

Dipole Operator from Atoms to Crystals

Using perturbation theory, the induced dipole moment at frequency $p\omega$ due to interaction with p photons is $d(p\omega) = \alpha_p(\omega)\mathcal{E}^p$. Here, the (hyper-) polarizabilities are

$$\alpha_p(\omega) = \frac{(-e)^{p+1}}{\hbar^p} \sum_{m_0 \dots m_p} \sum_{k=1}^{p+1} f_{m_0} x_{m_0 m_1} x_{m_1 m_2} \dots x_{m_p m_0} D_{m_0 m_1 \dots m_p}(\omega), \quad (1)$$

with $f_m \equiv f(E_m)$ the probability of occupancy in the unperturbed situation and

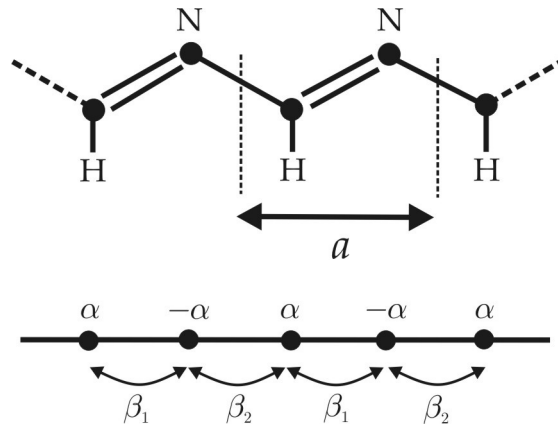
$$D_{m_0 m_1 \dots m_p}(\omega) = \sum_{k=1}^{p+1} \frac{1}{(\omega_{m_1 m_0} + s_{k1}\omega)(\omega_{m_2 m_0} + s_{k2}\omega) \dots (\omega_{m_p m_0} + s_{kp}\omega)},$$

where $s_{k1} = 1 - (p+1)\delta_{k1}$ and $s_{k,j} = s_{k,j-1} + 1 - (p+1)\delta_{kj}$ [1]. Here, $x_{nm} = \langle n|x|m \rangle$ and $\omega_{nm} = (E_n - E_m)/\hbar$. For instance,

$$\alpha_1(\omega) = \frac{2e^2}{\hbar} \sum_{m,n} f_n |x_{nm}|^2 \frac{\omega_{nm}}{\omega_{nm}^2 - \omega^2}, \quad (2)$$

$$\alpha_2(\omega) = \frac{3e^3}{\hbar^2} \sum_{m,n,l} f_n x_{nm} x_{ml} x_{ln} \frac{\omega\omega_{ml} + \omega_{mn}\omega_{ln}}{(\omega_{mn} - 2\omega)(\omega_{mn} + \omega)(\omega_{ln} + 2\omega)(\omega_{ln} - \omega)}. \quad (3)$$

We apply these expressions to a simple polymer chain (polymethineamine):



It consists of alternating C and N atoms along the backbone and, in addition, is dimerized with alternating single and double bonds. We only consider the π - orbitals directed perpendicularly to the molecule. Only nearest neighbour interactions are included and the orbitals are taken to be orthogonal. Hence, the tight-binding Hamiltonian is of the form

$$\vec{H} = \begin{pmatrix} \alpha & \beta_1 & 0 & \cdots \\ \beta_1 & -\alpha & \beta_2 & \cdots \\ 0 & \beta_2 & \alpha & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

We take the values $\alpha = 0.5$ eV, $\beta_1 = -2.0$ eV and $\beta_2 = -2.5$ eV and the lattice constant $a = 2\text{\AA}$ for polymethineimine. For $\alpha = 0$, $\beta_1 = -2.0$ eV and $\beta_2 = -3.0$ eV the same model describes polyacetylene. All bond lengths are assumed identical and the number of unit cells in the chain is N . In the π -orbital basis, the x -operator is of the form

$$\vec{X} = \begin{pmatrix} x_1 & 0 & 0 & \cdots \\ 0 & x_2 & 0 & \cdots \\ 0 & 0 & x_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

with $x_n = na/2$. Hence, in the presence of a long-axis electric field, the Hamiltonian becomes $\vec{H} + eF\vec{X}$. If an infinite chain is considered in k -space the two orbitals per unit cell lead to the Hamiltonian

$$\vec{H} = \begin{pmatrix} \alpha & \beta_1 e^{ika/2} + \beta_2 e^{-ika/2} \\ \beta_1 e^{-ika/2} + \beta_2 e^{ika/2} & -\alpha \end{pmatrix}$$

