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INTERMOLECULAR INTERACTIONS

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Introduction

1.1 Energy and length scales in matter

Earth, at temperatures around -20 to $+40^oC$ is very rich in forms of matter. We see different phases, namely solids, liquids, gases; we see also composite materials which are weakly bound. Almost all organic materials are like that. The structure of matter is determined on several very different scales of energy and lengths. When discussing these scales, we need to keep in mind that matter, as we know it on earth exists in room temperature, i.e close to $T \approx 300K$, which dictates a “thermal” energy, i.e. average kinetic energy per degree of freedom of $E_{therm} = k_B T \approx 0.025eV$.

1. Neutrons and protons interact via the strong, weak and electromagnetic forces make up a positively charged nucleus; the size of the nucleus is typically a femtometer ($10^{-6}nm$). It is positively charged and the energy to pull out a proton or a neutron from a stable nucleus or to excite vibrational motion within it is measured in *millions* of electron volts (10^6eV $\approx 10^7$kcal/mole).

2. Nuclei and electrons interact via the electromagnetic forces to make an atom. The electrons do not fall into the nucleus due to the quantum mechanical effect that squeezing an electron into a small region of space increases its kinetic energy (Heisenberg’s uncertainty principle). Thus, the atom is held by a combination of attractive electromagnetic forces and repulsive forces of quantum mechanical origin. It has a typical radius of $0.1 - 0.5nm$. The energy required to pull an electron out of an atom or to excite an electron ranges from keVs for core electrons down to $\sim 1 - 4 \times 10^2$ kcal/mole for the valence electrons. These energies are much smaller than the energies that make up the nuclei and therefore have almost no effect on the nuclear structure.

3. Atoms interact via electromagnetic forces and form molecules. The

energy needed to pull an atom out of a molecule is on the order of $\sim$ 100kcal/mole and to the energy of vibrational motion of atoms in a molecule is typically 2kcal/mole. These energies are not too different from the energies of the valence electrons in atoms. Therefore atoms do not keep their identity when forming the molecular bonds. Molecules come in all sizes. The smallest molecule is H_2 with a length of $0.07nm$ however the DNA of a living cell is also a molecule and it is composed of thousands of atoms hence having lengths on the order of $10-100nm$. In addition to molecules, atoms can interact to give molecules of "infinite" size, i.e. solids.

4. Molecules interact too. The forces are of electromagnetic origin mixing with the quantum mechanical nature of electrons. These interactions determine many properties of materials. For example, the freezing and boiling temperatures of materials, or the way proteins and DNA/RNA fold, or the tendency of salts to dissolve in water and the surface tension of water. The strength of the such non-covalent intercations can be measured by their boiling temperature T_b at 1atm. It is possible to prove that the binding energy is $\varepsilon \approx 20k_BT_b/n$. [1] In the table below we show the bond energy, as estimated by the boiling point and the more accurate value measured directly by experiment. It is seen that the energies associated with non-covalent interactions have quite a range, starting from 10^{-2} kcal/mole and reaching approximately 10kcal/mole. This range of forces are due to different mechanisms by which they appear and this is the subject of the present lecture.

	T_b/K	n	Bond energy (kcal/moles)	
			$20k_BT_b/n$	Experiment
He	4.2	12	0.014	0.022
Ar	87	12	0.29	0.28
Xe	166	12	0.55	0.56
CH_4	111.5	12	0.62	0.36-0.60
H_2O	373.2	4	3.71	4.77

5. Several types of molecular interactions are possible:
    (a) "Exchange" interactions.
    (b) Electrostatic interactions: these are interactions due to static poles, dipoles, quadrupoles etc. The most well known is the attractive hydrogen bond, which is due mainly to dipole-dipole attraction.
    (c) Inductive attractive interactions: This interaction is caused by a static pole in one molecule which induces a static pole in another and then interacts with it.

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[1] Consider water. The heat of evaporation of a mole of molecules at constant temperature and pressure (1 atm) is the change in enthalpy, given by $\Delta H_{vap} = T_b\Delta S$ where ΔS is the change, due mainly to translational and rotational entropy. The former $\Delta S_{tr} = k_B \ln\frac{v_{liq}}{v_{vap}}$, is estimated through the ratio of molar volumes: typically 1000 (the molecular mass of H_2O is $1+1+16 = 18$, (1 mole is 18 g), which is 18 cm^3 (water density is 1 in cgs units) while the molar volume of ideal gas is 22.4 L $\approx 20\times 10^3$) and $\Delta S_{tr} \approx 7.1k_B$, and the latter is on the order of $\approx 2.5k_B$. So, all in all $\Delta S \approx 10k_B$ and $\Delta H_{vap} \approx 10k_BT_b$. This heat is the bond energy per molecule. If each molecule in the liquid phase is connected to n neighbors and if each bond has energy ε then the energy required to release a molecule is $n\varepsilon/2$ (divide by two since ε is shared by two molecules). Thus, $n\varepsilon/2 = 10k_BT_b \Longrightarrow \varepsilon \approx 20k_BT_b/n$.

(d) Dispersive attractive interactions: This is the interaction between correlated fluctuations on both molecules.

2

Electric fields and potentials

2.1 The concepts of electric field and electric potential

Consider a charge e_a at position $\boldsymbol{r}^a = (x^a, y^a, z^a)$ in 3D space and a "test charge" q placed at position $\boldsymbol{r} = (x, y, z)$.The force exerted on q depends on its position $\boldsymbol{r}$ and its charge q and is given by the law due to Charles Augustin de Coulomb (c. 1780):

$$\mathbf{F}(q, \boldsymbol{r}) = q \times \frac{1}{4\pi\epsilon_0} \frac{e_a (\boldsymbol{r} - \boldsymbol{r}^a)}{|\boldsymbol{r} - \boldsymbol{r}^a|^3}. \tag{2.1}$$

Here, ϵ_0 is a constant called "vacuum permittivity". This force is radial, directed along the line connecting the two charges; it is proportional to both q and e and to the square of the inverse displacement $|\mathbf{r}{-}\mathbf{r}_a|$ between them.

Michael Faraday noticed the that the force is linearly dependent on q. He thus introduced the idea of an electric field $\mathbf{E}(\mathbf{r})$ due to a charge e_a: the electric field determines the force on a test charge q at point $\boldsymbol{r}$ through the linear relation $\mathbf{F} = q\mathbf{E}(\mathbf{r})$. Thus, the electric field of charge e_a located at point $\mathbf{r}_a = (x_a, y_a, z_a)$ in 3D space is:

$$\mathbf{E}_a(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{e_a (\boldsymbol{r} - \boldsymbol{r}^a)}{|\boldsymbol{r} - \boldsymbol{r}^a|^3}, \tag{2.2}$$

and the field from many charges $a = 1, 2, \ldots$ is just the sum of fields from each charge:

$$\mathbf{E}(\boldsymbol{r}) = \sum_a \mathbf{E}_a(\boldsymbol{r}).$$

This result is due to the fact that when several forces $\boldsymbol{F}_a$ operate on the test charge then the total force is just the sum $\boldsymbol{F} = \sum_a \boldsymbol{F}_a$.

