Dipole-Dipole Interaction Between Many Dipoles- Classical Energy & Quantum Mechanical Hamiltonian

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Abstract

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1 Multipole Expansion

I find the geometry of these light harvesting complexes interesting. I want to know if the fact that the FMO structure is almost 2D makes it more efficient. The picture of 7 dipole moments talking to each other is a complicated one, so I will start with two dipole moments, where I consider one dipole sitting in the electric field of the other. I then argue what the classical and quantum mechanical expressions for multiple dipoles should be. I will apply the theory to quantum dots.

This is based on chapter-4 of the classic book of Jackson: Classical Electrodynamics (third edition). I follow Jackson in using SI units, so sorry about the 4π and ϵ_0s floating around.

In the spirit of modelling a cow as a sphere (with the head, legs and tail as small perturbations), I will consider the charge of an entity that has an electron-hole pair density due to photons as a charge distribution $\rho(\mathbf{x})$, which is nonvanishing only inside a sphere of radius R. The potential outside the sphere (spherically symmetric problem, so the first thing that comes to mind is to span using Spherical Harmonics) is

$$\Phi(\mathbf{x}) = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} q_{lm} \frac{Y_{lm}(\theta, \phi)}{r^{l+1}}$$

the notation is used for convenience (will come back to this), $Y_{lm}(\theta, \phi)$ are the usual Spherical Harmonics (see section below for their form). The above potential is said to be written in multipole expansion: the $l = 0$ term is monopole term, $l = 1$ termS are the dipole terms, etc.

Now for a given charge distribution $\rho(\mathbf{x})$, what are the coefficients q_{lm} in the above expansion? Since

$$\Phi(\mathbf{x}) = \frac{1}{4\pi\epsilon_0}\int \frac{\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}d\mathbf{x}'$$

according to the addition theorem of Spherical Harmonics (page-110 of Jackson for example)

$$\frac{1}{|\mathbf{x}-\mathbf{x}'|} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\frac{(r')^l}{r^{l+1}}Y_{lm}^*(\theta',\phi')Y_{lm}(\theta,\phi)$$

now one can see that is indeed the reason for the form of the multipole expansion and this ties the whole story together in the following way:

$$\begin{aligned}
\Phi(\mathbf{x}) &= \frac{1}{4\pi\epsilon_0}\int \frac{\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}d\mathbf{x}' \\
&= \frac{1}{4\pi\epsilon_0}\int \left[4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\frac{(r')^l}{r^{l+1}}Y_{lm}^*(\theta',\phi')Y_{lm}(\theta,\phi)\right]\rho(\mathbf{x}')d\mathbf{x}' \\
&= \frac{1}{\epsilon_0}\left[\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\int (r')^l\, Y_{lm}^*(\theta',\phi')\rho(\mathbf{x}')d\mathbf{x}'\right]\frac{Y_{lm}(\theta,\phi)}{r^{l+1}}
\end{aligned}$$

therefore simple comparison with

$$\Phi(\mathbf{x}) = \frac{1}{4\pi\epsilon_0}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{l+1}}$$

gives me the "multipole moments"

$$q_{lm} = \int (r')^l\, Y_{lm}^*(\theta',\phi')\rho(\mathbf{x}')d\mathbf{x}'.$$

Symmetries of the Spherical Harmonic functions can be used to show that $q_{l-m} = (-1)^m q_{lm}^*$. Let me play with these

$$\begin{aligned}
q_{00} &= \int Y_{00}^*(\theta',\phi')\rho(\mathbf{x}')d\mathbf{x}' \\
&= \frac{1}{\sqrt{4\pi}}\int \rho(\mathbf{x}')d\mathbf{x}' = \frac{1}{\sqrt{4\pi}}q
\end{aligned}$$

for the total charge q. Let me put this back in the first term of $\Phi(\mathbf{x})$

$$\begin{aligned}
\Phi_{00}(\mathbf{x}) &= \frac{4\pi}{\epsilon_0}\frac{1}{\sqrt{4\pi}}q\frac{Y_{00}(\theta,\phi)}{r} \\
&= \frac{q}{\epsilon_0}\frac{1}{r}
\end{aligned}$$

Moving on to the dipole terms

$$\begin{aligned} q_{10} &= \int r' Y_{10}^*(\theta', \phi') \rho(\mathbf{x}') d\mathbf{x}' \\ &= \left[\frac{3}{4\pi}\right]^{1/2} \int \left[r' \cos\theta'\right] \rho(\mathbf{x}') d\mathbf{x}' \\ &= \left[\frac{3}{4\pi}\right]^{1/2} \int z' \rho(\mathbf{x}') d\mathbf{x}' \\ &= \left[\frac{3}{4\pi}\right]^{1/2} p_z \end{aligned}$$

$$\begin{aligned} \Phi_{10}(\mathbf{x}) &= \frac{1}{3\epsilon_0} q_{10} \frac{Y_{10}(\theta, \phi)}{r^2} \\ &= \frac{1}{4\pi\epsilon_0} p_z \frac{\cos\theta}{r^2} \end{aligned}$$

for $\mathbf{p} = \int \mathbf{x}' \rho(\mathbf{x}') d\mathbf{x}'$, the electric dipole moment.