The momentum operator becomes $p_x = m/\hbar(dH/dk)$ and we find the eigenvalues and matrix elements (Ω is the Berry connection defined below)

$$E_{v,c} = \mp E, \quad E = \sqrt{\alpha^2 + \varepsilon^2}, \quad \varepsilon = \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(ka)}$$

$$p_{cv} = \frac{ma}{\hbar} \left\{ -2\alpha\beta_1\beta_2 \sin(ka) + i(\beta_1^2 - \beta_2^2)E \right\} / (2\varepsilon E)$$

$$\Omega_{cc} - \Omega_{vv} = -a\alpha(\beta_1^2 - \beta_2^2) / (2\varepsilon^2 E).$$

Infinite chain

For an infinite chain, states are labeled by band n and k -vector so that

$$\alpha_1(\omega) = \frac{2e^2}{\hbar} \sum_{m,n,k,k'} f_{nk} |x_{nk,mk'}|^2 \frac{\omega_{mk',nk}}{\omega_{mk',nk}^2 - \omega^2},$$

For an infinite chain, the naive x operator is ill defined. However, the momentum is well behaved and for non-degenerate levels, the commutator relation $x_{nk,mk'} = p_{nk,mk'} / (im\omega_{nk,mk'})$

allows for simple reformulations. We have generally $p_{nk, mk'} = p_{nm}(k)\delta_{kk'}$. For the interband case $n \neq m$, we therefore immediately find

$$\alpha_1^{inter}(\omega) = \frac{2e^2}{\hbar m^2} \sum_{m \neq n, k} f_{nk} \frac{|p_{nm}(k)|^2}{\omega_{nm}(k)(\omega_{nm}^2(k) - \omega^2)}.$$

We now compute the polarizability per length Na and rewrite as an integral

$$\alpha_1^{inter}(\omega) / Na = \frac{e^2}{\pi \hbar m^2} \sum_{m \neq n} \int_{-\pi/a}^{\pi/a} f_{nk} \frac{|p_{nm}(k)|^2}{\omega_{nm}(k)(\omega_{nm}^2(k) - \omega^2)} dk. \quad (4)$$

For the intraband case $n = m$, we symmetrize in k and k' and so

$$\alpha_1^{intra}(\omega) = \frac{e^2}{\hbar} \sum_{n, k, k'} (f_{nk} - f_{nk'}) |x_{nk, nk'}|^2 \frac{\omega_{nk', nk}}{\omega_{nk', nk}^2 - \omega^2}. \quad (5)$$

We will again rely on the commutator trick and subsequently carefully take the $k' \rightarrow k$ limit

$$\alpha_1^{intra}(\omega) = \frac{e^2}{\hbar m^2} \sum_{n, k, k'} (f_{nk} - f_{nk'}) \frac{|p_{nk, nk'}|^2}{\omega_{nk', nk}(\omega_{nk', nk}^2 - \omega^2)}.$$

We may now take the limit $k' \rightarrow k$ by expanding $f_{nk'} \approx f_{nk} + f'_{nk} \hbar \omega_{nk', nk}$ with $f' = df / dE$. In this manner,

$$\alpha_1^{intra}(\omega) = \frac{e^2}{m^2 \omega^2} \sum_{n, k} f'_{nk} |p_{nk, nk}|^2.$$

