Lecture 32  Chapt 21

Announce:
- last quiz this today
- Remember to send me an email of exam time
- Breast cancer awareness thing Thursday night
- By the way, we are ending up with 9 quizzes (I’ll take the best 8) and on average 8 HW (I’ll take the best 7) so that gives 19 % quiz, 11 % HW, 47 % 3 exams, and 23 % final. People with 9 homeworks will have slightly different percentages (19%, 12 %, 46 %, and 23 %).

Outline:

- dipoles and multipoles
- Poisson equation

Review

Coulomb’s law which everyone remembers from physics

\[ u(r) = \frac{1}{4\pi \varepsilon} \frac{q_A q_B}{r} \quad \text{where} \quad \varepsilon = \varepsilon_0 D \quad \text{where} \ D \text{ is the dielectric constant} \]

Force

\[ \vec{f} = -\nabla u = -\frac{\partial u}{\partial r} \frac{1}{4\pi \varepsilon_0} \frac{q_A q_B}{Dr^2} \hat{r} \]

Field represents what would happen to a particle of \( q=1 \) if it were present at any point in space.

\[ \vec{E}(r) = \frac{\vec{f}}{q_B} = \frac{1}{4\pi \varepsilon_0} \frac{q_A}{Dr^2} \hat{r} \]

(remember that force is units of N, so field is N/C or V/m)

Gauss’s law

\[ \Phi = \int_{\text{surface}} \vec{E} \cdot d\vec{s} = \int_{\text{volume}} \frac{\rho}{\varepsilon_0} dV = \frac{\sum q}{\varepsilon_0} \]

Potential

\[ \psi = \psi_r - \psi_\infty = \frac{W_{\text{surf}}}{q_{\text{test}}} = -\int_{\infty}^{r} \vec{E} \cdot d\vec{l} \]

or just \( u(r) = q_{\text{test}} \psi(r) \)

Field and potential are connected like force and energy: \( \vec{E} = -\nabla \psi \)
**Multipoles**

Last time we talked about calculating interaction energies and forces for some charges acting on other charges. One way to try and simplify the calculation is to consider groups of charges as single entities. Thus, instead of talking about the field from two charges, we could talk about the field from one dipole. Four charges are a quadrupole, eight an octopole and so on.

Remember from last time that for a single charge

\[ \psi = \frac{1}{4\pi\varepsilon_0} \frac{q_A}{r^2} \]

It turns out that for a distribution of charge (say a blob with charge density, \( \rho \))

\[ \psi = \frac{1}{4\pi\varepsilon_0} \int_{\text{Volume}} \frac{\rho}{r^2} dV \]

If you try to solve this it turns out that you will derive the Legendre polynomials such that

\[ \int_{\text{Volume}} (r')^n P_n(\cos \theta) \rho dV \]

(sketch diagram, \( r \) is dist. from center of volume to test point, \( r' \) is dist from center of volume to volume element, \( r'' \) is distance from volume element to test point. Theta is angle between \( r \) and \( r' \).)

OR

\[ \psi = \frac{1}{4\pi\varepsilon_0} \sum_{n=0}^{\infty} \frac{1}{r^{n+1}} \int_{\text{Volume}} (r')^n P_n(\cos \theta) \rho dV \]

(Notice the subtle difference in \( r \). Before we had to integrate over \( r'' \), which was a nasty variable to handle. Now, we are integrating over \( r' \) which is only within our volume. So it is nasty, but we only have to deal with it one time and then as long as our object (volume) doesn’t change we don’t have to re-evaluate the integral. The thing that is now difficult to handle is \( r \) but that is a constant, from some fixed point – the center – of the volume. Does everyone see how this has made our lives easier? The \( \rho dV \) integral is now pretty easy.)

So, we have made our favorite thing – a power series, an expansion!

Normally we rewrite things a bit:

\[ \psi = \psi_{mon} + \psi_{dip} + \psi_{quad} + \cdots \]

where
\[ \psi_{\text{mon}} = \frac{q_{\text{mon}}}{4\pi \varepsilon_0 r} \]
\[ \psi_{\text{dip}} = \frac{\hat{r} \cdot \mu}{4\pi \varepsilon_0 r^2} \]

where \( \mu = \int \rho \, dV = \sum_{i=1}^{n} q_i \hat{r}_i \)

and so on with more complicated tensor stuff as we continue.

Remind me how this has made our lives easier? We can calculate the monopole, dipole, quad etc. moments ahead of time – those do not have anything to do with anything except the charge distribution. Then it is relatively easy for us to calculate the potential or the interaction energy with some other charge (or dipole or…) later on.

When is the dipole term really important? when the total charge is zero.