Atomic units

Atomic unit of length is the Bohr radius a_0, of energy is the Hartree energy E_h, of charge is the electron charge e, of mass is the electron mass m_e. The equations we give in the text do not refer to units but the examples will employ often atomic units. Sometimes we will use other units. Here are useful conversion factors:

Symbol	SI Conversion
Length a_0	$5.292\,10^{-11} M$
Energy E_h	$4.360\,10^{-18} J$
Electron mass m_e	$9.109\,10^{-31} kg$
Electron charge e	$1.602\,10^{-19} C$
Action $\hbar = h/2\pi$	$1.055\,10^{-34} J\,s$
Perm. $(4\pi\epsilon_0)^{-1}$	$8.988\,10^{9} M^2 N/C^2$

2.2 Gauss' law

Gauss' law states that the flux of the electric field through a closed surface is equal to the amount of charge contained within the closed surface. Let us first consider an infinitesimal surface area element (see explanation on the right) $d^2\mathbf{S}$ suppose this are is at $\mathbf{x}$ then the flux is

$$d\Phi = \mathbf{E}\cdot d^2\mathbf{S}$$

We integrate the flux to get the total flux:

$$\Phi\left[S\right] = \oiint_S \mathbf{E}\cdot d^2\mathbf{S} \tag{2.3}$$

(the symbol $\oiint_S$ is an integral over a closed surface). Gauss proved that the charge Q contained within the volume enclosed by the surface S divided by the dielectric constant is equal to the total flux $\Phi\left[S\right]$:

$$\frac{Q}{\epsilon_0\epsilon} = \Phi\left[S\right] \tag{2.4}$$

Let us consider a point charge at the origin and take the surface S to be a sphere of radius r. The total charge is $Q = 1$. From the symmetry of the problem it is clear that $\mathbf{E}$ must be spherically symmetric, i.e. it is radial (points away from or into origin) and has the same value for a given r. Thus the flux is just the field times the area of the sphere:

$$\frac{Q}{\epsilon_0\epsilon} = \Phi = E\times 4\pi r^2 \tag{2.5}$$

and indeed we see that Coulomb's law $E = \frac{Q}{4\pi\epsilon_0\epsilon r^2}$ is also a result of Gauss' law. Similarly, for an infinite line of charge along the z axis with linear density λ we take a cylinder around the line. Then $E\times 2\pi r\times L = \frac{L\lambda}{\epsilon\epsilon_0}$ so

$$E_\perp = \frac{\lambda}{2\pi\epsilon_0\epsilon r} \tag{2.6}$$

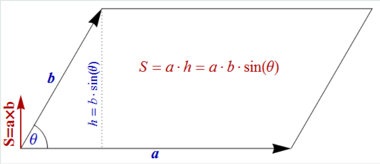
See on the right a calculation of the field from an charged infinite plane.

2.3 Work around a loop is zero

When a test particle is displaced by an infinitesimal amount $\mathbf{\Delta r}$ under the action of a force $\boldsymbol{F}$ the work done on it equals $\Delta W = -\mathbf{F}\cdot\Delta\mathbf{r}$. If the particle is a charge q at position $\boldsymbol{r}$ and the force is due to an electric field then the work is $\Delta W = -\mathbf{E}\left(\boldsymbol{r}\right)\cdot\Delta\mathbf{r}$ and along a path Γ in space the total work is a sum of such terms, which is a "line integral":

$$W\left[\Gamma\right] = -q\int_\Gamma \mathbf{E}\left(\boldsymbol{r}\right)\cdot d\boldsymbol{r}. \tag{2.8}$$

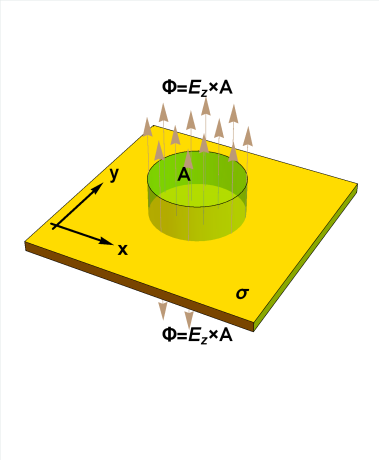
An *amazing quality* of electric fields is this: the work $W\left[\Gamma\right]$ depends not on the entire path Γ but only on the endpoints $\mathbf{r}_1$ and $\mathbf{r}_2$. Therefore, only endpoints count! An extreme example is when we start and



The surface area element

A surface area element is a parallelogram formed between two vectors $\mathbf{a}$ and $\mathbf{b}$ and the height is $h = b\sin\left(\theta\right)$ so the area is: $S = ah = ab\sin\left(\theta\right)$. This area element is described by vector $\mathbf{S}\equiv\mathbf{a}\times\mathbf{b}$ of length S perpendicular to the plane containing $\mathbf{a}$ and $\mathbf{b}$ (forming a right-handed rule). Infinitesimal sides $d\mathbf{a}$ and $d\mathbf{b}$ give infinitesimal area:

$$d^2\mathbf{S}\equiv d\mathbf{a}\times d\mathbf{b}$$



The field from an infinite charged plane of density σ

Take a cylinder of cross section A cutting the surface. The charge within the cylinder is $Q = \sigma A$ and by Gauss' law $\frac{\sigma A}{\epsilon_0\epsilon} = \Phi$ where the flux is $\Phi = 2E_z\times A$ (factor of 2 due to two bases of the cylinder). Thus

$$E_z = \frac{\sigma}{2\epsilon_0} \tag{2.7}$$

since the field is constant, in the z direction the potential is linear: $\varphi\left(\mathbf{r}\right) = -\frac{\sigma}{2\epsilon_0}z$.

end at the same point, i.e. the path is closed. Then the work must always be zero.

Since the work is a function of endpoints, we can choose one endpoint as a fixed reference point $\mathbf{r}_{ref}$ and then the work becomes a function of the second point $\mathbf{r}$. This work function, divided by the charge of the test particle q is called the *electric potential:*

$$\varphi\left(\mathbf{r}\right)=-\int_{\mathbf{r}_{ref}}^{\mathbf{r}}\mathbf{E}\left(\boldsymbol{r}\right)\cdot d\boldsymbol{r}. \tag{2.9}$$

Knowledge of the potential is equivalent to the knowledge of all line integrals $\varphi\left(\boldsymbol{r}\right)$. The work W_{12} needed to displace a charge q from $\boldsymbol{r}_1$ to $\boldsymbol{r}_2$ is thus just the charge times the potential *differences*: $W_{12}=q\left(\varphi\left(\boldsymbol{r}_2\right)-\varphi\left(\boldsymbol{r}_1\right)\right)$. The scalar function $\varphi\left(\boldsymbol{r}\right)$ thus encapsulates all information regarding the electric field. Knowledge of the field determines the potential through Eq. (2.9) while knowledge of the potential leads directly to the electric field since the derivative by r_i of the integral in Eq. (2.9) is equal to E_i, Thus:

$$E_i\left(\boldsymbol{r}\right)=-\varphi_i\left(\boldsymbol{r}\right). \tag{2.10}$$

Note that $i=x,y,z$ on the left hand side of this equation is the Cartesian coordinate of the vector $\boldsymbol{E}$ while i on the right hand side is the derivation variable (x, y or z) for the potential function derivative: $\varphi_x\left(\boldsymbol{r}\right)=\frac{\partial\varphi(\boldsymbol{r})}{\partial x}$, $\varphi_y\left(\mathbf{r}\right)=\frac{\partial\varphi(\boldsymbol{r})}{\partial y}$, etc.