Using $p_{nk, nk} = m d\omega_{nk} / dk$ we find after converting to an integral

$$\begin{aligned} \alpha_1^{intra}(\omega) / Na &= \frac{e^2}{2\pi \omega^2} \sum_n \int_{-\pi/a}^{\pi/a} f'_{nk} \left(\frac{d\omega_{nk}}{dk} \right)^2 dk \\ &\equiv -\frac{\varepsilon_0 \omega_p^2}{\omega^2}, \quad \omega_p^2 = -\frac{e^2}{2\pi \varepsilon_0} \sum_n \int_{-\pi/a}^{\pi/a} f'_{nk} \left(\frac{d\omega_{nk}}{dk} \right)^2 dk. \end{aligned} \quad (6)$$

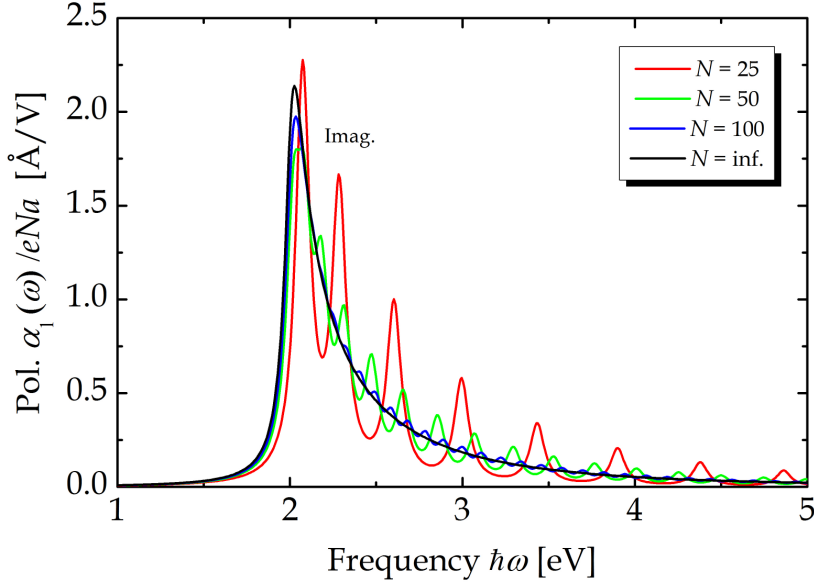


Figure 1. Polyacetylene polarizability per unit length for finite and infinite chains.

In the presence of a long-axis electrostatic field F , Eq.(2) still holds for the finite chain. The infinite-chain expression changes, however. If field-induced coupling between bands is ignored, the eigenstates belonging to a band n are determined by

$$\left\{ E_n(k) + ieF \frac{d}{dk} \right\} \Psi_p^{(n)}(k) = E_p^{(n)} \Psi_p^{(n)}(k).$$

Here, $E_n(k)$ is the band structure energy and index p is the Wannier-Stark ladder index. If the width of the Brillouin zone is $K = 2\pi / a$, the normalized solutions are

$$\Psi_p^{(n)}(k) = \frac{1}{\sqrt{K}} \exp \left\{ -\frac{i}{eF} \left(E_p^{(n)} k - \int_0^k E_n(k') dk' \right) \right\}.$$

The allowed states satisfy $\Psi_p^{(n)}(k+K) = \Psi_p^{(n)}(k)$. Thus, $E_p^{(n)} = p \cdot 2\pi eF / K + \bar{E}_n$ with p an integer and $\bar{E}_n = \int_0^K E_n(k) dk / K$. The transition frequencies are

$$\omega_{mn}(q-p) = (E_q^{(m)} - E_p^{(n)}) / \hbar = (q-p) \cdot 2\pi eF / \hbar K + \bar{E}_{mn} / \hbar = (q-p) \cdot eFa / \hbar + \bar{E}_{mn} / \hbar$$

The momentum matrix elements become

$$\langle \Psi_q^{(m)} | p_x | \Psi_p^{(n)} \rangle = \frac{1}{K} \int_0^K p_{mn}(k) \exp \left\{ \frac{i}{eF} \left(\hbar \omega_{mn}(q-p) k - \int_0^k E_{mn}(k') dk' \right) \right\} dk.$$

In turn, the response is

$$\alpha_1^{inter}(\omega) = \frac{2e^2}{\hbar m^2} \sum_{m,n,p,q} f_{n,p} \frac{\left| \langle \Psi_q^{(m)} | p_x | \Psi_p^{(n)} \rangle \right|^2}{\omega_{mn}(q-p)(\omega_{mn}^2(q-p) - \omega^2)}.$$