For example, let’s say we have two particles of charge +q and -q some distance, a apart. (like an HCl molecule) The dipole moment is (with the origin at the center):
\[ \mu = q \frac{a}{2} \hat{x} + (-q) \frac{a}{2} (-\hat{x}) = qa \hat{x} \]

(note that we could have chosen any origin)

The electrostatic potential is:
\[ \psi_{\text{dip}} = \frac{\hat{r} \cdot \mu}{4\pi \varepsilon_0 r^2} = \frac{q a \cos \theta}{4\pi \varepsilon_0 r^2} \]

(this is a lot easier than if we had done the individual charges Ex. 21.5)

The interaction energy with a particle of charge +q is:
\[ u = q_a \psi_{\text{dip}} = \frac{qq_a \cos \theta}{4\pi \varepsilon_0 r^2} \]

Note that
- charge-charge interaction \( r^{-1} \)
- charge-dipole interaction \( r^{-2} \)
- dipole-dipole interaction \( r^{-3} \)

Poisson Equation

What if we have a ridiculously complicated set of charges. Well, we could keep many terms in our multipole expansion. Or, we could do something a bit more clever.

Remember Gauss’s Law that we had last time (I think I left out the \( D \):
If we compare this to Gauss’s more general Theory:
\[
\oint \mathbf{D} \cdot d\mathbf{s} = \int \frac{\rho}{\varepsilon_0} \, dV
\]

We see that:
\[
\mathbf{D} \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \quad \text{or} \quad \nabla \cdot \mathbf{E} = \frac{\rho}{D \varepsilon_0}
\]

You may recognize this as one of Maxwell’s equations (quite different than Maxwell’s relations) though you may never have seen the differential form before. We can also restate this equation in terms of the potential which is often more useful:
\[
\mathbf{E} = -\nabla \psi
\]
so
\[
\nabla^2 \psi = -\frac{\rho}{D \varepsilon_0}
\]

This is Poisson’s equation. Big stuff. It gives us an easy way to solve for the potential even if we have a really complicated set of charges that sit within different media with varying dielectric constants. Note that if we have just point charges surrounded by a uniform dielectric, then Poisson’s equation reduces to Coulomb’s law.

Let’s do a quick example (just like 21.6 in the text)
We have a sphere of dielectric D with charge on the surface (total \(q\)), also surrounded by dielectric D
What is the potential at all points in space
\[
\nabla^2 \psi = -\frac{\rho}{D \varepsilon_0}
\]

What is the Laplacian in spherical coordinates (look it up table 17.1 p.313)? fortunately for us \(d\psi/d\phi = d\psi/d\theta = 0\)
\[
\nabla^2 \psi = \frac{1}{r^2} \left( \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) \right) = \frac{1}{r} \frac{d^2(r\psi)}{dr^2} = -\frac{\rho}{D \varepsilon_0}
\]
inside and outside the sphere, \(\rho = 0\) so
\[
\frac{d^2(r\psi)}{dr^2} = 0
\]
\[
\frac{d(r\psi)}{dr} = A_i \quad \text{(integrate once to get a constant)}
\]
\[ r \psi = A_1 r + A_2 \]
\[ \psi = A_1 + \frac{A_2}{r} \quad \text{(integrate again to get a second constant)} \]

(note that this solution is not unique… we have done it this way to match what we are about to see)

Now let’s think about what things look like outside the sphere. Gauss’s law tells us that the field and therefore the potential only depends on the total charge enclosed.

\[ \psi_{\text{out}} = \frac{q_{\text{tot}}}{4\pi \varepsilon_0 r} \]

Equating this with what we got before tells us that outside the sphere

\[ A_2 = \frac{q_{\text{tot}}}{4\pi \varepsilon_0} \quad A_1 = 0 \]

Taking this same approach inside the sphere tells us that

\[ \psi_{\text{in}} = \text{constant} \]

Of course, \( \psi_{\text{in}} \) must equal \( \psi_{\text{out}} \) at the surface of the sphere. Let’s call the radius \( a \).

\[ \psi_{\text{in}}(a) = C = \psi_{\text{out}}(a) = \frac{q_{\text{tot}}}{4\pi \varepsilon_0 a} \]

So, inside the sphere,

\[ \psi_{\text{in}} = \frac{q_{\text{tot}}}{4\pi \varepsilon_0 a} \quad \psi_{\text{out}}(r) = \frac{q_{\text{tot}}}{4\pi \varepsilon_0 r} \]

Note that there is no charge inside the sphere, so the field is zero, but the potential is not… just constant. Constant potential means no force though. This is why a charged (conducting) sphere shuts out RF interference (Dr. Chase’s lab)

Note that Poisson’s equation is critical in lots of current computational applications. For example, implicit solvent models use a variation on Poisson’s equation to estimate the electrostatic contribution to the free energy of solvation.

One critical step here is that when we are talking about electrostatic work \( \Delta G_{\text{el}} = w_{\text{el}} \)
\[ w_{el} = \frac{1}{2} \sum_i q_i \psi_i \]

(This is the work needed to assemble a bunch of charges, \( q_i \) in the potential \( \psi_i \))

Or if we want to know about the DG of going from vacuum to water – the electrostatic contribution to the solvation energy, then:

\[ w_{el} = \frac{1}{2} \sum_i q_i \Delta \psi_i = \frac{1}{2} \sum_i q_i (\psi_i^{\text{water}} - \psi_i^{\text{vacuum}}) \]

This is exactly the kind of treatment we use to calculate solvation energy of a protein.