Going back to Eq. (2.2), we can determine the electric potential of a single charge at the $\boldsymbol{r}^a$:

$$\varphi\left(\boldsymbol{r}\right)\equiv\frac{e_a}{4\pi\epsilon_0}\int_{\infty}^{\boldsymbol{r}}\frac{\left(\boldsymbol{r}-\boldsymbol{r}^a\right)}{\left|\boldsymbol{r}-\boldsymbol{r}^a\right|^3}\cdot d\boldsymbol{r}.$$

This results in:

$$\varphi\left(\mathbf{r}\right)=\frac{e_a}{4\pi\epsilon_0}\frac{1}{\left|\boldsymbol{r}-\boldsymbol{r}^a\right|}. \tag{2.11}$$

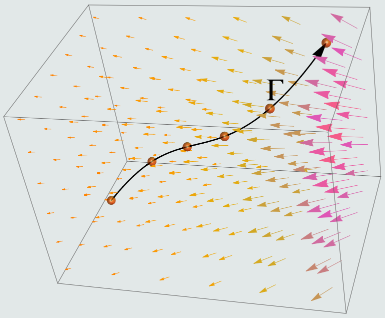
When we have a collection of charges, each e_a at position $\boldsymbol{r}^a$ the total potential is just the sum of each potential:

$$\varphi\left(\mathbf{r}\right)=\sum_a\frac{e_a}{4\pi\epsilon_0}\frac{1}{\left|\boldsymbol{r}-\boldsymbol{r}^a\right|} \tag{2.12}$$

Another example for potential is the potential from an infinite board of charge laying on the x-y as plane studied above. Since the field is constant the work is linear and so is the potential $\varphi\left(\mathbf{r}\right)=\frac{\sigma}{2\epsilon_0}z$.

The total potential of a charge distribution is always the sum of all $\frac{1}{r}$ terms from each of the charges (Eq 2.12). Thus we deduce from Eq. (2.17): $\varphi_{ii}\left(\mathbf{r}\right)=-\frac{1}{\epsilon_0}\sum_a e_a\delta\left(\boldsymbol{r}-\boldsymbol{r}^a\right)$. The function $\sum_a e_a\delta\left(\boldsymbol{r}-\boldsymbol{r}^a\right)$ is the density of charge $\rho\left(\mathbf{r}\right)$ at point $\mathbf{r}$ and so we reach the Poisson equation :

$$\varphi_{ii}\left(\mathbf{r}\right)=-\frac{1}{\epsilon_0}\rho\left(\mathbf{r}\right) \tag{2.13}$$



Electrostatic work for displacing a charge along a path

We show a path Γ stretching and winding in space, along which a charged particle can be displaced under the influence of a static electric field denoted as colored. The work along the path is equal to the line integral of Eq. (2.8).

It can be shown that this equation is equivalent to Gauss' law.

2.4 Far-field electric potential by a molecule: molecular multipoles

A molecule is composed of a set of charges e_a located at spatial positions $\boldsymbol{r}^a$. Thus the electric potential in space formed by the molecule is given by Eq. (2.12). The charges making up the molecule are the M nuclei and N electrons. The nuclei are indexed by $A = 1, \dots M$, where nucleus A has Z_A protons, each of charge $+e$ positioned at $\mathbf{R}_A$; the electrons are indexed by $n = 1, \dots, N$, where electron n has charge $-e$ positioned at $\boldsymbol{x}_n$. The same potential of Eq. (2.12) as can be written as:

$$\varphi(\mathbf{r}) = \sum_a \frac{e_a}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \boldsymbol{r}^a|} = \sum_{A=1}^{M} \frac{eZ_A}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{R}_A|} - \sum_{n=1}^{N} \frac{e}{4\pi\epsilon_0} \frac{1}{|\boldsymbol{r} - \boldsymbol{x}_n|}$$

The structure of this potential is not easy to grasp, but it becomes simple if we distance ourselves from the molecule, where we are at the "far-field". What is "far"? Where is "far"? This is determined of course by the location and size of the molecule (see discussion on the right).

We have a molecule with center of charge at the origin $\boldsymbol{x}_{cc} = 0$ and we want to calculate the potential at a point displaced by $\mathbf{r}$ from the molecule (see figure (2.1)). This point is "in the far-field" if the molecule is *small* relative to the distance r, i.e. $r \gg R$. In this case, we assume for all constituents$|\boldsymbol{r}| \gg |\boldsymbol{r}^a|$ so $\frac{r^a}{r} \ll 1$.

Using the identity $(\boldsymbol{r} - \boldsymbol{r}^a)^2 = r^2 - 2\boldsymbol{r} \cdot \boldsymbol{r}^a + (r^a)^2$ we have. The scalar product $\boldsymbol{A} \cdot \boldsymbol{B}$ between two vectors, $\boldsymbol{A}$ and $\boldsymbol{B}$ is clearer if written in terms of components: $\boldsymbol{A} \cdot \boldsymbol{B} = \sum_{i=x,y,z} A_i B_i$. We will simplify notations further and use the Einstein convention, that repeated Cartesian indices are summed over; then: $\boldsymbol{A} \cdot \boldsymbol{B} = A_i B_i$. Using this notation we have: $(\boldsymbol{r} - \boldsymbol{r}_a)^2 = r^2 - 2r_i r_i^a + r_a^2$ which can then ve written as: $(\boldsymbol{r} - \boldsymbol{r}_a)^2 = r^2 \left(1 - 2\frac{r_i r_i^a}{r^2} + \frac{r_a^2}{r^2}\right)$ and so:

$$\frac{1}{|\boldsymbol{r} - \boldsymbol{r}_a|} = \frac{1}{\sqrt{1 - 2\frac{r_i r_i^a}{r^2} + \frac{r_a^2}{r^2}}} \times \frac{1}{r} \tag{2.20}$$

Using Taylor's expansion to 1st and second order (see development on the right), we find the "multipole" expansion for the Coulomb potential:

$$\frac{1}{|\boldsymbol{r} - \boldsymbol{r}_a|} = \frac{1}{r}\left[1 + \frac{r_i r_i^a}{r^2} + \frac{3r_i r_i^a r_j r_j^a - (r^a)^2 r^2}{2r^4} + \dots\right]$$

Derivatives of $\frac{1}{r}$

The derivatives of $\frac{1}{r} = \frac{1}{\sqrt{r_x^2 + r_y^2 + r_z^2}}$ are central in electrostatics. When $r \neq 0$:

$$\left(\frac{1}{r}\right)_i = -\frac{r_i}{r^3} \tag{2.14}$$

A second derivative gives:

$$\left(\frac{1}{r}\right)_{ij} = \frac{\partial}{\partial r_j}\left(-\frac{r_i}{r^3}\right) = \frac{3r_i r_j - r^2 \delta_{ij}}{r^5} \tag{2.15}$$

By summing over $i = j$:

$$\left(\frac{1}{r}\right)_{ii} = 0, \tag{2.16}$$

Including $r = 0$ gives:

$$\left(\frac{1}{r}\right)_{ii} = -4\pi\delta(\mathbf{r}). \tag{2.17}$$

Where's the molecule? What's its size?