$$\begin{aligned} q_{11} &= \int r' Y_{11}^*(\theta', \phi') \rho(\mathbf{x}') d\mathbf{x}' \\ &= -\left[\frac{3}{8\pi}\right]^{1/2} \int r' e^{-i\phi} \sin\theta \rho(\mathbf{x}') d\mathbf{x}' \\ &= -\left[\frac{3}{8\pi}\right]^{1/2} (p_x - ip_y). \end{aligned}$$

$$\begin{aligned} \Phi_{11}(\mathbf{x}) &= \frac{1}{3\epsilon_0} q_{11} \frac{Y_{11}(\theta, \phi)}{r^2} \\ &= \frac{1}{8\pi\epsilon_0} (p_x - ip_y) \frac{e^{i\phi} \sin\theta}{r^2} \end{aligned}$$

$$\begin{aligned} \Phi_{1-1}(\mathbf{x}) &= \frac{1}{4\pi\epsilon_0} \frac{4\pi}{3} q_{1,-1} \frac{Y_{1-1}(\theta, \phi)}{r^2} \\ &= \frac{1}{8\pi\epsilon_0} (p_x + ip_y) \frac{e^{-i\phi} \sin\theta}{r^2} \end{aligned}$$

note: $q_{1-1} = \left[\frac{3}{8\pi}\right]^{1/2} (p_x + ip_y)$. Of course the scalar potential $\Phi(\mathbf{x})$ is define as

$$\mathbf{E}(\mathbf{x}) = -\boldsymbol{\nabla}\Phi(\mathbf{x}).$$

Lets consider a dipole $\mathbf{p}$ along the z-axis (at $\mathbf{x}_0$), then working through the differentiation (there is actually a very subtle point as pointed out by Jackson on page 147-148), one gets the electric field at point $\mathbf{x}$ due to this dipole ($\mathbf{n}$ is the unit vector directed from $\mathbf{x}_0$ to $\mathbf{x}$)

$$\mathbf{E}(\mathbf{x}) = \frac{1}{4\pi\epsilon_0}\left[-\frac{\mathbf{p}}{|\mathbf{x}-\mathbf{x}_0|^3} + \frac{3\mathbf{n}(\mathbf{p}\cdot\mathbf{n})}{|\mathbf{x}-\mathbf{x}_0|^3} - \frac{4\pi}{3}\mathbf{p}\delta(\mathbf{x}-\mathbf{x}_0)\right]$$

(I think, the last term originates from Gauss's law and it insures that integral over the electric field $\int_{r<R} \mathbf{E}(\mathbf{x})d\mathbf{x} = -\mathbf{p}/3\epsilon_0$). In any event, we have the electric field due to an electric dipole, which is a happy occasion, because we can ask, what happens if you put another dipole in the vicinity of the first dipole, i.e. in the above electric field. Basically the way I remember how to do this problem is through a combination of intuition and dimensional analysis (a much more elegant derivation is given on page 150 of Jackson).

Imagine a charge particle in an electric field (can be easily generalized to electromagnetic field), the force on the particle is then (I never know what convention of the sign of e is being used, so be careful with my signs)

$$\begin{aligned} \mathbf{F} &= -e\mathbf{E} \\ [F] &= g.cm.s^{-2} \end{aligned}$$

the electrostatic energy (work done on the particle, in the case of an EM field) is

$$\begin{aligned} W &= \mathbf{F}\cdot\mathbf{r} = -e\mathbf{E}\cdot\mathbf{r} = -\mathbf{E}\cdot\mathbf{p} \\ [W] &= g.cm^2.s^{-2} = erg \end{aligned}$$