Since only $p-q$ enters, one sum can be performed providing a factor $\hbar\omega_{mn}/eFa$. Partitioning bands into valence bands (v) and conduction bands (c) finally leads to

$$\alpha_1^{inter}(\omega) = \frac{2e}{m^2 Fa} \sum_{m \in c, n \in v} \sum_{q=q_0}^{\infty} \frac{\left| \langle \Psi_q^{(m)} | p_x | \Psi_0^{(n)} \rangle \right|^2}{\omega_{mn}^2(q) - \omega^2}, \quad (7)$$

where $q_0 = -\text{int}(\bar{E}_{mn}/eFa)$.

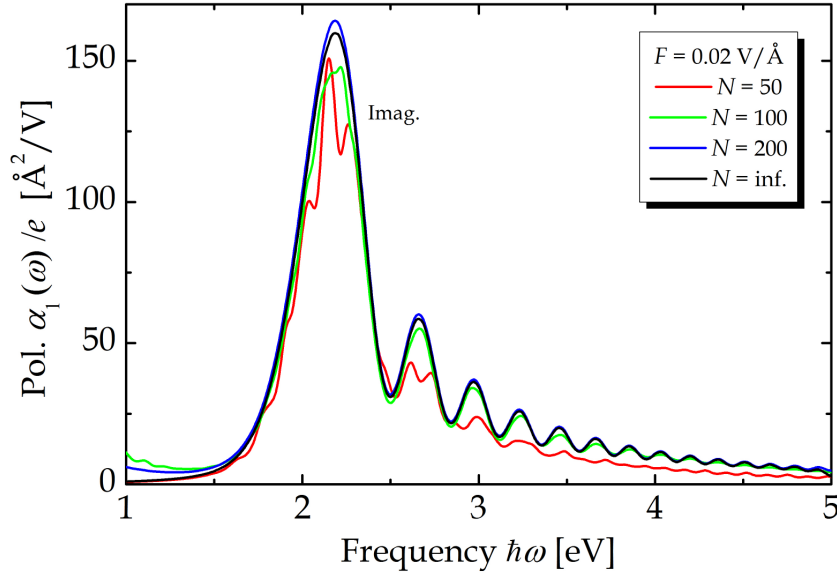


Figure 2. Polyacetylene polarizability in a field for finite and infinite chains.

The Systematic Way

As is apparent from the previous section, problems only arise whenever we are dealing with intraband factors $x_{nk,nk'}$. We therefore formally write

$$x_{nk,mk'} = \begin{cases} x_{nk,nk'}^i & n = m \\ p_{nk,mk'} / (im\omega_{nk,mk'}) & n \neq m \end{cases}.$$

The intraband dipole operator x^i is defined via the relation $x^i_{nk,mk'} = \delta_{nm} x^i_{nk,nk'}$ and its commutator with simple operators O such as p_x or H [2] for which $O_{nk,mk'} = O_{nm}(k)\delta_{kk'}$

$$\langle nk|[x^i,O]|mk'\rangle = i\delta_{kk'}(O_{nm})_{;k}, \quad (O_{nm})_{;k} \equiv \frac{dO_{nm}}{dk} - iO_{nm}(\Omega_{nm} - \Omega_{mm}). \quad (8)$$

Here, “;k” is the symbol for generalized derivative and by writing the band states as $|nk\rangle = V^{-1/2}u_{nk}e^{ikx}$ we have defined the Berry connection as $\Omega_{nm}(k) = iV_{UC}^{-1} \int u_{nk}^* \frac{d}{dk} u_{mk} d^3r$ with the normalization $\delta_{nm} = V_{UC}^{-1} \int u_{nk}^* u_{mk} d^3r$. We see that $\langle nk|[x^i,O]|nk'\rangle = i\delta_{kk'} dO_{nm}/dk$. To prove Eq.(8), we follow Blount [3] and write

$$-i \frac{d}{dk} |nk\rangle = \frac{-i}{V^{1/2}} \frac{du_{nk}}{dk} e^{ikx} + x |nk\rangle.$$