The molecule is composed of a M nuclei and N electrons. So we can think of it as "localized", i.e. we can ask "where" is the molecule and "what's its size". Since nuclei move very slowly relative to electrons we use their positions for determining where the molecule is, we take their charge-weighted average position:

$$\boldsymbol{x}_{cc} = \frac{\sum_{A=1}^{M} Z_A \mathbf{R}_A}{\sum_{A=1}^{M} Z_A} \tag{2.18}$$

What is the *spatial extent* of the molecule? Here we can average over the deviance of each charge from the center of charge:

$$D^2 = \frac{\sum_A Z_A (\mathbf{R}_A - \boldsymbol{x}_{cc})^2}{\sum_A Z_A}. \tag{2.19}$$

This definition does not take into account the breadth of the electronic cloud which protrudes (bulges out) by about 1.5Å; hence D should be enlarged by about 3Å beyond the value of Eq. 2.19.

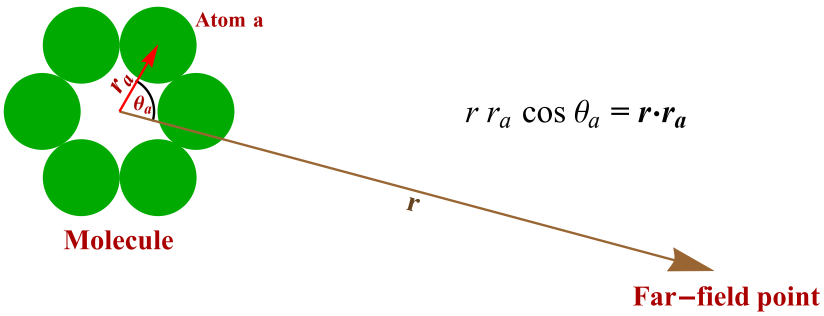


Figure 2.1: The molecule and its atoms; nucleus a is at position $\mathbf{r}_a$, the far-field potential is measured at a distant point $\mathbf{r}$, making an angle θ with $\mathbf{r}_a$.

Finally, we rearrange:

$$\frac{1}{|\mathbf{r}-\mathbf{r}_a|} = \frac{1}{r}\left[1+\frac{r_i r_i^a}{r^2}+\frac{3r_i\left(3r_i^a r_j^a-\left(r^a\right)^2\delta_{ij}\right)r_j}{2r^4}+\dots\right]$$

where we used the fact that $r^2 = r_i r_i = r_i \delta_{ij} r_j$ (check that this is correct). Multiplying by e_a and summing over a we have finally the following expression for the far-field potential:

$$\varphi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\left[\frac{Q}{r}+\frac{\mu_i r_i}{r^3}+\frac{r_i\Theta_{ij}r_j}{r^5}+\dots\right] \;(r \text{ in far-field}) \qquad (2.21)$$

where Q, μ_j and Θ_{ij} are the charge, *dipole moment* and *quadrupole moment*, defined as:

$$\begin{aligned} Q &= \sum_a e_a \\ \mu_i &= \sum_a e_a r_i^a \\ \Theta_{ij} &= \frac{1}{2}\sum_a e_a\left(3r_i^a r_j^a-\left(r^a\right)^2\delta_{ij}\right) \end{aligned}$$

The expansion of Eq. (2.21) is a series of additive terms, each involving multiplication between instances of the position vector $\mathbf{r}$, describing *where* we are evaluating the potential, and a *moment* tensor which is a purely molecular property that can be calculated and tabulated once and for all. For very large $r = |\mathbf{r}|$ only a small number of terms is required for reasonably accurate estimation of the potential. The first potential term on the right of Eq. (2.21) is a Coulomb potential of the total charge Q; it is isotropic (the same in all directions) and drops off slowly with distance, as r^{-1}. When the molecule is neutral, this potential is zero and the next term on the right of Eq. (2.21) becomes noticeable, the dipole $\boldsymbol{\mu}$ exerts a potential which decays as r^{-2}. This potential has an interesting of directionality as shown in the gray box on the right. When the dipole is zero the next term, the

Taylor expansion of $\frac{1}{\sqrt{1-2\zeta}}$

Taylor expansion of a function $f(\zeta)$around ζ is a power series in the variable ζ:

$$f(\zeta) = f(0) + f'(0)\,\zeta + \frac{1}{2}f''(0)\,\zeta^2 + \dots$$

where the first term on the right is the “zeroth order” term , the second, linear in ζ is the first order term the third, quadratic in ζ is the second order term and so . For the function $f(\zeta) = 1/\sqrt{1-2\zeta}$, we have $f'(\zeta) = 1/(1-2\zeta)^{3/2}$ so $f'(0) = 1$ and similarly $f''(\zeta) = 3/(1-2\zeta)^{5/2}$ so $f''(0) = 3$, thus the expansion, to second order is:

$$\frac{1}{\sqrt{1-2\zeta}} = 1 + \zeta + \frac{3}{2}\zeta^2 + \dots$$

quadrupole Θ becomes important and it decays as r^{-3} and has an even more interesting angular distribution.

2.5 *The point-dipole*

Consider two charges, a charge e at $\mathbf{R}/2$ and a second charge $-e$ at $-\mathbf{R}/2$. These two charges are a neutral system, and at distance $r \gg R$ the potential they form was estimated in Eq. (2.21):

$$\varphi_D(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\frac{\mu_i r_i}{r^3} \quad (\mathbf{r}\text{ far field}) \tag{2.22}$$

where:

$$\mu_i = e \times \frac{R_i}{2} + -e \times \frac{-R_i}{2} = eR_i$$

Strictly speaking, the potential is a far-field potential and only valid for $r \gg R$. However, what happens if we take the limit of $R \to 0$ i.e. go to an infinitely small, point-like, dipole? Of course, we want to keep the dipole μ constant, so at the same time that R shrinks to zero we take the charge difference to infinity, $e \to \infty$. What will the potential and the electric field look like in this limit?

The dipole potential is expected to be valid at all points $r \neq 0$ because our idealized *point dipole* has no finite length scale R so all points are now "far field".

