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▸ Equation Format

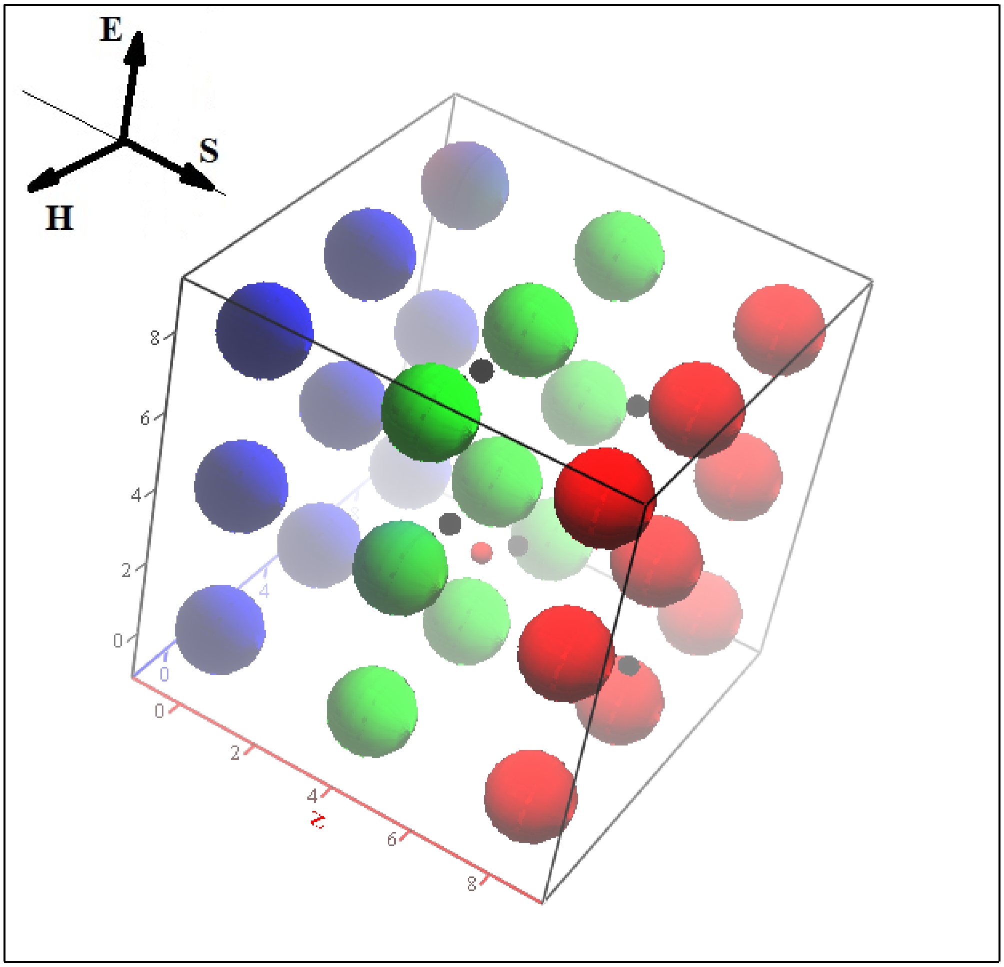
Reference:C:\Users\Franc\new folder\Physical Constants.xmcd

Reference:C:\Users\Franc\new folder\unit vectors.xmcd

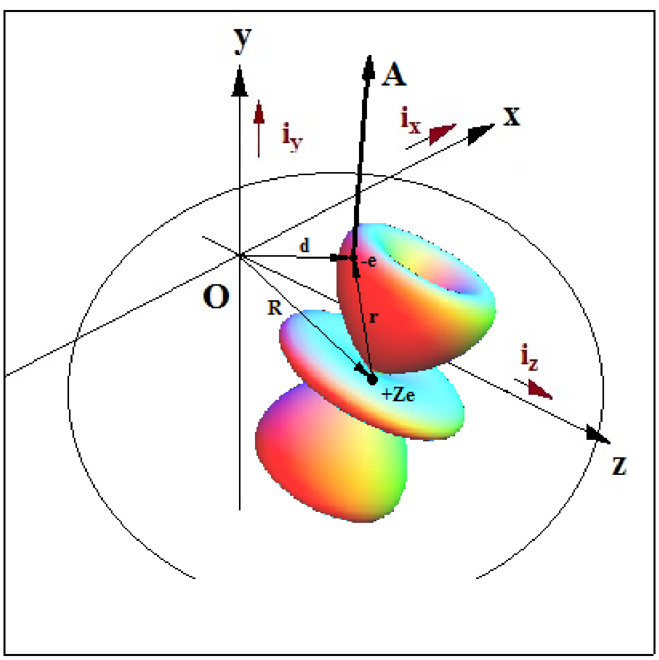
▸ Unit of measure

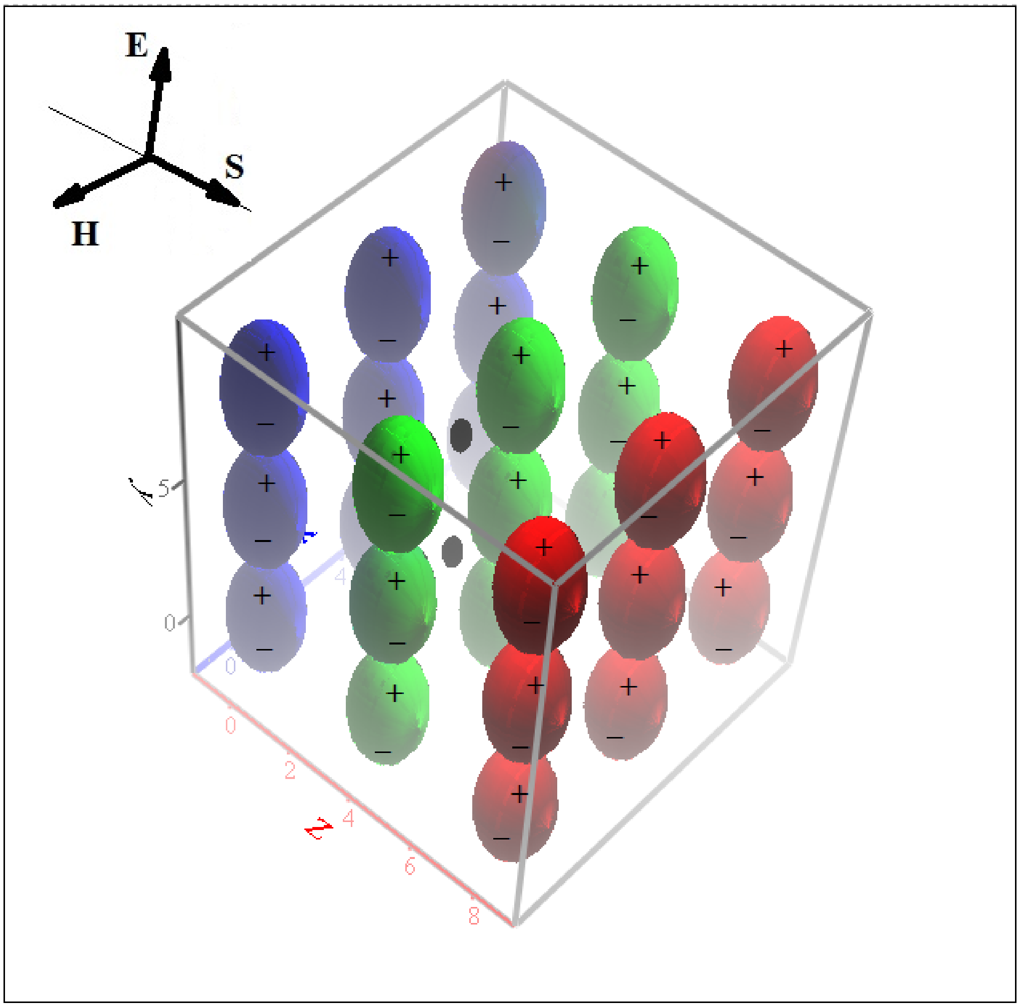
1
INTERACTION EM FIELD-CRYSTAL

Spheres



Dipole approximation





▸ Taylor series of the EM vector potential A (moving at light speed)

▾ Electric field

Since $\nabla \cdot \mathbf{B}(x,y,z,t) = 0$, eq. 6), a necessary and sufficient condition for ***solenoidal fields is***

$$\nabla \cdot \mathbf{V} = 0 \Rightarrow \mathbf{V} = \nabla \times \mathbf{U} \Rightarrow \nabla \cdot (\nabla \times \mathbf{U}) = 0$$

Option 1) so that I can place $\mathbf{B}(x,y,z,t) = \nabla \times \mathbf{A}(x,y,z,t)$ $[\ \mathbf{A}\ ] = \frac{Wb}{m}$ a1)

Option 2) if I choose instead $\mathbf{H}(x,y,z,t) = \nabla \times \mathbf{A}(x,y,z,t)$ then the unit is $[\ \mathbf{A}\ ] =$ Ampère

As a result of the Option 2) $\mathbf{B}(x,y,z,t) = \mu \cdot \nabla \times \mathbf{A}(x,y,z,t)$

Next I would always consider **Option 1)**. Now substitute a1) in the first Maxwell equation, here rewritten:

$$\nabla \times \mathbf{E}(x,y,z,t) = -\frac{\partial}{\partial t}\mathbf{B}(x,y,z,t) \qquad \text{a2)}$$

obtaining: $\nabla \times \mathbf{E}(x,y,z,t) = -\frac{\partial}{\partial t}\left(\nabla \times \mathbf{A}(x,y,z,t)\right)$ a3)

leaving the right hand side free, I have

$$\nabla \times \mathbf{E}(x,y,z,t) + \frac{\partial}{\partial t}\left(\nabla \times \mathbf{A}(x,y,z,t)\right) = 0\cdot\frac{T}{s} = 0\cdot\frac{volt}{m^2} \qquad a4)$$

and collecting the rotor operators, results

$$\nabla \times \left(\mathbf{E}(x,y,z,t) + \frac{\partial}{\partial t}\mathbf{A}(x,y,z,t)\right) = 0\cdot\frac{volt}{m^2} \qquad [\ \mathbf{A}\ ] = \frac{Wb}{m} \qquad a5)$$

Generally if $\nabla \times \mathbf{U} = 0 \Rightarrow \mathbf{U} = -\nabla\varphi$ $\qquad \nabla \times \nabla\varphi = 0$

$\nabla \times \mathbf{V} = 0 \quad \Rightarrow \quad \mathbf{V} = \nabla\varphi$ Lamellar field (conservative and irrotational)

$\mathbf{V}\cdot(\nabla \times \mathbf{V}) = 0$ Composed lamellar field

resulting:

$$\mathbf{E}(x,y,z,t) + \frac{\partial}{\partial t}\mathbf{A}(x,y,z,t) = -\nabla\varphi(x,y,z,t) \qquad a6)$$

Electric field

The electric field is linked to the vector potential by the relation (Electromagnetics: eq. 29)):

$$\frac{volt}{m} \qquad \boxed{\mathbf{E}(\mathbf{r},t) = -\nabla\varphi(\mathbf{r},t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r},t)} \qquad \frac{Wb}{m\cdot s} = 1\cdot\frac{volt}{m} \qquad 3)$$

furthermore the time derivative of the vector potential can be rewritten as the following scalar product:

$$\frac{\partial}{\partial t}\mathbf{A}(\mathbf{r},t) = \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r},t) = \frac{\partial}{\partial \mathbf{r}}\mathbf{A}(\mathbf{r},t)\cdot\frac{\partial}{\partial t}\mathbf{r} = \mathbf{v}\cdot\nabla\mathbf{A}(\mathbf{r},t) \qquad 4)$$