Thus, because $\langle mk'|nk\rangle = \delta_{nm}\delta_{kk'}$ the inner product with $\langle mk'|$ yields

$$\langle mk'|x|nk\rangle = \Omega_{mn}(k)\delta_{kk'} - i\delta_{nm} \frac{d}{dk} \delta_{kk'}$$

Similarly, interchanging quantum numbers, we find $\langle nk|x|mk'\rangle = \Omega_{nm}(k)\delta_{kk'} - i\delta_{nm} d\delta_{kk'}/dk'$. Comparison with the complex conjugate of the result above then shows that $d\delta_{kk'}/dk' = -d\delta_{kk'}/dk$. Note, that $\Omega_{mn}(k) = p_{mn}(k)/(im\omega_{mn}(k))$ for $n \neq m$ as one can demonstrate using perturbation theory to compute $u_{nk+\delta k}$. For the intraband dipole operator we then find

$$\langle nk|x^i|mk'\rangle = \delta_{nm} \left\{ \Omega_{nm}(k)\delta_{kk'} - i \frac{d}{dk'} \delta_{kk'} \right\}.$$

The problem is how to make sense of the last term. To solve this, we consider the commutator and apply the completeness relation

$$\begin{aligned} \langle nk|[x^i,O]|mk'\rangle &= \sum_{l,k''} \left\{ \langle nk|x^i|lk''\rangle \langle lk''|O|mk'\rangle - \langle nk|O|lk''\rangle \langle lk''|x^i|mk'\rangle \right\} \\ &= \sum_{k''} \left[\left[\Omega_{nm}(k)\delta_{kk''} - i \frac{d}{dk''} \delta_{kk''} \right] \langle nk''|O|mk'\rangle - \langle nk|O|mk''\rangle \left[\Omega_{mm}(k)\delta_{k'l''} - i \frac{d}{dk'} \delta_{k'l''} \right] \right] \\ &= \delta_{kk'} \left[\Omega_{nm}(k) - \Omega_{mm}(k) \right] O_{nm}(k) - i \sum_{k''} \left\{ \left[\frac{d}{dk''} \delta_{kk''} \right] \langle nk''|O|mk'\rangle - \langle nk|O|mk''\rangle \left[\frac{d}{dk'} \delta_{k'l''} \right] \right\} \\ &= \delta_{kk'} \left[\Omega_{nm}(k) - \Omega_{mm}(k) \right] O_{nm}(k) - i \sum_{k''} \left\{ \left[\frac{d}{dk''} \delta_{kk''} \right] \langle nk''|O|mk'\rangle + \langle nk|O|mk''\rangle \left[\frac{d}{dk''} \delta_{k'l''} \right] \right\}. \end{aligned}$$

We now use “integration by parts” to transfer the derivatives of the Kronecker deltas to the matrix elements (a more rigorous would involve converting the sum to an integral and the Kronecker deltas to delta functions before integration). After subsequently summing over k'' we find

$$\langle nk|[x^i, O]|mk'\rangle = \delta_{kk'} \left\{ [\Omega_{nm}(k) - \Omega_{mm}(k)] O_{nm}(k) + i \frac{d}{dk} O_{nm}(k) \right\},$$

which is precisely Eq.(8). Applying this to the linear intraband polarizability Eq.(5) we find

$$\begin{aligned} \alpha_1^{intra}(\omega) &= \frac{e^2}{\hbar} \sum_{n,k,k'} (f_{nk} - f_{nk'}) |x_{nk,nk'}^i|^2 \frac{\omega_{nk',nk}}{\omega_{nk',nk}^2 - \omega^2} \\ &= \frac{e^2}{\hbar^2} \sum_{n,k,k'} \langle nk|[x^i, f(H)]|nk'\rangle \langle nk'|[x^i, H]|nk\rangle \frac{1}{\omega_{nk',nk}^2 - \omega^2}. \end{aligned}$$

Accordingly, we find

$$\alpha_1^{intra}(\omega) = \frac{e^2}{\hbar^2 \omega^2} \sum_{n,k} \frac{df_{nk}}{dk} \frac{dE_{nk}}{dk}. \quad (9)$$