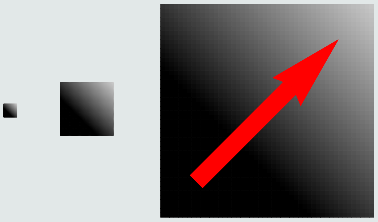
What about the electric field? This is obtained from the potential by a derivative (Eq. (2.10)):

$$(E_D)_j(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\mu_i\left(\frac{1}{r}\right)_{ji} \tag{2.23}$$

For $r > 0$ the derivative is: $\left(\frac{1}{r}\right)_{ji} = -\left(\frac{r_j}{r^3}\right)_i = 3\frac{r_i r_j}{r^5} - \frac{\delta_{ij}}{r^3}$. Note that this means that $\sum_i \left(\frac{1}{r}\right)_{ii} = 0$ for all $r > 0$ and that this is not fully compatible with Poisson's equation $\sum_i \left(\frac{1}{r}\right)_{ii} = -4\pi\delta(\mathbf{r})$. The way to fix this then is to demand that $\left(\frac{1}{r}\right)_{xx} = \frac{3x^2-r^2}{r^5} - \frac{4\pi}{3}\delta(\mathbf{r})$ or: $\left(\frac{1}{r}\right)_{ji} = 3\frac{r_i r_j}{r^5} - \frac{\delta_{ij}}{r^3} - \frac{4\pi}{3}\delta_{ij}\delta(\mathbf{r})$ and the electric field of a point dipole is:

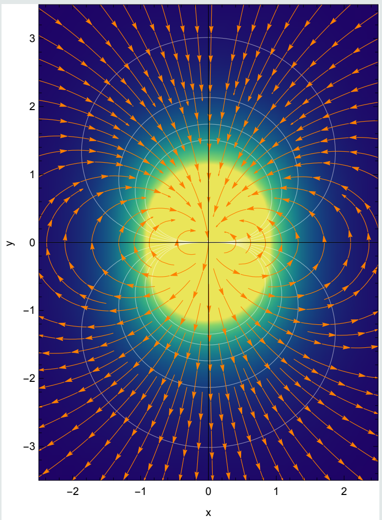
$$(E_D)_j(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\left[3\frac{(\mu_i r_i)\,r_j}{r^5} - \frac{\mu_j}{r^3} - \frac{4\pi}{3}\mu_j\delta(\mathbf{r})\right] \tag{2.24}$$

Note the new feature, of a delta function field right at the center of the dipole. This field exists at a singular point and it results from the electric field "imprisoned" in between the two point charges as they approach each other when $R \to 0$.



Feeling for the moment

We show 3 snapshots of a board, the first from very far away, is barely seen as a gray point; zooming in 4 times closer, the lower-left is slightly blacker than the upper-right; 4 times closer still we the board is seen in full detail. Red arrow represents the dipole vector. Zooming in and out is what moments allow us to do: from afar we only notice only the monopole - the overall charge - of a charge distribution; as we zoom in we first feel the potential of its dipole and then more details.



Point dipole potential and field

2D contour plot in x-y plane of the potential $\varphi_D(\boldsymbol{r}) = \frac{\mu}{4\pi\epsilon_0}\frac{y}{r^3}$ of dipole $\mu\hat{\boldsymbol{y}}$ and the electric field lines $(E_D)_j(\boldsymbol{r}) = \frac{\mu}{4\pi\epsilon_0}\left[\frac{3yr_j}{r^5} - \left(\frac{1}{r^3} + \frac{4\pi}{3}\delta(\boldsymbol{r})\right)\delta_{jy}\right]$ going from positive into negative poles.

2.6 *Quantum mechanical expressions for the potential*

Up to now we have not talked about the quantum state of the molecule. All we assumed are that the charges e_a from which the molecule is contrived are at given positions $\mathbf{r}_a$. However, molecules obey the laws of quantum mechanics and in quantum mechanics the low lying states of the molecules do not in general allow determination of the exact position of charges. Suppose that the molecule is in a quantum state described by the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2 \ldots)$. The potential it creates at far-field position $\mathbf{r}$ will not be a deterministic number. If we measure it many times, under exactly the same conditions, we will find its value.

The quantum mechanical formalism requires that the positions of the charges are $\mathbf{r}_a$ become quantum mechanical operators, and acquire a "hat" symbol to remind us: $\hat{\mathbf{r}}_a$. This way, the potential becomes an quantum operator $\hat{\varphi}(\mathbf{r}) = \sum_a \frac{e_a}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}-\hat{\mathbf{r}}_a|}$. The measurable potential in space is the expectation value of this $\mathbf{r}$ dependent potential:

$$\langle\varphi\rangle(\mathbf{r}) = \langle\Psi\,|\hat{\varphi}(\mathbf{r})|\,\Psi\rangle = \left\langle \Psi \left| \sum_a \frac{e_a}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{r}-\hat{\boldsymbol{r}}^a|} \right| \Psi \right\rangle .$$

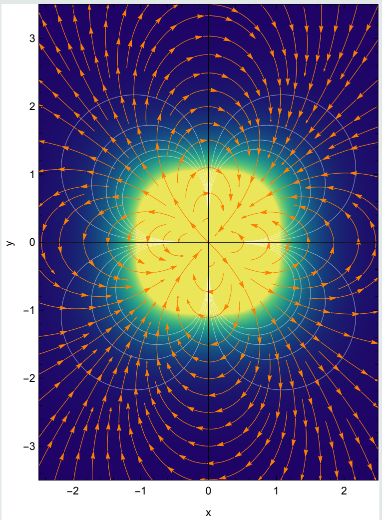
The dipole and quadrupole moments become operators as:

$$\begin{aligned} \hat{\mu}_i &= \sum_a e_a \hat{r}_i^a \\ \hat{\Theta}_{ij} &= \frac{1}{2}\sum_a e_a \left(3\hat{r}_i^a\hat{r}_j^a - \delta_{ij}\left(\hat{r}^a\right)^2\right) \end{aligned}$$

and their expectation values determine the potential:

$$\langle\varphi\rangle(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\left[\frac{Q}{r} + \frac{\langle\hat{\mu}_i\rangle r_i}{r^3} + \frac{r_i\langle\hat{\Theta}_{ij}\rangle r_j}{r^5} + \ldots\right].$$

Note,again, that we are using the Einstein summation convention by which repeated Cartesian indices are summed.



Quadrupole potential and field

2D contour plot superimposed on electric field lines for the quadruple potential $V_\Theta(\boldsymbol{r}) = \frac{\Theta_{ij}(3r_ir_j-\delta_{ij}r^2)}{r^5}$ for $\Theta = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} ea_0^2$.

2.7 *Energy of a molecule in an electric potential*

In the previous section we looked into the potential created by a molecule. Now let us consider the effect of an external potential on a given molecule.

The energy of a collection of charges in a electric potential $\varphi(\boldsymbol{r})$ is defined as the work required to bring the collection from infinity to its final location in the field $\mathbf{E}(\boldsymbol{r}) = -\nabla\varphi(\boldsymbol{r})$. Since this work is simply the product of the charges and the potential, we find:

$$W_{es} = e_a\varphi(\boldsymbol{r}_a) \tag{2.25}$$

(once again, note that repeated indices are summed over).