A(r,t) time derivative

where $\mathbf{r}$ is the position, at time t, of the vector potential. Therefore I can write:

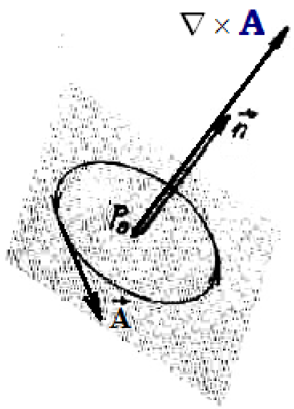
$$\frac{\partial}{\partial t}\mathbf{A}(\mathbf{r},t) = \nabla\mathbf{A}(\mathbf{r},t)\cdot\frac{\partial}{\partial t}\mathbf{r} = \mathbf{v}\cdot\nabla\mathbf{A}(\mathbf{r},t) \qquad 5)$$

unites of measure

the vector $\mathbf{v}$ is the speed of the EM field through the lattice namely slightly less than the light speed c, that is $|\mathbf{v}| = \frac{c}{\eta}$,

where η is the refraction index of the crystal. The propagation direction is that of the wave vector $\mathbf{k}$ with unit vector $\frac{]}{|]}$

orthogonal to $\mathbf{A}(\mathbf{r},t)$. Namely $\mathbf{v} = \frac{c}{\eta}\cdot\frac{\mathbf{k}}{|\mathbf{k}|}$. 6)



$\mathbf{A}\cdot\nabla\times\mathbf{A} = 0$ Composed lamellar field

Option 1) $\mathbf{A}\cdot\mathbf{B} = 0$ **Option 2)** $\mathbf{A}\cdot\mathbf{H} = 0$

$\mathbf{A}$ is orthogonal to $\mathbf{B}$ or $\mathbf{H}$

$\mathbf{S} = \mathbf{E}\times\mathbf{H}$

$\mathbf{E}$ is orthogonal to $\mathbf{H}$ or $\mathbf{B}$ and parallel coplanar to $\mathbf{A}$

Substituting 5) in 3) I get:

$$\mathbf{E}(\mathbf{r},t) = -\nabla\,\varphi(\mathbf{r},t) - \mathbf{v}\cdot\nabla\,\mathbf{A}(\mathbf{r},t) \qquad 7)$$

▸ unites of measure

furthermore, collecting the gradient operators, I can write:

$$\mathbf{E}(\mathbf{r},t) = -\nabla\left(\varphi(\mathbf{r},t) + \mathbf{v}\cdot\mathbf{A}(\mathbf{r},t)\right) = -\nabla\,(\Phi) \qquad 8)$$

so that I can define the scalar potential: $\boxed{\Phi(\mathbf{r},t) = \varphi(\mathbf{r},t) + \mathbf{v}\cdot\mathbf{A}(\mathbf{r},t)}$ 9)

while the potential energy is $U(\mathbf{r},t) = -q_e\cdot\left(\varphi(\mathbf{r},t) + \mathbf{v}\cdot\mathbf{A}(\mathbf{r},t)\right)$ 10)

which is useful to define the Lagrangian.

▾ Lagrange equations system

Lagrangian coordinates for a system with n degree of freedom : position vector $\mathbf{q_i} = \mathbf{r}_i$, i=1,..n, conjugated momenta: $\mathbf{p_i} = m\cdot\mathbf{q'_i}$, i=1,..n,

Kinetic energy : T, Potential energy : U

Lagrangian : $\mathbf{L}(q, q_2, ...q_n, q'_1, q'_{2.n}, ...q', t) = \mathbf{T}(q'_1, q'_2, ...q'_n, t) - \mathbf{U}(q_1, q_2, ...q_n)$

Lagrange equations' system

$$\boxed{\frac{d}{dt}\frac{\partial}{\partial \mathbf{q'_i}}\mathbf{L_i} - \frac{\partial}{\partial \mathbf{q}_i}\mathbf{L_i} = 0} \qquad i = 1, 2, 3 .. n$$

Conjugated momenta can be written as functions of the Lagrangian $\mathbf{p_i} = \frac{\partial}{\partial \mathbf{q'_i}}\mathbf{L}$ $i = 1, 2, 3 .. n$

the kinetic energy as well: $T = \frac{1}{2\cdot m}\cdot\sum_{i=1}^{n}\mathbf{p_i}^2 = \frac{1}{2\cdot m}\cdot\sum_{i=1}^{n}\left(\frac{\partial}{\partial \mathbf{q'_i}}\mathbf{L}\right)^2$

$$T_i = \frac{p_i^2}{2\cdot m} = \frac{p_i\cdot p_i}{2\cdot m} = \frac{p_i\cdot m\cdot q'_i}{2\cdot m} = \frac{p_i\cdot q'_i}{2}$$

$$T = \frac{1}{2}\cdot\sum_{i=1}^{n}\left(p_i\cdot q'_i\right)$$

$$T(q_i) = \frac{m_i\cdot q'^2_i}{2}$$

Finally the Lagrangian is: $$L = \frac{1}{2}\cdot\sum_{i=1}^{n}\left(p_i\cdot q'_i\right) - U$$

Lagrange equations system

The Lagrangian within the Gauss System

$$L_i = \frac{m\cdot q'^2_i}{2} + \frac{Q^2\cdot A^2}{2\cdot c^2\cdot m} - \frac{Q\cdot A\cdot q'_i}{c} - Q\cdot V(q) \qquad \text{Gauss System}$$

For one electron ($Q=-q_e$) in a crystal lattice:

$$L = \frac{m\cdot q'^2}{2} + q_e\cdot V(q) + \frac{q_e^2\cdot A^2}{2\cdot c^2\cdot m} + \frac{q_e\cdot A\cdot q'}{c} \qquad \text{Gauss System}$$

The Lagrangian within the Gauss System

Consider as Lagrangian variables, the position $q = r$, and $p = m\cdot q'$, $q' = v$.

Electric potential at q: $V(q) = \varphi(q,t)$, while the potential energy is $U(q,t) = -q_e\cdot\left(\varphi(q,t) + q'\cdot A(q,t)\right)$

The Lagrangian of the system I deal with is:

$$L(q,q',t) = \frac{1}{2}\cdot p\cdot q' + q_e\cdot V(q) + q_e\cdot q'\cdot A(q,t) \qquad q_e = 1.602\times 10^{-19}\,C \qquad 11)$$

For one atomic electron, the Lagrange equation is: $$\frac{d}{dt}\frac{\partial}{\partial q'}L(q,q',t) - \frac{\partial}{\partial q}L(q,q',t) = 0 \qquad 12)$$

Remark:

If I define the new Lagrangian $L_1(q,q',t) = L(q,q',t) + f(t)$, the differential equation doesn't varies, indeed:

$$\frac{d}{dt}\frac{\partial}{\partial q'}\left(L(q) + f(t)\right) - \frac{\partial}{\partial q}\left(L(q) + f(t)\right) = \frac{d}{dt}\frac{\partial}{\partial q'}L(q) - \frac{\partial}{\partial q}L(q) \qquad 13)$$

because: $\frac{\partial}{\partial q'}f(t) = 0 \qquad \frac{\partial}{\partial q}f(t) = 0$

Accordingly I can add, to the Lagrangian L, the arbitrary, but useful term, $-q_e\cdot\frac{\partial}{\partial t}\left(q\cdot A(q,t)\right)$ without affecting the analysis of the dynamic behavior of the system.

I can write: $$L_1(q,q',t) = L(q,q',t) - q_e\cdot\frac{\partial}{\partial t}\left(q\cdot A(q,t)\right) \qquad 14)$$

after a substitution of 11) $$L_1(q,q',t) = \frac{1}{2}\cdot p\cdot q' + q_e\cdot V(q) + q_e\cdot q'\cdot A(q,t) - q_e\cdot\frac{\partial}{\partial t}\left(q\cdot A(q,t)\right) \qquad 15)$$

the partial derivatives is $\frac{\partial}{\partial t}(\mathbf{q}\cdot\mathbf{A}(\mathbf{q},t)) = \mathbf{A}(\mathbf{q},t)\cdot\mathbf{q'} + \mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)$ 16)

which substituted in 15) gives:

$$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} + q_e\cdot V(\mathbf{q}) + q_e\cdot\mathbf{q'}\cdot\mathbf{A}(\mathbf{q},t) - q_e\cdot\left(\mathbf{A}(\mathbf{q},t)\cdot\mathbf{q'} + \mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)\right) \quad 17)$$

or $$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} + q_e\cdot V(\mathbf{q}) + q_e\cdot\mathbf{q'}\cdot\mathbf{A}(\mathbf{q},t) - q_e\cdot\mathbf{A}(\mathbf{q},t)\cdot\mathbf{q'} - q_e\cdot\mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t) \quad 18)$$

simplifying I get: $$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} + q_e\cdot V(\mathbf{q}) - q_e\cdot\mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t) \quad 19)$$

Consider an EM ***plane wave*** propagating in the crystal along a path aligned with the optical axis z. This implies that the electromagnetic field is orthogonal to the z propagation direction. As a result I indicate the electric field as transversal:

$$\mathbf{E_T}(\mathbf{q},t) = -\nabla V(\mathbf{q},t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)$$

which, for a constant potential V, simplify to:

$$\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t) = -\mathbf{E_T}(\mathbf{q},t)$$ transversal electric field intensity 20)

$$\mathbf{E_T}(\mathbf{q},t) = E_x(x,y,z,t)\cdot\mathbf{i_x} + E_y(x,y,z,t)\cdot\mathbf{i_y}$$

the Lagrangian 19), finally, is: $$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} + q_e\cdot V(\mathbf{q}) + q_e\cdot\mathbf{q}\cdot\mathbf{E_T}(\mathbf{q},t) \quad 21)$$

Time harmonic Field decomposition

for n electrons I get: $$\mathbf{L_1} = \frac{1}{2}\cdot\sum_{i=1}^{n}(\mathbf{p_i}\cdot\mathbf{q'_i}) + q_e\cdot\sum_{i=1}^{n}V(\mathbf{q_i}) + q_e\cdot\sum_{i=1}^{n}(\mathbf{q_i}\cdot\mathbf{E_T}(\mathbf{q},t)) \quad 22)$$

The modified Lagrangian correspondingly is:

$$\mathbf{L_1} = \sum_{i=1}^{n}\left[\frac{1}{2}\cdot(\mathbf{p_i}\cdot\mathbf{q'_i}) + q_e\cdot V(\mathbf{q_i}) + q_e\cdot\mathbf{q_i}\cdot\mathbf{E_T}(\mathbf{q},t)\right] \quad 23)$$

