\omega t}}{2\hbar} \sum_n |x_{gn}|^2 \left(\frac{1}{\omega_{ng}^* + \omega} + \frac{1}{\omega_{ng} - \omega}\right) + c.c., \end{aligned} \tag{23}$$

were $c.c.$ represents the complex conjugate of the previous term. Using orthogonality of $\exp(-i\omega t)$ and $\exp(+i\omega t)$, and the definition given in Equation (1), we get the complex polarizability

$$\alpha(-\omega; \omega) = \frac{q^2}{\hbar} \sum_n |x_{gn}|^2 \left(\frac{1}{\omega_{ng}^* + \omega} + \frac{1}{\omega_{ng} - \omega}\right). \tag{24}$$

The real an imaginary parts of the polarizability, $\alpha(-\omega; \omega)$, given by Equation (24) are just α_0 and $\alpha_{\pi/2}$, respectively.

One additional comment needs to be made about the damping factor in Equation (14). The astute reader may notice that the introduction of complex

internal frequencies prior to applying perturbation theory leads to divergences that invalidate the use of perturbation theory. Furthermore, even without the damping factors, perturbation theory does not - in principle - hold on resonance (when the internal frequency and the electric field frequency are the same) because the coefficients $c_n^{(1)}$ can become larger than unity, leading to probability non-conservation. However, the ad hoc addition of damping in Equation (16) leads to a theory that accurately fits experiment. Methods for dealing with such divergence are described in the paper by Orr and Ward,[2] and references therein.

References

[1] R. W. Boyd, Nonlinear Optics Academic, Press, New York (1992).

[2] B. J. Orr and J. F. Ward, Mol. Phys. **20**, 513, (1971).