Let us develop the potential around a central position of the molecule, which we take as the origin. Let us also assume that the potential varies slowly over the molecule. Thus we can use the Taylor expansion around $\mathbf{r} = 0$ which, using the Einstein convention gives:

$$\varphi\left(\boldsymbol{r}_a\right) = \varphi + \left(\boldsymbol{r}_a\right)_i \varphi_i + \frac{1}{2}\left(\boldsymbol{r}_a\right)_i \left(\boldsymbol{r}_a\right)_j \varphi_{ij} + \ldots \tag{2.26}$$

Because of the Laplace equation $\varphi_{ii} = 0$ we can add to the equation this also as:

$$\varphi\left(\boldsymbol{r}_a\right) = \varphi + \left(\boldsymbol{r}_a\right)_i \varphi_i + \frac{1}{2}\left(\boldsymbol{r}_a\right)_i \left(1 - \frac{1}{3}\delta_{ij}\right)\left(\boldsymbol{r}_a\right)_j \varphi_{ij} + \ldots \tag{2.27}$$

Multiplying by e_a and summing over a we obtain for the electrostatic energy of interaction of the molecule with the potential:

$$\hat{W}_{es} = Q\varphi + \mu_i\varphi_i + \frac{1}{3}\Theta_{ij}\varphi_{ij} + \ldots \tag{2.28}$$

we see that the same molecular quantities, the dipole moment μ_i and the quadrupole moment Θ_{ij} are involved in describing the interaction energy of the molecule with an external electric potential. The dipole μ_i couples to the potential gradient φ_i which is the electric field. The quadrupole Θ_{ij} couples to the derivatives, or non-homogeneity of the field.

Taylor expansion of a function of N variables

Taylor's expansion of a function $f\left(\boldsymbol{r}\right)$ where $\boldsymbol{r} = \left(r_x, r_y, r_z\right)$ near the origin (0) is a power series in the variables r_i, $i = x, y, z$. We write it in the condensed form:

$$f\left(\boldsymbol{r}\right) = f\left(\boldsymbol{0}\right) + f_i r_i + \frac{1}{2} r_i r_j f_{ij} + \ldots$$

The derivative is written as a subscript: $f_i \equiv \left(\frac{\partial f}{\partial r_i}\right)_{(0)}$ and we used the Einstein summation convention $i, j = x, y, z$.

As above the energy expression above must be considered as an identity for operators. If the state of the molecule is Ψ (typically, the groundstate) then the expectation value for the electrostatic energy is:

$$\begin{aligned} \left\langle W_{es}\right\rangle &= e_a\left\langle \Psi\left|\varphi\left(\hat{\boldsymbol{r}}_a\right)\right|\Psi\right\rangle \qquad (2.29) \\ &= Q\varphi + \left\langle \hat{\mu}_i\right\rangle \varphi_i + \frac{1}{3}\left\langle \hat{\Theta}_{ij}\right\rangle \varphi_{ij} + \ldots \end{aligned}$$

This expression, while true, is usually not very useful because we do not know the ground state wave function. In chapter 4 (see page 27) we will use perturbation theory to estimate the energy $\left\langle W_{es}\right\rangle$.

3

Polarizability, dielectric materials and solvation

We have seen that molecules interact with electric field exerted on them. In this section, we would like to examine how their properties are affected. The field δE_j ($j = x, y, z$) exerts opposite forces an nuclei and on electrons displacing nuclei in the direction of the field and electrons in the opposite direction. Such a displacement will change the expectation value of the dipole moment and we call this change $\delta \langle \mu_i \rangle$ an "induced" dipole vector. Assuming a weak field δE_j we expect a linear relation

$$\delta \langle \mu_i \rangle = \alpha_{ij} \delta E_j \tag{3.1}$$

(summation over repeated indices assumed). The proportionality coefficient α_{ij} is a tensorial molecular property called *polarizability*. Note the units of polarizability, which is $4\pi\epsilon_0$ times volume. In homogeneous media $\alpha_{ij} = \alpha$ is a constant.

Polarizability is a most important property of matter responsible for subtle effects seen in neutral systems. Polarizability can be a result of various mechanisms. In spirit with the usual treatment of molecules and materials, we use the Born-Oppenheimer approximation. In such a case we differentiate between nuclei, which we treat as classical objects and electrons which we treat quantum mechanically.

We shall study 2 types of polarizability, one we designate by α_0 described by slow motion, rotation, of the molecular nuclei and thus uses classical mechanics and one by the fast motion of electrons described by quantum mechanics.

3.1 Electronic polarizability

Up to now we dealt with the polarizability due to orientation of polar molecules. However, even if the molecules have no dipole moment, they can still be polarized due to the distortion of their electronic cloud by an electric field. This kind of polarizability is called the electronic polarizability $\alpha^{(e)}$.

In order to compute the electronic polarizability we consider a neutral molecule with Hamiltonian $\hat{H}_0$ with its eigenfunctions and energies denoted by a superscript "(0)": $\hat{H}_0\psi_s^{(0)} = \mathcal{E}_s^{(0)}\psi_s^{(0)}$, where s indexes the eigenstates of $\hat{H}_0$ and the corresponding eigenstates of $\hat{H}$. The molecule is now placed in a homogeneous field so the interaction is $\delta\hat{V}^{(1)} = -\delta E_j\hat{\mu}_j$ (see Eq. (2.29) with $\delta E_j = -\varphi_j$, taken from Eq. (2.10)), so the full Hamiltonian of the molecule and field is: $\hat{H} = \hat{H}_0 + \delta\hat{V}^{(1)}$.

Brief reminder of perturbation theory

For a perturbed Hamiltonian $\hat{H} = \hat{H}_0 + \delta\hat{V}^{(1)}$, we write energy as a sum $\mathcal{E}_s = \mathcal{E}_s^{(0)} + \delta\mathcal{E}_s^{(1)} + \delta\mathcal{E}_s^{(2)} + ...$ where

$$\delta\mathcal{E}_s^{(1)} = \left\langle \psi_s^{(0)} \middle| \delta\hat{V}^{(1)} \middle| \psi_s^{(0)} \right\rangle, \tag{3.2}$$

$$\delta\mathcal{E}_s^{(2)} = \sum_{s'\neq s} \frac{\left|\left\langle \psi_s^{(0)} \middle| \delta\hat{V}^{(1)} \middle| \psi_{s'}^{(0)} \right\rangle\right|^2}{\mathcal{E}_{s'}^{(0)} - \mathcal{E}_s^{(0)}} \tag{3.3}$$

are respectively the first and second order energy corrections. The wave function of $\hat{H}$ is also written as a sum of $\psi_s(x) = \psi_s^{(0)}(x) + \delta\psi_s^{(1)}(x)$ where:

$$\delta\leftarrow_s^{(1)}(x) = \sum_{s'\neq s} \psi_{s'}^{(0)}(x) \frac{\left\langle \psi_{s'}^{(0)} \middle| \delta\hat{V}^{(1)} \middle| \psi_s^{(0)} \right\rangle}{\mathcal{E}_s^{(0)} - \mathcal{E}_{s'}^{(0)}} \tag{3.4}$$

is the first order correction.