For one particle with electric charge Q, I get:

$$U(\mathbf{q},t) = Q\cdot(\varphi(\mathbf{q},t) + \mathbf{q'}\cdot\mathbf{A}(\mathbf{q},t))$$

$$\mathbf{L}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - Q\cdot V(\mathbf{q}) - Q\cdot\mathbf{q'}\cdot\mathbf{A}(\mathbf{q},t)$$

$$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \mathbf{L}(\mathbf{q},\mathbf{q'},t) + Q\cdot\frac{\partial}{\partial t}(\mathbf{q}\cdot\mathbf{A}(\mathbf{q},t))$$

$$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - Q\cdot V(\mathbf{q}) - Q\cdot\mathbf{q'}\cdot\mathbf{A}(\mathbf{q},t) + Q\cdot\frac{\partial}{\partial t}(\mathbf{q}\cdot\mathbf{A}(\mathbf{q},t))$$

$$\frac{\partial}{\partial t}(\mathbf{q}\cdot\mathbf{A}(\mathbf{q},t)) = \mathbf{A}(\mathbf{q},t)\cdot\mathbf{q'} + \mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)$$

$$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - Q\cdot V(\mathbf{q}) - Q\cdot\mathbf{q'}\cdot\mathbf{A}(\mathbf{q},t) + Q\cdot\left(\mathbf{A}(\mathbf{q},t)\cdot\mathbf{q'} + \mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)\right)$$

$$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - Q\cdot V(\mathbf{q}) - Q\cdot\mathbf{q'}\cdot\mathbf{A}(\mathbf{q},t) + Q\cdot\mathbf{A}(\mathbf{q},t)\cdot\mathbf{q'} + Q\cdot\mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)$$

$$\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - Q\cdot V(\mathbf{q}) + Q\cdot\mathbf{q}\cdot\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)$$

$$\boxed{\mathbf{E_T}(\mathbf{q},t) = -\nabla V(\mathbf{q},t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t)}$$

which, for a constant potential V, simplify to:

$$\frac{\partial}{\partial t}\mathbf{A}(\mathbf{q},t) = -\mathbf{E_T}(\mathbf{q},t)$$

$$\mathbf{E_T}(\mathbf{q},t) = E_x(x,y,z,t)\cdot\mathbf{i_x} + E_y(x,y,z,t)\cdot\mathbf{i_y} \qquad E_z(x,y,z,t) = 0$$

$$\boxed{\mathbf{L_1}(\mathbf{q},\mathbf{q'},t) = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - Q\cdot V(\mathbf{q}) - Q\cdot\mathbf{q}\cdot\mathbf{E_T}(\mathbf{q},t)}$$

for n particles with electric charge Q, I get:

$$\boxed{\mathbf{L_1} = \sum_{i=1}^{n}\left[\frac{1}{2}\cdot(\mathbf{p_i}\cdot\mathbf{q'_i}) - Q\cdot V(\mathbf{q_i}) - Q\cdot\mathbf{q_i}\cdot\mathbf{E_T}(\mathbf{q},t)\right]}$$

Hamiltonian's calculation

Hamilton equations

Classical Hamilton equations

Kinetic energy : T
Potential energy : U
Hamiltonian :

$$\mathbf{H}(q_1, q_2, ...q_n, p_1, p_2, ...p_n, t) = T + U = 2\cdot T - \mathbf{L}(q_1, q_2, ...q_n, q'_1, q'_{2.n}, ...q', t)$$

$$\mathbf{H} = \frac{1}{2}\cdot\sum_{i=1}^{n}(\mathbf{p_i}\cdot\mathbf{q'_i}) + \mathbf{U}$$

$$\mathbf{L} = \frac{1}{2}\cdot\sum_{i=1}^{n}(\mathbf{p_i}\cdot\mathbf{q'_i}) - \mathbf{U}$$

$$\mathbf{H} = 2\cdot T - L = 2\cdot\frac{1}{2}\cdot\sum_{i=1}^{n}(\mathbf{p_i}\cdot\mathbf{q'_i}) - \mathbf{L} = \sum_{i=1}^{n}(\mathbf{p_i}\cdot\mathbf{q'_i}) - \mathbf{L} = \sum_{i=1}^{n}\left(\mathbf{q'_i}\cdot\frac{\partial}{\partial \mathbf{q'_i}}\mathbf{L}\right) - \mathbf{L}$$

The conjugated momenta can be written as functions of the Lagrangian $\mathbf{p_i} = \frac{\partial}{\partial \mathbf{q'_i}}\mathbf{L}$ $i = 1, 2, 3 .. n$

$$\mathbf{H} = \sum_{i=1}^{n}(\mathbf{p_i}\cdot\mathbf{q'_i}) - \mathbf{L} = \sum_{i=1}^{n}\left(\mathbf{q'_i}\cdot\frac{\partial}{\partial \mathbf{q'_i}}\mathbf{L}\right) - \mathbf{L}$$

$$\mathbf{H} = \sum_{i=1}^{n}\left(\mathbf{q'_i}\cdot\frac{\partial}{\partial \mathbf{q'_i}}\mathbf{L}\right) - \mathbf{L}$$

Hamilton equations: $\mathbf{q'}_i = \frac{\partial}{\partial \mathbf{p}_i}\mathbf{H}$ $i = 1, 2, 3 .. n$

$$\mathbf{p'}_i = -\frac{\partial}{\partial \mathbf{q}_i}\mathbf{H}$$

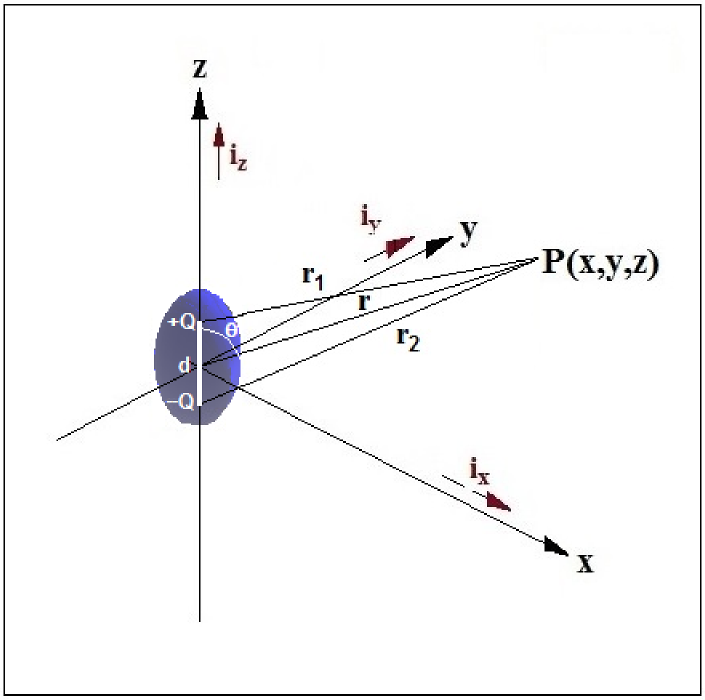
Hamilton equations

For one electron, the Hamiltonian is: $\mathbf{H} = \mathbf{p}\cdot\mathbf{q'} - \mathbf{L_1} = \mathbf{p}\cdot\mathbf{q'} - \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - q_e\cdot V(\mathbf{q}) - q_e\cdot\mathbf{q}\cdot\mathbf{E_T}(\mathbf{q}, t)$ 24)

namely: $\mathbf{H} = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - q_e\cdot V(\mathbf{q}) - q_e\cdot\mathbf{q}\cdot\mathbf{E_T}(\mathbf{q}, t)$ 25)

The effect of the electromagnetic field acting on the crystal, is the polarization of each atom or molecule part of it.

The electric dipole



$Q := q_e$

$Q = 1.602 \times 10^{-19} C$

$$V_1(P) = \frac{Q}{4\cdot\pi\cdot\varepsilon\cdot r_1} \qquad V_2(P) = \frac{-Q}{4\cdot\pi\cdot\varepsilon\cdot r_2} \qquad r_1 = r - \frac{d}{2}\cdot\cos(\theta) \qquad r_2 = r + \frac{d}{2}\cdot\cos(\theta)$$

Resulting Electric potential in P: $V(P) = V_1 + V_2 = \frac{Q}{4\cdot\pi\cdot\varepsilon\cdot r_1} + \frac{-Q}{4\cdot\pi\cdot\varepsilon\cdot r_2} = \frac{Q}{4\cdot\pi\cdot\varepsilon}\cdot\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$

$$V(r,\theta) = \frac{Q}{4\cdot\pi\cdot\varepsilon}\cdot\left(\frac{1}{r - \frac{d}{2}\cdot\cos(\theta)} - \frac{1}{r + \frac{d}{2}\cdot\cos(\theta)}\right) = \frac{Q}{4\cdot\pi\cdot\varepsilon\cdot r^2}\cdot\frac{\left(r + \frac{d}{2}\cdot\cos(\theta) - r + \frac{d}{2}\cdot\cos(\theta)\right)}{\left[1 - \left(\frac{d}{2\cdot r}\cdot\cos(\theta)\right)^2\right]}$$

$$\frac{Q}{4\cdot\pi\cdot\varepsilon\cdot r^2}\cdot\frac{\left(r + \frac{d}{2}\cdot\cos(\theta) - r + \frac{d}{2}\cdot\cos(\theta)\right)}{\left[1 - \left(\frac{d}{2\cdot r}\cdot\cos(\theta)\right)^2\right]} = \frac{Q}{4\cdot\pi\cdot\varepsilon\cdot r^2}\cdot\frac{d\cdot\cos(\theta)}{1 - \left(\frac{d}{2\cdot r}\cdot\cos(\theta)\right)^2}$$

$$x = \frac{d}{2\cdot r}$$

$$\frac{Q}{2\cdot\pi\cdot\varepsilon\cdot r}\cdot\frac{d\cdot\cos(\theta)}{2\cdot r\cdot\left[1 - \left(\frac{d}{2\cdot r}\cdot\cos(\theta)\right)^2\right]} = \frac{Q}{2\cdot\pi\cdot\varepsilon\cdot r}\cdot\frac{x\cdot\cos(\theta)}{\left[1 - (x\cdot\cos(\theta))^2\right]}$$

$x := x \quad \theta := \theta$

$$\frac{x\cdot\cos(\theta)}{\left[1 - (x\cdot\cos(\theta))^2\right]} \text{ series}, x, 2 \rightarrow x\cdot\cos(\theta)$$

$$\left[\frac{Q}{2\cdot\pi\cdot\varepsilon\cdot r}\cdot\frac{x\cdot\cos(\theta)}{\left[1 - (x\cdot\cos(\theta))^2\right]}\right] \approx \left(\frac{Q}{2\cdot\pi\cdot\varepsilon\cdot r}\cdot x\cdot\cos(\theta)\right)$$

$$\frac{Q}{2\cdot\pi\cdot\varepsilon\cdot r}\cdot\frac{d}{2\cdot r}\cdot\cos(\theta) = \frac{Q}{4\cdot\pi\cdot\varepsilon\cdot r^2}\cdot d\cdot\cos(\theta)$$

$$V(r,\theta) \approx \left(\frac{Q\cdot d}{4\cdot\pi\cdot\varepsilon\cdot r^2}\cdot\cos(\theta)\right) \qquad r \gg d$$

$Q := q_e \qquad d := 0.1\cdot\mu m$

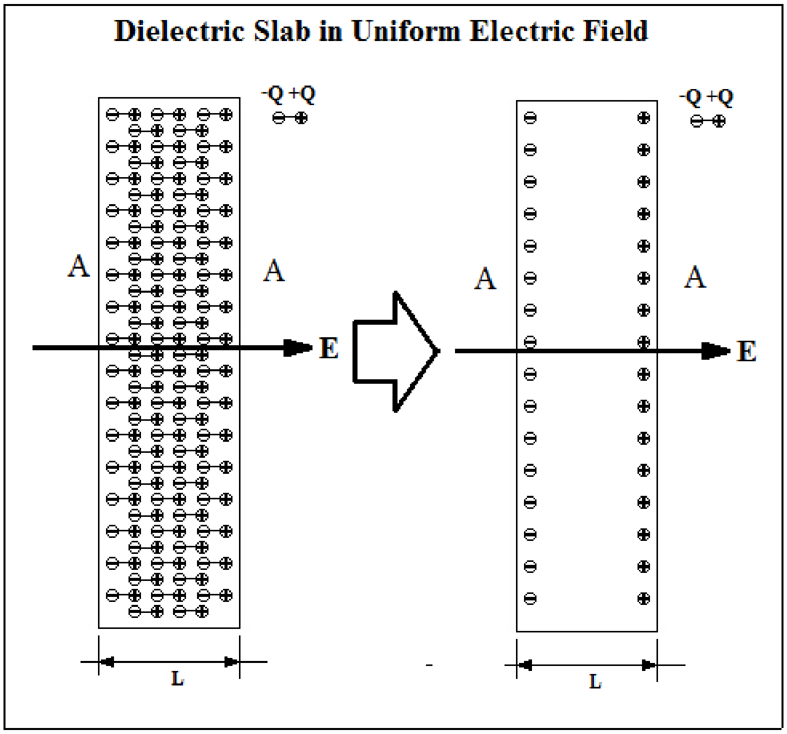
$r := r \qquad \theta := \theta \qquad Q := Q \qquad d := d \qquad \varepsilon := \varepsilon \qquad \boldsymbol{\mu} := Q\cdot d\cdot\mathbf{i_z}$

$$\boldsymbol{\mu} := \boldsymbol{\mu} \qquad \varepsilon := \varepsilon_0 \qquad V_d(r,\theta) := \frac{|\boldsymbol{\mu}|}{4\cdot\pi\cdot\varepsilon\cdot r^2}\cdot\cos(\theta)$$