Converting to an integral and using $df/dk = f' \cdot dE/dk$, this expression is seen to be identical to Eq.(6). We now consider $\alpha_2(\omega)$ in the special case of a two-band semiconductor. When only two-band contributions are retained, the general expression Eq.(3) can be reduced to

$$\begin{aligned} \alpha_2(\omega) &= \frac{3e^3}{\hbar^2} \sum_{m \neq n, k, k'} f_{nk} \frac{|x_{nk,mk'}^i|^2 (x_{nk,nk'}^i - x_{mk,mk'}^i) \omega_{mk',nk}^2}{(\omega_{mk',nk}^2 - 4\omega^2)(\omega_{mk',nk}^2 - \omega^2)} \\ &= \frac{3e^3}{\hbar^2 m^2} \sum_{m \neq n, k, k'} f_{nk} \frac{|p_{nk,mk'}|^2 (x_{nk,nk'}^i - x_{mk,mk'}^i)}{(\omega_{mk',nk}^2 - 4\omega^2)(\omega_{mk',nk}^2 - \omega^2)}. \end{aligned}$$

Because the intraband dipole operator has only diagonal elements we can rewrite as the commutator $\lim_{k' \rightarrow k} p_{nk,mk'} (x_{nk,nk'}^i - x_{mk,mk'}^i) = \lim_{k' \rightarrow k} \langle nk|[x^i, p_x]|mk'\rangle$. Thus,

$$\alpha_2(\omega) = \frac{3ie^3}{\hbar^2 m^2} \sum_{m \neq n, k} f_{nk} \frac{p_{nm}(k)(p_{mn})_{,k}}{(\omega_{mn}^2(k) - 4\omega^2)(\omega_{mn}^2(k) - \omega^2)}.$$

in agreement with Ref. [4].

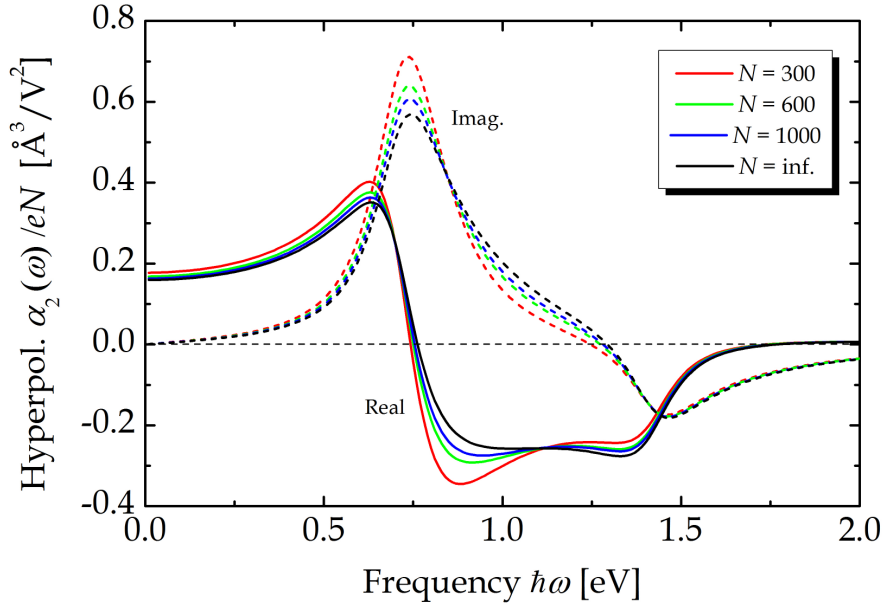


Figure 3. Polymethineamine hyperpolarizability for finite and infinite chains.