As a result of the field induced distortion of the ground state wave function ψ_g (we reserve the symbol $s = g$ for the ground state) the dipole expectation value changes by:

$$\delta\left\langle\hat{\mu}_i\right\rangle = \left\langle\psi_g\left|\hat{\mu}_i\right|\psi_g\right\rangle - \left\langle\psi_g^{(0)}\left|\hat{\mu}_i\right|\psi_g^{(0)}\right\rangle$$

plugging into this expression the first-order perturbation expression $\psi_g = \psi_g^{(0)} + \delta\psi_g^{(1)}$, we obtain:

$$\delta\left\langle\hat{\mu}_i\right\rangle = \left\langle\psi_g^{(0)}\left|\hat{\mu}_i\right|\delta\psi_g^{(1)}\right\rangle + c.c$$

where "$+c.c.$" means that we add the complex conjugate. Combining this expression with Eq. (3.4) and taking $\delta\hat{V}^{(1)} = -\delta E_j\hat{\mu}_j$ (Eq. (2.29)) we obtain:

$$\delta\left\langle\hat{\mu}_i\right\rangle = -\sum_{s\neq g} \frac{\left\langle\hat{\mu}_i\right\rangle_{gs}\left\langle\hat{\mu}_j\right\rangle_{sg}}{\mathcal{E}_g^{(0)} - \mathcal{E}_s^{(0)}}\delta E_j + c.c$$

where s indexes the excited states of the system and we used the following notation for the unperturbed matrix elements of an operator $\left\langle\psi_s^{(0)}\left|\hat{X}\right|\psi_{s'}^{(0)}\right\rangle \equiv$

$\langle \hat{X} \rangle_{ss'}$. Note that s may be a composite index, as for example in the hydrogen atom, where the bound eigenstates are indexed by 3 integers $\psi_s(\boldsymbol{r}) \equiv \psi_{nlm}(\boldsymbol{r})$: $l = 0, 1, 2, \ldots$ is the *angular momentum quantum number*, $n = l, l+1, \ldots$ is the *principal quantum number* and $m = -l, \ldots, l$ is the *magnetic quantum number.* This Eq. shows the linear relation between the imposed field and the induced dipole from which the polarizability tensor is given by (see Eq. (3.1)):

$$\alpha^{(e)}_{ji} = 2Re \sum_{s \neq g} \frac{\langle \hat{\mu}_i \rangle_{gs} \langle \hat{\mu}_j \rangle_{sg}}{\mathcal{E}^{(0)}_s - \mathcal{E}^{(0)}_g} \tag{3.5}$$

Note that in the denominator we have the excitation energies of the system, which are positive by definition and that when $i = j$ the numerator is also positive; thus we conclude that the diagonal elements of the polarizability tensor are positive . This is what we would expect from simple physical intuition: a field in the positive x direction will push the positive charges in the positive x direction and the negative charges in the negative x direction, thus inducing a positive dipole.

A material which has a large polarizability polarizes easily under the action of a field. For high polarizability a molecule should have low lying excitation energies $\mathcal{E}^{(0)}_s - \mathcal{E}^{(0)}_g$ from the ground state and correspondingly strong transition dipole matrix elements.

The evaluation of Eq. (3.5) can be quiet complicated. A useful approximation can be obtained when we assume that the denominator is a constant equal to the ionization potential of the system. In this case:

$$\alpha^{(e)}_{ji} \approx \frac{2e^2}{I} \left(\langle r_i r_j \rangle_g - \langle r_i \rangle_g \langle r_j \rangle_g \right) \tag{3.6}$$

Example: The polarizability of the hydrogen atom: The ground state is $g = 1, 0, 0$ or$\psi_{1,0,0}(\boldsymbol{r}) = Ne^{-r/a_0}$ and the energy is $\mathcal{E}^{(0)}_g = \frac{-E_h}{2}$. The ionization potential is just the negative of the ground state energy, so: $I = \frac{e^2}{2 \times 4\pi\epsilon_0 a_0}$. The integrals required for (3.6) are:

$$\langle 1s | r_i r_j | 1s \rangle = \frac{\delta_{ij}}{3} \frac{\int \psi_{100}(r)^2 r^2 \times 4\pi r^2 dr}{\int \psi_{100}(r)^2 \times 4\pi r^2 dr} = a_0^2$$

and thus the approximation for the hydrogen polarizability is:

$$\alpha_{ij} \approx (4\pi\epsilon_0) \times 4a_0^3 \delta_{ij}. \tag{3.7}$$

We note that an exact summation of Eq. (3.5) for the H atom yields $\alpha_{zz} = (4\pi\epsilon_0) \times \frac{9}{2} a_0{}^3$, a value verified by experiment. Hence our approximate estimate, about 90% of the exact value, is quite reasonable.

3.2 Langevin polarizability

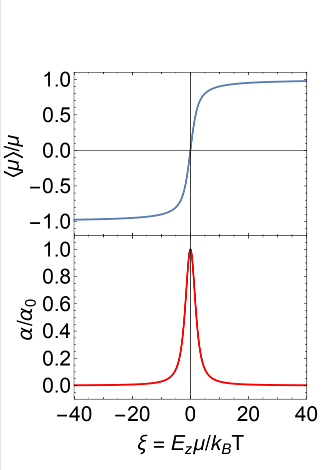
In the previous section, we calculated the electronic polarizability, assuming atomic nuclei are locked in place. In reality nuclei of molecules can move and of the molecule carries a permanent dipole, they can rotate so as to align with the field. Since nuclei are heavy we can use classical mechanics to treat this kind of effect. The effect of alignment becomes interesting when combined with temperature. The temperature wants to scramble everything (increase entropy) while the external fields tries to induce order. The race between two gives a combined effect of polarizability.

When the field is strong the average dipole is the product of the permanent dipole and the so called Langevin function:

$$\langle\mu_z\rangle = \mu\left(\coth\xi - \frac{1}{\xi}\right) \tag{3.8}$$

where $\xi = E_z\mu/k_BT$ and the polarizability is then:

$$\alpha = 3\alpha\left(\frac{3}{\xi^2} - \frac{3}{\sinh^2\xi}\right) \tag{3.9}$$



The polarization (top panel) and polarizability (bottom panel) of a gas of dipolar molecules. For strong fields practically all molecules become aligned with the field and the polarization saturates.

Consider a dilute gas of N identical polar molecules (molecules that have a permanent dipole, like NH_3 or H_2O) at temperature T. The dipole $\vec{\mu}_n$ of molecule n ($n = 1, 2, \ldots, N$) is a vector of a known constant magnitude $|\vec{\mu}_n| = \mu$ but it's orientation is unconstrained: it's dynamical. Due to collisions with the vessel wall or between molecules each dipole $\vec{\mu}_n$ fluctuates over time and the time-averaged dipole $\langle\vec{\mu}_n\rangle$ becomes independent of n, so we simply drop the index n and set it equal to $\langle\vec{\mu}\rangle$. Clearly, the total dipole moment is, on the average equal to $\left\langle\vec{\mu}^{tot}\right\rangle = N\langle\vec{\mu}\rangle$ (this is called the ergodic assumptions, by which the time average of one molecule equals the average over many molecules at a given time).