Electric field in P: $\mathbf{E} = -\nabla V_d(r,\theta) = -\frac{\partial}{\partial r}V_d(r,\theta)\cdot\mathbf{e_\rho} - \frac{1}{r}\cdot\frac{\partial}{\partial\theta}V_d(r,\theta)\cdot\mathbf{e_\theta} \qquad \mathbf{e_\rho} \rightarrow \begin{pmatrix}1\\0\\0\end{pmatrix} \qquad \mathbf{e_\theta} \rightarrow \begin{pmatrix}0\\1\\0\end{pmatrix}$

$$\mathbf{E_d}(r,\theta) := -\frac{\partial}{\partial r}V_d(r,\theta)\cdot\mathbf{e_\rho} - \frac{1}{r}\cdot\frac{\partial}{\partial\theta}V_d(r,\theta)\cdot\mathbf{e_\theta} \rightarrow \begin{pmatrix}\frac{\cos(\theta)\cdot|\boldsymbol{\mu}|}{2\cdot\pi\cdot r^3\cdot\varepsilon_0}\\ \frac{\sin(\theta)\cdot|\boldsymbol{\mu}|}{4\cdot\pi\cdot r^3\cdot\varepsilon_0}\\ 0\end{pmatrix} \qquad \mathbf{E_d}(r,\theta) \rightarrow \begin{pmatrix}\frac{\cos(\theta)\cdot|\boldsymbol{\mu}|}{2\cdot\pi\cdot r^3\cdot\varepsilon_0}\\ \frac{\sin(\theta)\cdot|\boldsymbol{\mu}|}{4\cdot\pi\cdot r^3\cdot\varepsilon_0}\\ 0\end{pmatrix}$$

Electric field due to the dipole only $\mathbf{E_d}(r,\theta) \rightarrow \begin{pmatrix}\frac{\cos(\theta)\cdot|\boldsymbol{\mu}|}{2\cdot\pi\cdot r^3\cdot\varepsilon_0}\\ \frac{\sin(\theta)\cdot|\boldsymbol{\mu}|}{4\cdot\pi\cdot r^3\cdot\varepsilon_0}\\ 0\end{pmatrix}$



The polarization is $P = \frac{Q \cdot L}{V} = \frac{Q \cdot L}{A \cdot L} = \frac{Q}{A} = \rho_A$ surface charge density

The electric dipole

Define the *dipole moment* as: $\boldsymbol{\mu} = -q_e \cdot \mathbf{d}$, which, substituted in the previous equation 25), yields:

$$\mathbf{H} = \frac{1}{2} \cdot \mathbf{p} \cdot \mathbf{q'} - q_e \cdot V(\mathbf{q}) + \boldsymbol{\mu} \cdot \mathbf{E_T}(\mathbf{q}, t) \qquad 27)$$

($\boldsymbol{\mu}$ and $\mathbf{E_T}$ are aligned only for isotropic materials) In this relation I distinguish three Hamiltonians:

Unperturbed Hamiltonian: $$\mathbf{H_0} = \frac{1}{2} \cdot \mathbf{p} \cdot \mathbf{q'} \qquad 28)$$

Relaxation Hamiltonian: $$\mathbf{H_r} = -q_e \cdot V(\mathbf{q}) \qquad 29)$$

Interaction Hamiltonian: $$\mathbf{H_1} = \boldsymbol{\mu} \cdot \mathbf{E_T}(\mathbf{q}, t) \qquad 30)$$

that is: $$\mathbf{H} = \mathbf{H_0} + \mathbf{H_1} + \mathbf{H_r} \qquad 31)$$

Define the dipole moment ***for n atoms or molecules*** as: $$\boldsymbol{\mu}_1 = -\sum_{i=1}^{n} \left(q_{e_i} \cdot \mathbf{d}_i\right) \qquad (C \cdot m) \qquad 32)$$

So that the Hamiltonian is:

$$\mathbf{H} = \sum_{i=1}^{n} \left(\frac{1}{2} \cdot \mathbf{p_i} \cdot \mathbf{q'_i}\right) - \sum_{i=1}^{n} \left(q_e \cdot V(\mathbf{q_i})\right) + \mu_1 \cdot \mathbf{E_T}(\mathbf{q}, t) \quad 33)$$

the resulting electric potential energy is $q_e \cdot V(\mathbf{q_1}, \mathbf{q_2}, .., \mathbf{q_n}) = \sum_{i=1}^{n} \left(q_e \cdot V(\mathbf{q_i})\right)$

that is: $$\boxed{\mathbf{H} = \frac{1}{2} \cdot \sum_{i=1}^{n} \left(\mathbf{p_i} \cdot \mathbf{q'_i}\right) - q_e \cdot V(\mathbf{q_1}, \mathbf{q_2}, .., \mathbf{q_n}) + \mu_1 \cdot \mathbf{E_T}(\mathbf{q}, t)} \quad 34)$$

Quadrupole approximation of the vector potential

I Rewrite the Taylor series of the vector potential but now I trunk the series to the first order term:

$$\mathbf{A}(\mathbf{d}, t) = \mathbf{A}(\mathbf{r} + \mathbf{r}, t) = \left[\mathbf{A}(\mathbf{r}, t) + \sum_{k=1}^{\infty} \left[\frac{1}{k!} \cdot (\mathbf{r} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right]^k\right] \approx \left[\mathbf{A}(\mathbf{r}, t) + (\mathbf{r} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right] \quad 35)$$

$$[\ \mathbf{A}\ ] = \frac{Wb}{m}$$

namely: $$\mathbf{A}(\mathbf{d}, t) = \mathbf{A}(\mathbf{r} + \mathbf{r}, t) \approx \left[\mathbf{A}(\mathbf{r}, t) + (\mathbf{r} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right] \quad 36)$$

then I substitute it in the equation of the electric field 3) namely:

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

$$\mathbf{E}(\mathbf{r}, t) = -\nabla \left[\Phi(\mathbf{r}, t) + \mathbf{v} \cdot \left[\mathbf{A}(\mathbf{r}, t) + (\mathbf{r} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right]\right] = -\nabla\ (U) \quad 37)$$

$$\boxed{\Phi_1(\mathbf{r}, t) = \Phi(\mathbf{r}, t) + \mathbf{v} \cdot \left[\mathbf{A}(\mathbf{r}, t) + (\mathbf{r} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right]} \quad 38)$$

Scalar potential $$\Phi(\mathbf{r}, t) + \mathbf{v} \cdot \left[\mathbf{A}(\mathbf{r}, t) + (\mathbf{r} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right] \quad 39)$$

potential energy $$U(\mathbf{r}, t) = -q_e \cdot \Phi_1 = -q_e \cdot \left[\Phi(\mathbf{r}, t) + \mathbf{v} \cdot \left[\mathbf{A}(\mathbf{r}, t) + (\mathbf{r} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right]\right] \quad 40)$$

The Lagrangian of n particles is:

$$\boxed{\mathbf{L} = \frac{1}{2} \cdot \sum_{i=1}^{n} \left(\mathbf{p_i} \cdot \mathbf{q'_i}\right) - \mathbf{U}} \quad 41)$$

($\mathbf{q}$ is the vector position and q_e the electron charge)

The Lagrangian of the system I deal with is:

$$V(\mathbf{q}) = \Phi(x, y, z, t) \quad \mathbf{L}(\mathbf{q}, \mathbf{q'}, t) = \frac{1}{2} \cdot \mathbf{p} \cdot \mathbf{q'} + q_e \cdot V(\mathbf{q}) - q_e \cdot \mathbf{q'} \cdot \left[\mathbf{A}(\mathbf{r}, t) + (\mathbf{q} \cdot \nabla) \cdot \mathbf{A}(\mathbf{r}, t)\right] \qquad \mathbf{q} = \mathbf{r} \quad 42)$$

$$\mathbf{q}\cdot\nabla = (x\cdot\mathbf{i_x} + y\cdot\mathbf{i_y} + z\cdot\mathbf{i_z})\cdot\left(\mathbf{i_x}\cdot\frac{\partial}{\partial x} + \mathbf{i_y}\cdot\frac{\partial}{\partial y} + \mathbf{i_z}\cdot\frac{\partial}{\partial z}\right) = x\cdot\frac{\partial}{\partial x} + y\cdot\frac{\partial}{\partial y} + z\cdot\frac{\partial}{\partial z} \quad 43)$$

$$(\mathbf{q}\cdot\nabla)\cdot\mathbf{A} = \left(x\cdot\frac{\partial}{\partial x} + y\cdot\frac{\partial}{\partial y} + z\cdot\frac{\partial}{\partial z}\right)\cdot\mathbf{A} \quad 44)$$

$$\left(x\cdot\frac{\partial}{\partial x} + y\cdot\frac{\partial}{\partial y} + z\cdot\frac{\partial}{\partial z}\right)\cdot\mathbf{A} = \left(x\cdot\frac{\partial}{\partial x}A_x + y\cdot\frac{\partial}{\partial y}A_x + z\cdot\frac{\partial}{\partial z}A_x\right)\cdot\mathbf{i_x} \ldots$$
$$+ \left(x\cdot\frac{\partial}{\partial x}A_y + y\cdot\frac{\partial}{\partial y}A_y + z\cdot\frac{\partial}{\partial z}A_y\right)\cdot\mathbf{i_y} \ldots$$
$$+ \left(x\cdot\frac{\partial}{\partial x}A_z + y\cdot\frac{\partial}{\partial y}A_z + z\cdot\frac{\partial}{\partial z}A_z\right)\cdot\mathbf{i_z}$$

$$\boxed{\mathbf{H} = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - q_e\cdot V(\mathbf{q}) - \mu\cdot\mathbf{E_T}(\mathbf{r},t) - \mathbf{M}\cdot\mathbf{B} + \frac{1}{2}\cdot q_e\cdot\mathbf{q}\cdot(\mathbf{q}\cdot\nabla)\cdot\mathbf{E} + \frac{{q_e}^2}{8\cdot m_e}\cdot(\mathbf{q}\times\mathbf{B})^2} \quad 45)$$

Magnetic Dipole moment $\mathbf{M} = \frac{-q_e}{2\cdot m_e}\cdot\mathbf{q}\times\mathbf{B}$ due to the magnetic interaction. 46)

Conjugated moment $\mathbf{p} = m_e\cdot\mathbf{q'} + q_e\cdot(\mathbf{q}\times\mathbf{B})$ 47)

Quadrupole term $\frac{1}{2}\cdot q_e\cdot\mathbf{q}\cdot(\mathbf{q}\cdot\nabla)\cdot\mathbf{E}$ 48)

Diamagnetic interaction (quadratic) $\frac{{q_e}^2}{8\cdot m_e}\cdot(\mathbf{q}\times\mathbf{B})^2$ 49)

The term $-\mu\cdot\mathbf{E_T}(\mathbf{q},t) - \mathbf{M}\cdot\mathbf{B}$, considering the maximum values, I find: $|\mu\cdot\mathbf{E_T}| = q_e\cdot|\mathbf{q}|\cdot|\mathbf{E_T}|$,

$$|\mathbf{M}\cdot\mathbf{B}| = \frac{q_e}{2\cdot m}\cdot|\mathbf{r}|\cdot m\cdot|\mathbf{r'}|\cdot|\mathbf{B}| = \frac{q_e}{2}\cdot|\mathbf{r}|\cdot|\mathbf{r'}|\cdot|\mathbf{B}|.$$

Furthermore $\frac{|\mathbf{M}\cdot\mathbf{B}|}{|\mu\cdot\mathbf{E_T}|} = \frac{\left(\frac{q_e}{2}\cdot|\mathbf{q}|\cdot|\mathbf{q'}|\cdot|\mathbf{B}|\right)}{(q_e\cdot|\mathbf{q}|\cdot|\mathbf{E_T}|)} = \frac{|\mathbf{q'}|}{2}\cdot\frac{|\mathbf{B}|}{|\mathbf{E_T}|} = \frac{|\mathbf{q'}|}{2}\cdot\frac{\eta}{c}$, but $|\mathbf{q'}| \ll \left(\frac{c}{\eta}\right) \Rightarrow \left[\left(\frac{\eta\cdot|\mathbf{q'}|}{c}\right) \ll 1\right]$,

so that:

$$|\mathbf{M}\cdot\mathbf{B}| \ll |\mu\cdot\mathbf{E_T}|. \quad 50)$$

Finally I can write the classical Hamiltonian:

$$\mathbf{H} \approx \left(\frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - q_e\cdot V(\mathbf{q}) - \mu\cdot\mathbf{E_T}(\mathbf{q},t)\right) \quad 51)$$

namely, for $|\mathbf{q'}| \ll \left(\frac{c}{\eta}\right)$ is acceptable the dipole approximation without taking into account of the magnetism.