The third order response consists of an interband and a mixed term

$$\begin{aligned}
 \alpha_3^{inter}(\omega) &= -\frac{4e^4}{\hbar^3 m^4} \sum_{m \neq n, k, k'} f_{nk} \frac{|p_{nk, mk'}|^4}{\omega_{mk', nk}^3 (\omega_{mk', nk}^2 - 9\omega^2)(\omega_{mk', nk}^2 - \omega^2)} \\
 &= -\frac{4e^4}{\hbar^3 m^4} \sum_{m \neq n, k} f_{nk} \frac{|p_{nm}(k)|^4}{\omega_{mn}^3(k) (\omega_{mn}^2(k) - 9\omega^2)(\omega_{mn}^2(k) - \omega^2)}. \\
 \alpha_3^{mixed}(\omega) &= \frac{4e^4}{\hbar^3 m^2} \sum_{m \neq n, k, k'} f_{nk} \frac{|p_{nk, mk'}|^2 (x_{nk, nk'}^i - x_{mk, mk'}^i)^2 (\omega_{mk', nk}^2 + \omega^2)}{\omega_{mk', nk} (\omega_{mk', nk}^2 - 9\omega^2)(\omega_{mk', nk}^2 - 4\omega^2)(\omega_{mk', nk}^2 - \omega^2)} \\
 &= \frac{4e^4}{\hbar^3 m^2} \sum_{m \neq n, k} f_{nk} \frac{|(p_{mn})_{;k}|^2 (\omega_{mn}^2(k) + \omega^2)}{\omega_{mn}(k) (\omega_{mn}^2(k) - 9\omega^2)(\omega_{mn}^2(k) - 4\omega^2)(\omega_{mn}^2(k) - \omega^2)}.
 \end{aligned}$$

The Velocity Gauge

An alternative approach to avoiding dipole matrix elements is to work in the “velocity gauge”. In this case, the perturbation is $H_1 = (e/m)p_x \mathcal{A} + (e^2/2m)\mathcal{A}^2$. The observable is then the induced current $j = -(e/m)(p_x + e\mathcal{A})$. The current is the time-derivative of the dipole moment $j = -i\omega d$ and the electric field is $\mathcal{E} = i\omega \mathcal{A}$. For the linear response, perturbation theory then shows that

$$\langle j \rangle = \left\{ \frac{2e^2}{\hbar m^2} \sum_{m,n} f_n |p_{nm}|^2 \frac{\omega_{mn}}{\omega_{mn}^2 - \omega^2} - \frac{e^2}{m} \sum_n f_n \right\} \mathcal{A}.$$

It follows that the polarizability is

$$\alpha_1(\omega) = \frac{1}{\omega^2} \left\{ \frac{2e^2}{\hbar m^2} \sum_{m,n} f_n |p_{nm}|^2 \frac{\omega_{mn}}{\omega_{mn}^2 - \omega^2} - \frac{e^2}{m} \sum_n f_n \right\}.$$

To prove the equivalence, we then use

$$\frac{\omega_{mn}}{\omega_{mn}^2 - \omega^2} = \frac{\omega^2}{\omega_{mn}(\omega_{mn}^2 - \omega^2)} + \frac{1}{\omega_{mn}}$$

so that

$$\alpha_1(\omega) = \frac{2e^2}{\hbar m^2} \sum_{m,n} f_n \frac{|p_{nm}|^2}{\omega_{mn}(\omega_{mn}^2 - \omega^2)} + \frac{1}{\omega^2} \left\{ \frac{2e^2}{\hbar m^2} \sum_{m,n} f_n \frac{|p_{nm}|^2}{\omega_{mn}} - \frac{e^2}{m} \sum_n f_n \right\}.$$

The first term is identical to the dipole expression and the last part vanishes if a *complete* set of states is considered. To see this, consider

$$\sum_m \frac{|p_{nm}|^2}{\omega_{mn}} = \frac{1}{2} \sum_m \left\{ \frac{p_{nm}p_{mn}}{\omega_{mn}} - \frac{p_{nm}p_{mn}}{\omega_{nm}} \right\} = \frac{im}{2} \sum_m \{p_{nm}x_{mn} - x_{nm}p_{mn}\} = \frac{im}{2} [p_x, x]_{nn} = \frac{\hbar m}{2}.$$

Hence, the two terms in the curly brackets cancel but only if a complete set of states is included. Otherwise, an additional contribution is found that diverges badly at low frequencies.

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