Then the electrostatic energy of a dipole $\mathbf{p}_2$ sitting (at $\mathbf{x}_2$) in a field (given above) due to a dipole $\mathbf{p}_1$(at $\mathbf{x}_1$) is

$$\begin{aligned} W_{12} &= -\mathbf{E}(\mathbf{x})\cdot\mathbf{p}_2 \\ &= \frac{1}{4\pi\epsilon_0}\left[\frac{\mathbf{p}_1\cdot\mathbf{p_2}}{|\mathbf{x}_2-\mathbf{x}_1|^3} - \frac{3(\mathbf{n}\cdot\mathbf{p}_1)(\mathbf{n}\cdot\mathbf{p_2})}{|\mathbf{x}_2-\mathbf{x}_1|^3}\right] \end{aligned}$$

where $\mathbf{n}$ is the unit vector directed from $\mathbf{x}_1$ to $\mathbf{x}_2$ ($\mathbf{x}_1 \neq \mathbf{x}_2$), which is the equation I was after. This is the dipole-dipole coupling energy that we have been talking about between two dipoles. If I ask, what is the electrostatic energy when I put $n-1$ dipoles $\mathbf{p}_i$ (at x_i, $i = 2...n$) in the electric field of a dipole $\mathbf{p}_1$ sitting at $\mathbf{x}_1$, then I would argue that the classical electrostatic energy of the system would be

$$\begin{aligned} W &= \sum_{i=2}^{n} W_{1i} \\ W_{1i} &= \frac{1}{4\pi\epsilon_0}\left[\frac{\mathbf{p}_1\cdot\mathbf{p}_i}{|\mathbf{x}_i-\mathbf{x}_1|^3} - \frac{3(\mathbf{n}\cdot\mathbf{p}_1)(\mathbf{n}\cdot\mathbf{p}_i)}{|\mathbf{x}_i-\mathbf{x}_1|^3}\right] \end{aligned}$$

To make a quantum mechanical calculation couplings "J", one then makes the above energy a part of the Hamiltonian by simply making it an operator (the usual procedure of constructing quantum mechanics from classical mechanics)

$$H_{dipole-dipole} == \frac{1}{4\pi\epsilon_0}\left[\frac{\mathbf{p_1}\cdot\mathbf{p_2}}{|\widehat{\mathbf{x}}_2-\widehat{\mathbf{x}}_1|^3} - \frac{3(\mathbf{n}\cdot\mathbf{p}_1)\,(\mathbf{n}\cdot\mathbf{p_2})}{|\widehat{\mathbf{x}}_2-\widehat{\mathbf{x}}_1|^3}\right]$$

$\widehat{}$ denotes an operator. This is then written using the spectral resolution of identity for the system

$$I = \sum_i |i\rangle\langle i|$$

$$H_{dipole-dipole} = \sum_{ij} J_{ij}|i\rangle\langle j|$$

for the couplings

$$J_{ij} = \frac{1}{4\pi\epsilon_0}\langle i|\left[\frac{\mathbf{p_1}\cdot\mathbf{p_2}}{|\widehat{\mathbf{x}}_2-\widehat{\mathbf{x}}_1|^3} - \frac{3(\mathbf{n}\cdot\mathbf{p}_1)\,(\mathbf{n}\cdot\mathbf{p_2})}{|\widehat{\mathbf{x}}_2-\widehat{\mathbf{x}}_1|^3}\right]|j\rangle.$$

In principle the fact that maybe nature has found optimal ways of orienting dipoles for energy transfer would be hidden in the geometry of the above expression. In another set of notes I will apply the above equation to quantum dots, where one should be able to use the spatial symmetry of the Hamiltonian (Hermite polynomials) to find simple relations between different dipole interaction terms.

Then I should be able to answer questions such as: Can I construct quantum dot arrays for which the quadrupole interaction is very strong? I am not going to touch the quadrupole stuff for now, because it gets very messy? I will focus on the dipole interaction and try to vary the size of the QDs (and perhaps the effective mass, i.e. the material). This analysis (generalization of it) would also work for 2DEG quantum dots, although other interactions will become important there as well.

2 Spherical Harmonics

The Spherical Harmonics (which in my opinion should always be held close to one's heart):

$$Y_{lm}(\theta,\phi) = (-1)^l\left[\frac{(2l+1)!}{4\pi}\right]^{1/2}\frac{1}{2^l l!}\left[\frac{(l+m)!}{(2l)!(l-m)!}\right]^{1/2} e^{im\phi}(\sin\theta)^{-m}\frac{d^{l-m}}{d(\cos\theta)^{l-m}}(\sin\theta)^{2l}$$

are normalized

$$\int Y^*_{l'm'}(\theta,\phi)Y_{lm}(\theta,\phi)d\Omega = \delta_{ll'}\delta_{mm'}.$$

$$
\begin{aligned}
Y_{00}(\theta,\phi) &= \left[\frac{1}{4\pi}\right]^{1/2} \\
Y_{10}(\theta,\phi) &= \left[\frac{3}{4\pi}\right]^{1/2} \cos\theta \\
Y_{11}(\theta,\phi) &= -\left[\frac{3}{8\pi}\right]^{1/2} e^{i\phi}\sin\theta \\
Y_{1-1}(\theta,\phi) &= +\left[\frac{3}{8\pi}\right]^{1/2} e^{-i\phi}\sin\theta \\
&\quad ....
\end{aligned}
$$