I look for the corresponding quantum-mechanical Hamiltonian.

QM Hamiltonian operator

Given the classical Hamiltonian $\mathbf{H} = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - q_e\cdot V(\mathbf{q}) - \mu\cdot\mathbf{E_T}(\mathbf{q},t)$ 51')

with the following substitution rules:

Quantization rules 52)

Classical Operator		Quantized Operator acting on kets or eigenfunctions
$\mathbf{p}$	$\leftrightarrow$	$-j\cdot\hbar\cdot\nabla$
$\mathbf{L}$	$\leftrightarrow$	$-j\cdot\hbar\cdot\mathbf{r}\times\nabla$,
$\mathbf{p}^2$	$\leftrightarrow$	$-\hbar^2\cdot\Delta$,
$\frac{\mathbf{p}\cdot\mathbf{q'}}{2} = \frac{\mathbf{p}^2}{2\cdot m}$	$\leftrightarrow$	$\frac{-\hbar^2}{2\cdot m}\cdot\Delta$,
Energy E	$\leftrightarrow$	$j\cdot\hbar\cdot\frac{\partial}{\partial t}$,
$\mathbf{l}^2 = (\mathbf{r}\times\mathbf{p})\cdot(\mathbf{r}\times\mathbf{p}) = r^2\cdot\left(\mathbf{p}^2 - p_r^2\right)$	$\leftrightarrow$	$r^2\cdot\left[-\hbar^2\cdot\Delta + \hbar^2\cdot\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\right]$ Sph. coord.
$\mathbf{r}\cdot\mathbf{p}$	$\leftrightarrow$	$-j\cdot\hbar\cdot r\cdot\frac{\partial}{\partial r} = -j\cdot\hbar\cdot r\cdot\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)$ Sph. coord.
A is the vector potential $\mathbf{A}\cdot\mathbf{p}$	$\leftrightarrow$	$\frac{j\cdot\hbar}{2}\cdot(\nabla\bullet\mathbf{A} + \mathbf{A}\cdot\nabla)$.

I get the quantized Hamiltonian: substitute to each classical operator the one given by the table of the correspondences (at first only the energy E).

Classical mechanical energy $E = T + U = H$,

In QM, E and H are operators acting on a ket: $\mathbf{E}\,|\,\Psi > = \mathbf{H}\,|\,\Psi >$. Namely, applying the previous substitutions rule I get:

the Hamiltonian $H = \frac{1}{2}\cdot\mathbf{p}\cdot\mathbf{q'} - q_e\cdot V(\mathbf{q}) - \mu\cdot\mathbf{E_T}(\mathbf{q},t) \leftrightarrow \mathbf{H} = \frac{-\hbar^2}{2\cdot m}\cdot\Delta - q_e\cdot V(\mathbf{q}) - \boldsymbol{\mu}\cdot\mathbf{E_T}(\mathbf{q},t)$

where $\boldsymbol{\mu}$ is the unknown linear operator corresponding to the vector dipole moment.

Resulting Hamiltonian operator: $\boxed{\mathbf{H} = \frac{-\hbar^2}{2\cdot m}\cdot\Delta - q_e\cdot V(\mathbf{q}) - \boldsymbol{\mu}\cdot\mathbf{E_T}(\mathbf{q},t)}$ 53)

Hamiltonian for macroscopic systems and small interactions close to equilibrium.

I distinguish three partial Hamiltonian:

$$\mathbf{H} = \mathbf{H_0} + \mathbf{H_{int}} + \mathbf{H_r} \quad 54)$$

Unperturbed Hamiltonian $\mathbf{H_0}$

Interaction Hamiltonian $\mathbf{H_{int}}$ 55)

Relaxation Hamiltonian $\mathbf{H_r}$

Unperturbed Hamiltonian $\mathbf{H_0} = \frac{-\hbar^2}{2 \cdot m} \cdot \Delta$ 56)

Interaction Hamiltonian $\mathbf{H_{int}} = \boldsymbol{\mu} \cdot \mathbf{E_T}(\mathbf{q}, t)$ 57)

Relaxation Hamiltonian $\mathbf{H_r} = q_e \cdot V(\mathbf{q})$ 58)

Finally after a substitution in eq $j \cdot \hbar \cdot \frac{\partial}{\partial t} | \ \Psi > = \mathbf{H} | \ \Psi >$, I obtain the ***Schrödinger equation of motion:***

$$j \cdot \hbar \cdot \frac{\partial}{\partial t} | \ \Psi_k > = \left(\frac{-\hbar^2}{2 \cdot m} \cdot \Delta - q_e \cdot V(\mathbf{q}) - \boldsymbol{\mu} \cdot \mathbf{E_T}(\mathbf{q}, t) \right) | \ \Psi_k > \quad 59)$$

If the system is in a stationary state of energy $E_k = \hbar \cdot \omega_k$, with $| \ \Psi_k(\mathbf{q}, t) > = e^{\frac{-j}{\hbar} \cdot E_k \cdot t} | \ \psi_k(\mathbf{q}) >$, substituting in the previous equation, I get:

$$j \cdot \hbar \cdot \frac{\partial}{\partial t} e^{\frac{-j}{\hbar} \cdot E_k \cdot t} | \ \psi_k(\mathbf{q}) > = \left(\frac{-\hbar^2}{2 \cdot m} \cdot \Delta - q_e \cdot V(\mathbf{q}) - \boldsymbol{\mu} \cdot \mathbf{E_T}(\mathbf{q}, t) \right) e^{\frac{-j}{\hbar} \cdot E_k \cdot t} | \ \psi_k(\mathbf{q}) > \quad 60)$$

On the left side, only the exponential is a function of time, so that the derivative become:

$$\frac{\partial}{\partial t} e^{\frac{-j}{\hbar} \cdot E_k \cdot t} | \ \psi_k > = \frac{\partial}{\partial t} e^{\frac{-j}{\hbar} \cdot E_k \cdot t} | \ \psi_k > = -\frac{E_k \cdot e^{-\frac{E_k \cdot t \cdot j}{\hbar}} \cdot j}{\hbar} | \ \psi_k >$$

$$-j \cdot \hbar \cdot \frac{E_k \cdot e^{-\frac{E_k \cdot t \cdot j}{\hbar}} \cdot j}{\hbar} | \ \psi_k > = \mathbf{H} \, e^{\frac{-j}{\hbar} \cdot E_k \cdot t} | \ \psi_k >$$

resulting the following time independent eigenvalue equation:

$$\mathbf{H} | \ \psi_k(\mathbf{q}) > = E_k | \ \psi_k(\mathbf{q}) > \quad 61)$$

where E_k is the eigenvalue corresponding to the eigenket $| \ \psi_k(\mathbf{q}) >$. The set of all eigenvalues constitutes the discrete spectrum of the operator **H**.

The time independent Schrödinger equation now is:

$$\left(\frac{-\hbar^2}{2 \cdot m} \cdot \Delta - q_e \cdot V(\mathbf{q}) - \boldsymbol{\mu} \cdot \mathbf{E_T}(\mathbf{q}, t) \right) | \ \psi_k(\mathbf{q}) > = E_k | \ \psi_k(\mathbf{q}) > . \quad 62)$$

expanding, results: $\frac{-\hbar^2}{2 \cdot m} \cdot \Delta | \ \psi_k > - q_e \cdot V(\mathbf{q}) | \ \psi_k > - \boldsymbol{\mu} \cdot \mathbf{E_T}(\mathbf{q}, t) | \ \psi_k > = E | \ \psi_k >$

Consider the unperturbed Hamiltonian (in absence of $V(\mathbf{q})$ and $\mathbf{E_T}(\mathbf{q}, t)$):

$$\mathbf{H_0} | \ \psi_k > = \frac{-\hbar^2}{2 \cdot m} \cdot \Delta | \ \psi_k > = E_k | \ \psi_k > .$$

The Schrödinger equation is: $\frac{-\hbar^2}{2 \cdot m} \cdot \Delta | \ \psi_k > = E_k | \ \psi_k >$ 63)

Solution of the one-dimensional Schrödinger equation

Impose the condition that the unperturbed Hamiltonian be ***symmetrical***, (or also ***inversion invariant***) that is:

$$\mathbf{H_0}(p,q) = \mathbf{H_0}(p,-q) \text{ symmetry condition} \qquad 64)$$

As a result I can write: $\mathbf{H_0}(p,q) \mid \psi_k(q) > = E_k \mid \psi_k(q) >$ 65)

and also $\mathbf{H_0}(p,-q) \mid \psi_k(-q) > = E_k \mid \psi_k(-q) >$ 66)

and for the hypotheses made $\mathbf{H_0}(p,q) \mid \psi_k(-q) > = E_k \mid \psi_k(-q) >$ 67)

that is possible only if the kets $\mid \psi_k(q) >$ and $\mid \psi_k(-q) >$ are eigenfunctions of the same operator corresponding to tl

same non-degenerated eigenvalue E_k. And therefore the eigenkets $\mid \psi_k(q) >$ and $\mid \psi_k(-q) >$ are multiple one of the other. Namely $\mid \psi_k(-q) > = c_0 \mid \psi_k(q) >$ where c_0 is a complex constant. As a consequence of that, I have:

$$\mathbf{H_0}(p,q) \mid \psi_k(q) > = \mathbf{H_0}(p,q) \mid \psi_k[-(-q)] > = \mathbf{H_0}(p,q)\cdot c_0 \mid \psi_k(-q) > = \mathbf{H_0}(p,q)\cdot {c_0}^2 \mid \psi_k(q) > \qquad 68)$$

so that ${c_0}^2 = \pm 1 \Rightarrow \mid \psi_k(-q) > = \pm \mid \psi_k(q) >$ therefore the eigenkets are all even (**Even functions: ψ(t)=ψ(-t)**) o all odd (**Odd functions: ψ(t)=-ψ(-t)**). Namely the eigenkets form ***a finite disparity.***
What are the consequences of the ***finite disparity*** on the interaction Hamiltonian?

Let's consider, therefore, the Interaction Hamiltonian: $\mathbf{H_{int}} = -\mu\cdot\mathbf{E_T}(q,t)$, valid for a single dipole .

For a multitude of dipoles present in the lattice of a crystal, I must address the problem statistically. To do that, I need th matrix elements built with the eigenfunctions of the unperturbed symmetrical Hamiltonian and forming ***a finite dispari***

$$\mathbf{H1_{int}}_{i,j} = \left(-< \psi_i \mid \mu\cdot\mathbf{E_T}(q,t) \mid \psi_j >\right) \approx \left(-< \psi_i \mid \mu \mid \psi_j >\cdot\mathbf{E_T}(q,t)\right) = -\mu_{i,j}\cdot\mathbf{E_T}(q,t) \qquad 69)$$

where the matrix element is:

$$\mu_{i,j} = < \psi_i \mid \mu \mid \psi_j > = < \psi_i \mid \sum_k (-q_e\cdot q_k) \mid \psi_j > = -q_e\cdot\sum_k < \psi_i \mid q_k \mid \psi_j > \qquad 70)$$

(q_k is the Lagrangean coordinate while q_e is the electron charge)

explicitly: $\mu_{i,j} = -q_e\cdot\sum_k \left(< \psi_i \mid q_k \mid \psi_j >\right) = -q_e\cdot\sum_k \int \overline{\psi_i}\cdot\psi_j\cdot q_k \, dq_k$

$$\text{namely: } \boxed{\mu_{i,j} = -q_e\cdot\sum_k \int \overline{\psi_i}\cdot\psi_j\cdot q_k \, dq_k} \qquad 71)$$

I distinguish two cases:

a) If the eigenkets of the unperturbed Hamiltonian, $\mathbf{H_0}$, are all even (or all odd), it follows that both $\mid \psi_i >$ and $\mid \psi_j >$ are all even, (or all odd), then the product $\overline{\psi_i}\cdot\psi_j$ is odd and the integral is null, it follows that also $\mu_{i,j} = 0$.

b) If an eigenket is even and the other is odd, then the integrals of the product $\overline{\psi_i}\cdot\psi_j$, are different from zero, and therefore also the corresponding dipolar moment $\mu_{i,j} \neq 0$.

It follows that the elements $\mu_{i,i}$ of the main diagonal of the matrix, are all zero if the unperturbed Hamiltonian $\mathbf{H_0}$ is *invariant by inversion* or *symmetrical*. It follows that using the statistical operator **ρ ,** the statistical average of the component α of the dipole moment operator is :

$$<\mu_\alpha> = \mathrm{Tr}(\rho\cdot\mu_\alpha) = \mathrm{Tr}\left[\begin{pmatrix}\rho_{1,1} & \rho_{1,2}\\ \rho_{2,1} & \rho_{2,2}\end{pmatrix}\cdot\begin{pmatrix}0 & \mu_\alpha\\ \overline{\mu_\alpha} & 0\end{pmatrix}\right] = \mathrm{Tr}\left[\begin{pmatrix}\overline{\mu_\alpha}\cdot\rho_{1,2} & \mu_\alpha\cdot\rho_{1,1}\\ \overline{\mu_\alpha}\cdot\rho_{2,2} & \mu_\alpha\cdot\rho_{2,1}\end{pmatrix}\right] = \overline{\mu_\alpha}\cdot\rho_{1,2} + \mu_\alpha\cdot\rho_{2,1}$$

$$\alpha = x, y, z$$

$$<\mu_x> = \overline{\mu_x}\cdot\rho_{1,2} + \mu_x\cdot\rho_{2,1}$$

$$<\mu_y> = \overline{\mu_y}\cdot\rho_{1,2} + \mu_y\cdot\rho_{2,1}$$

$$<\mu_z> = \overline{\mu_z}\cdot\rho_{1,2} + \mu_z\cdot\rho_{2,1}$$

And will be null also the elements of the main diagonal of the interaction Hamiltonian operator $\mathbf{H1_{int}}_{i,i}$ in matrix form, whose generic element is given by:

$$\mathbf{H1_{int}}_{i,j} = -\mu_{i,j}\cdot\mathbf{E_T}\,. \qquad 72)$$

so I can write $\mathbf{H_0} = \begin{pmatrix}E_1 & 0\\ 0 & E_2\end{pmatrix}$ $\qquad \mu_\alpha = \begin{pmatrix}0 & \mu_\alpha\\ \overline{\mu_\alpha} & 0\end{pmatrix}$ $\qquad \alpha = x, y, z$ 73)

$$\mu_x = \begin{pmatrix}0 & \mu_x\\ \overline{\mu_x} & 0\end{pmatrix} \qquad \mu_y = \begin{pmatrix}0 & \mu_y\\ \overline{\mu_y} & 0\end{pmatrix} \qquad \mu_z = \begin{pmatrix}0 & \mu_z\\ \overline{\mu_z} & 0\end{pmatrix}$$

Furthermore it results that $\mu_\alpha = \mu_\alpha^{\dagger}$ Hermitian matrix $\alpha = x, y, z$ 74)

in fact: $$\mu_\alpha^{\dagger} = \left(\overline{\mu_\alpha}\right)^T = \left[\overline{\begin{pmatrix}0 & \mu_\alpha\\ \overline{\mu_\alpha} & 0\end{pmatrix}}\right]^T = \begin{pmatrix}0 & \overline{\mu_\alpha}\\ \overline{\overline{\mu_\alpha}} & 0\end{pmatrix}^T = \begin{pmatrix}0 & \mu_\alpha\\ \overline{\mu_\alpha} & 0\end{pmatrix} = \mu_\alpha$$

the interaction Hamiltonian operator in matrix form is:

$$\mathbf{H1_{int}} = -\mu\cdot\mathbf{E_T}(\mathbf{q}, t) = -\sum_\alpha (\mu_\alpha\cdot E_\alpha) = \sum_\alpha \begin{pmatrix}0 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & 0\end{pmatrix} \qquad 75)$$

explicitly:

$$\mathbf{H1_{int}} = \begin{pmatrix}0 & -\mu_x\cdot E_x\\ -\overline{\mu_x}\cdot E_x & 0\end{pmatrix} + \begin{pmatrix}0 & -\mu_y\cdot E_y\\ -\overline{\mu_y}\cdot E_y & 0\end{pmatrix} + \begin{pmatrix}0 & -\mu_z\cdot E_z\\ -\overline{\mu_z}\cdot E_z & 0\end{pmatrix}$$

Now I look for the time evolution of the expectation value of the discrete operator dipole moment.

The differential equation that let's study the time evolution of the expectation value of an operator, is the one known frc

QM (eq. (18.1)), that for the vectorial operator dipole moment is:

$$\frac{d}{dt}<\mu_\alpha> - <\frac{\partial}{\partial t}\mu_\alpha> = \frac{1}{j\cdot\hbar}\cdot\left(<[\mu_\alpha, \mathbf{H}]>\right) \qquad 76)$$

Assuming that the dipole moment decrease exponentially with *transversal time constant* *(or damping constant)* T_2

Check the accuracy

The differential equation is

$$\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2} = \frac{1}{j\cdot\hbar}\cdot\left(<[\mu_\alpha, \mathbf{H}]>\right) \qquad 77)$$

The Hamiltonian appearing in the commutator of eq 77), is formed by the sum of the unperturbed Hamiltonian and the interaction one:

$$\mathbf{H} = \mathbf{H_0} + \mathbf{H1_{int}} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \begin{pmatrix} 0 & -\mu_\alpha\cdot E_\alpha \\ \overline{-\mu_\alpha\cdot E_\alpha} & 0 \end{pmatrix} = \begin{pmatrix} E_1 & -\mu_\alpha\cdot E_\alpha \\ \overline{-\mu_\alpha\cdot E_\alpha} & E_2 \end{pmatrix}$$

namely:

$$\mathbf{H} = \begin{pmatrix} E_1 & -\mu_\alpha\cdot E_\alpha \\ \overline{-\mu_\alpha\cdot E_\alpha} & E_2 \end{pmatrix} \qquad 78)$$

Now I can calculate the commutator between the dipole moment operator, and the Hamiltonian present in the right side
77):

$$[\mu_\alpha, \mathbf{H}] = \mu_\alpha\cdot\mathbf{H} - \mathbf{H}\cdot\mu_\alpha = \begin{pmatrix} 0 & \mu_\alpha \\ \overline{\mu_\alpha} & 0 \end{pmatrix}\cdot\begin{pmatrix} E_1 & -\mu_\alpha\cdot E_\alpha \\ \overline{-\mu_\alpha\cdot E_\alpha} & E_2 \end{pmatrix} - \begin{pmatrix} E_1 & -\mu_\alpha\cdot E_\alpha \\ \overline{-\mu_\alpha\cdot E_\alpha} & E_2 \end{pmatrix}\cdot\begin{pmatrix} 0 & \mu_\alpha \\ \overline{\mu_\alpha} & 0 \end{pmatrix}$$

$\mu_\alpha := \mu_\alpha \qquad E_1 := E_1 \qquad E_2 := E_2 \qquad E_\alpha := E_\alpha$

$$\begin{pmatrix} 0 & \mu_\alpha \\ \overline{\mu_\alpha} & 0 \end{pmatrix}\cdot\begin{pmatrix} E_1 & -\mu_\alpha\cdot E_\alpha \\ \overline{-\mu_\alpha\cdot E_\alpha} & E_2 \end{pmatrix} - \begin{pmatrix} E_1 & -\mu_\alpha\cdot E_\alpha \\ \overline{-\mu_\alpha\cdot E_\alpha} & E_2 \end{pmatrix}\cdot\begin{pmatrix} 0 & \mu_\alpha \\ \overline{\mu_\alpha} & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & E_2\cdot\mu_\alpha - E_1\cdot\mu_\alpha \\ E_1\cdot\overline{\mu_\alpha} - E_2\cdot\overline{\mu_\alpha} & 0 \end{pmatrix}$$

that is:

$$[\mu_\alpha, \mathbf{H}] = \begin{bmatrix} 0 & \mu_\alpha\cdot(E_2 - E_1) \\ \overline{-\mu_\alpha}\cdot(E_2 - E_1) & 0 \end{bmatrix}$$

I know that $(E_2 - E_1) = \omega_0\cdot\hbar$ substituting in the previous result, I obtain tha the commutator is:

$$[\mu_\alpha, \mathbf{H}] = \begin{pmatrix} 0 & \mu_\alpha \\ \overline{-\mu_\alpha} & 0 \end{pmatrix}\cdot(E_2 - E_1) = \begin{pmatrix} 0 & \mu_\alpha \\ \overline{-\mu_\alpha} & 0 \end{pmatrix}\cdot\omega_0\cdot\hbar$$

so that, finally, the commutator results to be

$$[\mu_\alpha, \mathbf{H}] = \begin{pmatrix} 0 & \mu_\alpha \\ \overline{-\mu_\alpha} & 0 \end{pmatrix}\cdot\omega_0\cdot\hbar \qquad 79)$$

furthermore it is ***anti-Hermitian***, that is:

$$[\,\mu_\alpha, \mathbf{H}\,] = -\left([\,\mu_\alpha, \mathbf{H}\,]\right)^{\dagger} \qquad \mu_\alpha = \begin{pmatrix} 0 & \mu_\alpha \\ \overline{\mu_\alpha} & 0 \end{pmatrix} \tag{80)}$$

Now I substitute this result 80) in the differential equation of the motion of the average value 77) below rewritten:

$$\boxed{\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2} = \frac{1}{j\cdot\hbar}\cdot\left(<[\,\mu_\alpha, \mathbf{H}\,]>\right)} \tag{77')}$$

obtaining:

$$\boxed{\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2} = \frac{\omega_0}{j}<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}>} \tag{81)}$$

Deriving once both sides of 81), , with respect to the time, I get

$$\frac{d^2}{dt^2}<\mu_\alpha> + \frac{1}{T_2}\cdot\frac{d}{dt}<\mu_\alpha> = \frac{\omega_0}{j}\frac{d}{dt}<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}> \tag{82)}$$

Let me consider again the equation of the motion of an operator average $<\mathbf{A}>$:

$$\frac{d}{dt}<\mathbf{A}> - <\frac{\partial}{\partial t}\mathbf{A}> = \frac{1}{j\cdot\hbar}\cdot\left(<[\,\mathbf{A}, \mathbf{H}\,]>\right)$$

it is composed by three terms.

now place : $\mathbf{A} = \begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}$

1) average of the time derivative of the operator:

a) $$<\frac{\partial}{\partial t}\mathbf{A}> = <\frac{\partial}{\partial t}\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}> = -\frac{1}{T_2}\cdot\left[<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}>\right]$$

2) time derivative of the average of the operator:

b) $$\frac{d}{dt}<\mathbf{A}> = \frac{d}{dt}<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}> = \frac{1}{j\cdot\hbar}\cdot\left[<[\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}, \mathbf{H}\,]>\right] - \frac{1}{T_2}\cdot\left[<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}>\right]$$

Substituting those results in the left side of eq. 82) I get:

$$\frac{d^2}{dt^2}<\mu_\alpha> + \frac{1}{T_2}\cdot\frac{d}{dt}<\mu_\alpha> = \frac{\omega_0}{j}\left[\frac{1}{j\cdot\hbar}\cdot\left[<[\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}, \mathbf{H}\,]>\right] - \frac{1}{T_2}\cdot\left[<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}>\right]\right] \tag{83)}$$

in it there is the term $<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}>$ which can be obtained from eq. 81):

$$<\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}> = \frac{j}{\omega_0}\cdot\left(\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2}\right)$$

substituting in eq. 83), I have:

$$\frac{d^2}{dt^2}<\mu_\alpha> + \frac{1}{T_2}\cdot\frac{d}{dt}<\mu_\alpha> = \frac{\omega_0}{j}\left[\frac{1}{j\cdot\hbar}\cdot\left[<[\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix},\mathbf{H}]>\right]\ldots \atop + \frac{-1}{T_2}\cdot\frac{j}{\omega_0}\cdot\left(\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2}\right)\right] \qquad 84)$$

Calculation of the expectation value of the commutator: $<[\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix},\mathbf{H}]> \quad \alpha = x, y, z$

knowing that the Hamiltonian is $\boxed{\mathbf{H} = \begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}}$ 78')

substituting into the commutator I get:

$$[\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix},\mathbf{H}] = [\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix},\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}]$$

calculating the commutator results:

$$[\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix},\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}] = \begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}\cdot\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix} - \begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}\cdot\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}$$

the expectation value is:

$$<[\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix},\mathbf{H}]> = <\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}\cdot\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}> - <\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}\cdot\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}>$$

After a simplification

$$\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}\cdot\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix} \rightarrow \begin{pmatrix}-E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & E_2\cdot\mu_\alpha\\ -E_1\cdot\overline{\mu_\alpha} & E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\end{pmatrix}$$

$$\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}\cdot\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix} \rightarrow \begin{pmatrix}E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & E_1\cdot\mu_\alpha\\ -E_2\cdot\overline{\mu_\alpha} & -E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\end{pmatrix}$$

results:

$$<[\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix},\mathbf{H}]> = <\begin{pmatrix}-E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & E_2\cdot\mu_\alpha\\ -E_1\cdot\overline{\mu_\alpha} & E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\end{pmatrix}> - <\begin{pmatrix}E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & E_1\cdot\mu_\alpha\\ -E_2\cdot\overline{\mu_\alpha} & -E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\end{pmatrix}>$$

$$<A> - <B> = <(A - B)>$$

$$\begin{pmatrix} -E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & E_2\cdot\mu_\alpha \\ -E_1\cdot\overline{\mu_\alpha} & E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} \end{pmatrix} - \begin{bmatrix} E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & E_1\cdot\mu_\alpha \\ -E_2\cdot\overline{\mu_\alpha} & -\left(E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\right) \end{bmatrix} \text{ factor } \rightarrow \begin{bmatrix} -2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & -\mu_\alpha\cdot(E_1-E_2) \\ -\overline{\mu_\alpha}\cdot(E_1-E_2) & 2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} \end{bmatrix}$$

knowing that $E_2 - E_1 = \omega_0\cdot\hbar$

the expectation value is:

$$<\left[\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}, \mathbf{H}\right]> = <\begin{bmatrix} -2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & -\mu_\alpha\cdot(E_1-E_2) \\ -\overline{\mu_\alpha}\cdot(E_1-E_2) & 2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} \end{bmatrix}> \qquad 85)$$

Furthermore I can write the expectation value in a simplified form, as follows:

$$<\begin{bmatrix} -2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} & -\mu_\alpha\cdot(E_1-E_2) \\ -\overline{\mu_\alpha}\cdot(E_1-E_2) & 2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha} \end{bmatrix}> = -2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot\left[<\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}>\right] + \omega_0\cdot\hbar\cdot\left[<\begin{pmatrix} 0 & \mu_\alpha \\ \overline{\mu_\alpha} & 0 \end{pmatrix}>\right]$$

calculate the expectation value of the Pauli matrix $\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$<\sigma_3> = <\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}> = \mathrm{Tr}\left[\rho\cdot\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] = \mathrm{Tr}\left[\begin{pmatrix} \rho_{1,1} & \rho_{1,2} \\ \rho_{2,1} & \rho_{2,2} \end{pmatrix}\cdot\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] = \mathrm{Tr}\left(\begin{pmatrix} \rho_{1,1} & -\rho_{1,2} \\ \rho_{2,1} & -\rho_{2,2} \end{pmatrix}\right) = \rho_{1,1} - \rho_{2,2}$$

$$<\begin{pmatrix} 0 & \mu_\alpha \\ \overline{\mu_\alpha} & 0 \end{pmatrix}> = <\mu_\alpha>$$

finally resulting:

$$<\left[\begin{pmatrix} 0 & \mu_\alpha \\ -\overline{\mu_\alpha} & 0 \end{pmatrix}, \mathbf{H}\right]> = -2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2}) + \omega_0\cdot\hbar\cdot\left(<\mu_\alpha>\right) \qquad 86)$$

substituting in eq.:84) I get:

$$\frac{d^2}{dt^2}<\mu_\alpha> + \frac{1}{T_2}\cdot\frac{d}{dt}<\mu_\alpha> = \frac{\omega_0}{j}\left[\frac{1}{j\cdot\hbar}\cdot\left[-2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2}) + \omega_0\cdot\hbar\cdot\left(<\mu_\alpha>\right)\right] \ldots + \frac{-1}{T_2}\cdot\frac{j}{\omega_0}\cdot\left(\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2}\right)\right] \qquad 84')$$

and after a simplification of the right side, I get:

$$\frac{d^2}{dt^2}<\mu_\alpha> + \frac{1}{T_2}\cdot\frac{d}{dt}<\mu_\alpha> = \frac{2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot\omega_0\cdot(\rho_{1,1}-\rho_{2,2})}{\hbar} - \omega_0^2\cdot\left(<\mu_\alpha>\right) - \frac{\frac{d}{dt}<\mu_\alpha>}{T_2} - \frac{<\mu_\alpha>}{T_2^2}$$

collecting the derivatives at the left side and living the constant term at the right side, I find:

$$\frac{d^2}{dt^2}<\mu_\alpha> + \frac{2}{T_2}\cdot\frac{d}{dt}<\mu_\alpha> + \left(\omega_0^2 + \frac{1}{T_2^2}\right)\cdot\left(<\mu_\alpha>\right) = \frac{2\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot\omega_0\cdot(\rho_{1,1}-\rho_{2,2})}{\hbar} \qquad 87)$$

This equation, formally is like to the equation of a classical harmonic oscillator forced by the electric field E_α .

Solving the equation

$$\frac{d^2}{dt^2}<\mu_\alpha> + \frac{2}{T_2}\cdot\frac{d}{dt}<\mu_\alpha> + (<\mu_\alpha>)\cdot\left(\omega_0^2 + \frac{1}{T_2^2}\right) = \frac{2\cdot\omega_0\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})}{\hbar} \qquad 87')$$

This equation can be rewritten as a function of the density operator , placing:

$$\rho_{1,1}-\rho_{2,2} = <\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}> = <\mathbf{D}> \qquad 88)$$

Let me consider again the equation of the motion of an operator average $<\mathbf{A}>$:

$$\frac{d}{dt}<\mathbf{A}> - <\frac{\partial}{\partial t}\mathbf{A}> = \frac{1}{j\cdot\hbar}\cdot(<[\mathbf{A},\mathbf{H}]>)$$

rewritten for the new operator **D**: $\frac{d}{dt}<\mathbf{D}> - <\frac{\partial}{\partial t}\mathbf{D}> = \frac{1}{j\cdot\hbar}\cdot(<[\mathbf{D},\mathbf{H}]>)$ 89)

place the average derivative $<\frac{\partial}{\partial t}\mathbf{D}> = -\frac{<\mathbf{D}> - (<\mathbf{D}>)^e}{T_1}$ 90)

substituting 88) into 87), results: $\frac{d}{dt}<\mathbf{D}> + \frac{<\mathbf{D}> - (<\mathbf{D}>)^e}{T_1} = \frac{1}{j\cdot\hbar}\cdot(<[\mathbf{D},\mathbf{H}]>)$ 91)

The hamiltonian be: $\mathbf{H} = \begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}$ 78'')

it let me calculate the commutator on the right side of 89):

$$[\mathbf{D},\mathbf{H}] = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\cdot\begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix} - \begin{pmatrix}E_1 & -\mu_\alpha\cdot E_\alpha\\ -\overline{\mu_\alpha}\cdot E_\alpha & E_2\end{pmatrix}\cdot\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \begin{pmatrix}0 & -2\cdot E_\alpha\cdot\mu_\alpha\\ 2\cdot E_\alpha\cdot\overline{\mu_\alpha} & 0\end{pmatrix}$$

resulting: $[\mathbf{D},\mathbf{H}] = -2\cdot E_\alpha\cdot\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix} = -2\cdot E_\alpha\cdot\boldsymbol{\mu_\alpha}$

remember that $\boldsymbol{\mu_\alpha} = \boldsymbol{\mu_\alpha}^\dagger$ Hermitian matrix 74')

finally the average is $<[\mathbf{D},\mathbf{H}]> = -2\cdot E_\alpha\cdot(<\boldsymbol{\mu_\alpha}>)$ been $<\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}> = <\boldsymbol{\mu_\alpha}>$

Previously I found that eq 81): $\frac{d}{dt}<\boldsymbol{\mu_\alpha}> + \frac{<\boldsymbol{\mu_\alpha}>}{T_2} = \frac{\omega_0\cdot\hbar}{j\cdot\hbar}<\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}>$ 81')

from which I have $\frac{1}{j\cdot\hbar}<\begin{pmatrix}0 & \mu_\alpha\\ -\overline{\mu_\alpha} & 0\end{pmatrix}> = \frac{1}{j\cdot\hbar}<\boldsymbol{\mu_\alpha}> = \frac{1}{\omega_0\cdot\hbar}\cdot\left(\frac{d}{dt}<\boldsymbol{\mu_\alpha}> + \frac{<\boldsymbol{\mu_\alpha}>}{T_2}\right)$

$$\omega_0 = \frac{E_2 - E_1}{\hbar}$$

After a substitution in eq. 89), I find that:

$$\frac{d}{dt}<\mathbf{D}> + \frac{<\mathbf{D}> - (<\mathbf{D}>)^e}{T_1} = \frac{-2\cdot E_\alpha}{j\cdot\hbar}\cdot(<\mu_\alpha>) = \frac{-2\cdot E_\alpha}{(\omega_0\cdot\hbar)}\cdot\left(\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2}\right)$$

$$\frac{d}{dt}<\mathbf{D}> + \frac{<\mathbf{D}> - (<\mathbf{D}>)^e}{T_1} = \frac{-2\cdot E_\alpha}{(\omega_0\cdot\hbar)}\cdot\left(\frac{d}{dt}<\mu_\alpha> + \frac{<\mu_\alpha>}{T_2}\right) \qquad 92)$$

Equilibrium density operator: $(<\mathbf{D}>)^e = (\rho_{1,1} - \rho_{2,2})_e \qquad <\mathbf{D}> = \rho_{1,1} - \rho_{2,2}$
substituting in eq. 90), it assumes the form:

$$\frac{d}{dt}(\rho_{1,1} - \rho_{2,2}) + \frac{\rho_{1,1} - \rho_{2,2} - (\rho_{1,1} - \rho_{2,2})_e}{T_1} = \frac{-2\cdot E_\alpha}{\hbar\cdot\omega_0}\cdot\left[\frac{\partial}{\partial t}<\mu_\alpha> + \frac{1}{T_2}\cdot(<\mu_\alpha>)\right] \qquad 93)$$

Now, I will describe the time evolution of the ***polarization*** per unit of crystal volume (M_{ar} states for arithmetic average where are present N_p dipoles.

The polarization is: $$\mathbf{P}_\alpha = \frac{\sum_{i=1}^{N_p}(<\mu_\alpha>)_i}{V} = \frac{N_p}{V}\cdot\frac{\sum_{i=1}^{N_p}(<\mu_\alpha>)_i}{N_p} = N_V\cdot M_{ar}(<\mu_\alpha>)$$

$$\boxed{\mathbf{P}_\alpha = N_V\cdot M_{ar}(<\mu_\alpha>)} \qquad m^{-3}\cdot C\cdot m = \frac{C}{m^2} \qquad 94)$$

Spatial dipolar moment average value $$M_{ar}(<\mu_\alpha>) = \frac{\sum_{i=1}^{N_p}(<\mu_\alpha>)_i}{N} \qquad 95)$$

Active centers (or polarized molecules) density: $N_V = \frac{N_p}{V}$. 96)

Now I will try to modify eq. 87) at the light of the previous definition (94), 95), 96)). I rewrite eq. 87):

$$\boxed{\frac{\partial^2}{\partial t^2}<\mu_\alpha> + \frac{2}{T_2}\cdot\frac{\partial}{\partial t}<\mu_\alpha> + (<\mu_\alpha>)\cdot\left(\omega_0^2 + \frac{1}{T_2^2}\right) = \frac{-2\cdot\omega_0\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1} - \rho_{2,2})}{\hbar}} \qquad 87')$$

Multiply both sides of eq. 87) by N_V :

$$\boxed{\frac{\partial^2}{\partial t^2}\left[N_V\cdot(<\mu_\alpha>)\right] + \frac{2}{T_2}\cdot\frac{\partial}{\partial t}\left[N_V\cdot(<\mu_\alpha>)\right] \ldots = \frac{-2\cdot N_V\cdot\omega_0\cdot E_\alpha\cdot\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1} - \rho_{2,2})}{\hbar} \\ + N_V\cdot(<\mu_\alpha>)\cdot\left(\omega_0^2 + \frac{1}{T_2^2}\right)} \qquad 98)$$

then I calculate a spatial average of both sides:

$$\frac{\partial^2}{\partial t^2}\left[N_V\cdot\frac{\sum_{i=1}^{N_p}(<\mu_\alpha>)_i}{V}\right]+\frac{2}{T_2}\cdot\frac{\partial}{\partial t}\left[N_v\cdot\frac{\sum_{i=1}^{N_p}(<\mu_\alpha>)_i}{V}\right]\ \ldots = \frac{-2\cdot N_V\cdot\omega_0\cdot E_\alpha}{\hbar}\cdot\frac{\sum_{i=1}^{N_p}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]_i}{V}$$
$$+N_V\cdot\left[\frac{\sum_{i=1}^{N_p}(<\mu_\alpha>)_i}{V}\right]\cdot\left(\omega_0^{\,2}+\frac{1}{T_2^{\,2}}\right)$$

as previously defined $\frac{\sum_{i=1}^{N_p}(<\mu_\alpha>)_i}{N}=M_{ar}(<\mu_\alpha>)$ which substituted into the equation gives

$$\frac{\partial^2}{\partial t^2}\left(N_V\cdot M_{ar}(<\mu_\alpha>)\right)+\frac{2}{T_2}\cdot\frac{\partial}{\partial t}\left(N_v\cdot M_{ar}(<\mu_\alpha>)\right)\ \ldots = \frac{-2\cdot N_V\cdot\omega_0\cdot E_\alpha\cdot M_{ar}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]}{\hbar}$$
$$+N_V\cdot M_{ar}(<\mu_\alpha>)\cdot\left(\omega_0^{\,2}+\frac{1}{T_2^{\,2}}\right)$$

The α component of the polarization is: $P_\alpha = N_V\cdot M_{ar}(<\mu_\alpha>)$ So the equation assumes the simple form:

$$\frac{\partial^2}{\partial t^2}P_\alpha+\frac{2}{T_2}\cdot\frac{\partial}{\partial t}P_\alpha+P_\alpha\cdot\left(\omega_0^{\,2}+\frac{1}{T_2^{\,2}}\right)=\frac{-2\cdot N_V\cdot\omega_0\cdot E_\alpha\cdot M_{ar}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]}{\hbar}\qquad 99)$$

To a random distribution of the molecules corresponds a random distribution of the components μ_α and $\overline{\mu_\alpha}$, resulting tl $\mu_\alpha\cdot\overline{\mu_\alpha}$ and $\rho_{1,1}-\rho_{2,2}$ are uncorrelated, so that I can write:

$$\text{spatial average value: } M_{ar}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]=M_{ar}\left(\mu_\alpha\cdot\overline{\mu_\alpha}\right)\cdot M_{ar}(\rho_{1,1}-\rho_{2,2})\qquad 100)$$

If, instead, the molecules have all the same orientation, then $\mu_\alpha\cdot\overline{\mu_\alpha}$ is statistically independent from $\rho_{1,1}-\rho_{2,2}$, finally resulting:

$$M_{ar}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]=\mu_\alpha\cdot\overline{\mu_\alpha}\cdot M_{ar}(\rho_{1,1}-\rho_{2,2})\qquad 101)$$

Now I consider the case of a low correlation between $\mu_\alpha\cdot\overline{\mu_\alpha}$ and $\rho_{1,1}-\rho_{2,2}$ namely:

$$\text{spatial average value: } M_{ar}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]=M_{ar}\left(\mu_\alpha\cdot\overline{\mu_\alpha}\right)\cdot M_{ar}(\rho_{1,1}-\rho_{2,2}).\qquad 100'')$$

Than I can write:

$$M_{ar}\left[N_V\cdot(\rho_{1,1}-\rho_{2,2})\right]=M_{ar}(N_V\cdot\rho_{1,1})-M_{ar}(N_V\cdot\rho_{2,2})=N_V\cdot\left(M_{ar}(\rho_{1,1})-M_{ar}(\rho_{2,2})\right)$$

$$N_V=\frac{N_p}{V}\qquad M_{ar}\left[N_V\cdot(\rho_{1,1}-\rho_{2,2})\right]=\frac{N_p}{V}\cdot\left(M_{ar}(\rho_{1,1})-M_{ar}(\rho_{2,2})\right)=\frac{N_p}{V}\cdot\left[\frac{\sum_j(\rho_{1,1})_j}{N_p}\right]-\frac{N_p}{V}\cdot\left[\frac{\sum_j(\rho_{2,2})_j}{N_p}\right]$$

$$M_{ar}\left[N_V\cdot(\rho_{1,1}-\rho_{2,2})\right] = \frac{\sum_j (\rho_{1,1})_j}{V} - \frac{\sum_j (\rho_{2,2})_j}{V} = N_1 - N_2$$

The spatial average value is $M_{ar}\left[N_V\cdot(\rho_{1,1}-\rho_{2,2})\right] = N_1 - N_2$

$$P_\alpha = N_V\cdot M_{ar}\left(<\mu_\alpha>\right) = N_1 - N_2 \qquad 102)$$

Molecular density at energetic level 1: $N_1 = \frac{\sum_j (\rho_{1,1})_j}{V}$

Molecular density at energetic level 2: $N_2 = \frac{\sum_j (\rho_{2,2})_j}{V}$

Going back to equation 99) for the polarization operator,

$$\frac{\partial^2}{\partial t^2}P_\alpha + \frac{2}{T_2}\cdot\frac{\partial}{\partial t}P_\alpha + P_\alpha\cdot\left(\omega_0{}^2 + \frac{1}{T_2{}^2}\right) = \frac{-2\cdot N_V\cdot\omega_0\cdot E_\alpha\cdot M_{ar}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]}{\hbar} \qquad 99')$$

and substituting 102) I obtain the macroscopic equations:

$$N_V\cdot\frac{d}{dt}\left(M_{ar}(\rho_{1,1}-\rho_{2,2})\right) \;\ldots\; + \frac{N_V\cdot M_{ar}(\rho_{.1,1}-\rho_{2,2}) - N_V\cdot M_{ar}\left[(\rho_{1,1}-\rho_{2,2})_e\right]}{T_1} = \frac{-2\cdot E_\alpha\cdot N_V}{\hbar\cdot\omega_0}\cdot\left(\frac{\partial}{\partial t}M_{ar}\left(<\mu_\alpha>\right) + \frac{1}{T_2}\cdot M_{ar}\left(<\mu_\alpha>\right)\right)$$

$E_{\alpha loc}$ is the average value of the transversal field acting on each molecule

$N_1 - N_2 = N_V\cdot M_{ar}(\rho_{1,1}-\rho_{2,2})$ $\quad E_{\alpha loc} = N_V\cdot E_\alpha$ $\quad (N_1 - N_2)_e = N_V\cdot M_{ar}\left[(\rho_{1,1}-\rho_{2,2})_e\right]$

$$\frac{d}{dt}(N_1 - N_2) + \frac{N_1 - N_2 - (N_1 - N_2)_e}{T_1} = \frac{-2\cdot E_{\alpha loc}}{\hbar\cdot\omega_0}\cdot\left(\frac{\partial}{\partial t}P_\alpha + \frac{1}{T_2}\cdot P_\alpha\right) \qquad 103)$$

Polarization $\quad P_\alpha = N_V\cdot M_{ar}\left(<\mu_\alpha>\right)$

$$\frac{\partial^2}{\partial t^2}P_\alpha + \frac{2}{T_2}\cdot\frac{\partial}{\partial t}P_\alpha + P_\alpha\cdot\left(\omega_0{}^2 + \frac{1}{T_2{}^2}\right) = \frac{-2\cdot N_V\cdot\omega_0\cdot E_\alpha\cdot M_{ar}\left[\mu_\alpha\cdot\overline{\mu_\alpha}\cdot(\rho_{1,1}-\rho_{2,2})\right]}{\hbar}$$

The effect of the time harmonic electromagnetic field on the dielectric material is finally described by the two equations:

$$\frac{\partial^2}{\partial t^2}P_\alpha + \frac{2}{T_2}\cdot\frac{\partial}{\partial t}P_\alpha + P_\alpha\cdot\left(\omega_0{}^2 + \frac{1}{T_2{}^2}\right) = \frac{-2\cdot\omega_0\cdot E_{\alpha loc}\cdot M_{ar}\left(\mu_\alpha\cdot\overline{\mu_\alpha}\right)\cdot(N_1 - N_2)}{\hbar} \qquad 104)$$