In the presence of an electric field E_z pointing in the z direction the energy of each dipole is determined by its z-component: $\mathcal{E} = -E_z\mu_z$ (see Eq. (2.29) with $E_j = -\varphi_j$, taken from Eq. (2.10)) and it is energetically favorable for each molecular dipole to orient with the field, i.e. in the positive z direction. In the x or y direction there is no preference so we can assume at the outset: $\langle\mu_x\rangle = \left\langle\mu_y\right\rangle = 0$, while

$$\langle\mu_z\rangle = \frac{\int_{-\mu}^{\mu} e^{\frac{E_z\mu_z}{k_BT}}\mu_z d\mu_z}{\int_{-\mu}^{\mu} e^{\frac{E_z\mu_z}{k_BT}} d\mu_z}.$$

For very weak fields we Taylor expand the exponential to first order: $e^x \approx 1 + x$, hence:

$$\begin{aligned}\langle\mu_z\rangle &\approx \frac{\int_{-\mu}^{\mu}\left(1+\frac{E_z\mu_z}{k_BT}\right)\mu_z d\mu_z}{\int_{-\mu}^{\mu}\left(1+\frac{E_z\mu_z}{k_BT}\right)d\mu_z} \\ &= \frac{1}{3}\frac{E_z}{k_BT}\mu^2\end{aligned}$$

Thus, the average dipole $\langle\vec{\mu}\rangle$ points in the z direction and is *created* by the field because when the field is zero the dipole is zero. In fact, it is linear with the field and the polarizability is the proportionality constant (Eq. (3.1)):

$$\alpha^{(L)} = \frac{\mu^2}{3k_BT}. \tag{3.10}$$

This formula was first derived by the French physicist Paul Langevin and it represents the "Langevin polarizability". It shows that the polarizability grows as the inverse temperature. In ideal cases, if the gas is sufficiently dilute the polarizability can grow indefinitely as $T \to 0$. Furthermore, we see that the polarizability is proportional to the square of the constant dipole moment magnitude μ. The Langevin polarizability is often useful for liquids, however, if the dipole density is high a correction must be applied fue to the interaction between nearby dipoles, as done by Onsager in 1938.

In strong fields we may not linearize the Boltzmann distribution. Yet in our case, a full analytical integral of the Boltzmann distribution is not difficult. We thus give the results in the margin, showing saturation effects in high electric field.

Combining the results of this section and the previous, we find that for polar molecules the total polarizability is a sum of the Langevin and the electronic polarizability, leading to the Langevin-Debye equation:

$$\alpha = \alpha^{(e)} + \alpha^{(L)} \tag{3.11}$$

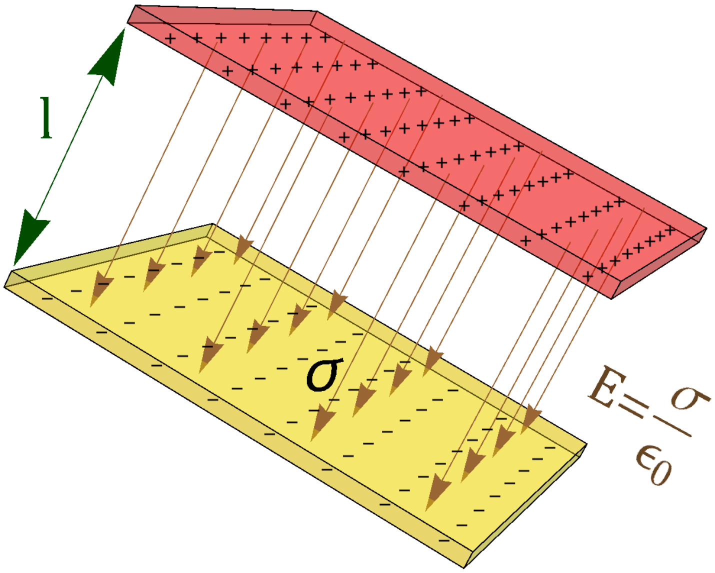


Figure 3.1: A charge Q is transferred between two plates of area A a distance l apart. The electric field between the plates is $E = \epsilon_0^{-1}Q/A$. The device is a *capacitor* of and the ratio of charge Q and potential difference $\Delta\varphi = El$ is the capacitance: $C = A\epsilon_0/l$.

3.3 *The planar capacitor and dielectric materials*

A planar capacitor (or condensor or Leyden jar as it was called by it's 1745 inventors Ewald Georg von Kleist and separately Andreas Cunaeusand Pieter van Musschenbroek), is an electronic device composed of two parallel plates of area A displaced by $l \ll \sqrt{A}$ (see Fig 3.1). The capacitor can store charge and energy. As we shall see below, from an electronic perspective A and l determine the capacitance $C = A\epsilon_0/l$

of the the capacitor. The overall charge of the capacitor is neutral but charge can be transferred between the plates. When one plate is charged Q' the other is charged $-Q'$ and charge is smeared on each plate so as to have even distribution with charge density $\sigma = Q'/A$ then the fiel d inside the capacitor is has field lines going from the positive to the negative plate (see Fig. 3.1). The electric field inside the capacitor must be constant)not dependent on space and zero outside of the capacitor. The magnitude is twice the field from a single plane (Eq. 2.7):

$$E_z = \frac{Q'}{A\epsilon_0} = C^{-1}\frac{Q'}{l}$$

The capacitor is a device to store energy. To see this, let us suppose we charge it little by little. Every time we transfer a small packet of positive charge dQ' from the negative to the positive plate . If the plates are already charged by the amount Q' then the next packet dQ' will involve investment of energy in the form of work (since we are forcing positive charge to go from the negative plate which attracts it to the positive plate which repels it). The work is the force on the packet $E_z dQ'$ times the distance between the plates l, so the energy we invested in this step is:

$$d\mathcal{E}\left(Q'\right) = E_z dQ' \times l = C^{-1}Q'dQ'.$$

The total work in charging the capacitor with charge Q is then just the integral on Q':

$$\mathcal{E}\left(Q\right) = \frac{1}{2}C^{-1}Q^2$$

The stored energy can be regained by allowing the charge to go back from the positive plate to the negative one. As this happens we can use the energy to light a bulb or do work.

Michael Faraday discovered circa 1837, that when an insulating material (a substance that does not readily conduct electricity) is placed to separate the capacitor plates, the stored energy of a Q-charged capacitor decreases by a material-dependent factor $\epsilon \geq 1$ called the *dielectric constant*:

$$\epsilon \equiv \frac{\mathcal{E}_{vacuum}\left(Q\right)}{\mathcal{E}_{material}\left(Q\right)} = \frac{C_{material}}{C_{vacuum}}$$

In Fig. 3.2 we explain the effect in terms of the creation of a layer of charge on the sides of the dielectric material.

A list of some materials and their dielectric constants is given in Table 3.1. It can be seen that some materials, water for example have huge dielectric constants. Thus a capacitor with water between its plate will store 80 times less energy than that with air in between the plates.

Material	ϵ
Vacuum	$\equiv 1$
Air	1.0006
Water	80 (20^oC)
Methanol	30
Ammonia	17 (20^oC)
Graphite	10-15
Diamond	5.5-10
Silicon	11.7
Ideal Metal	$\equiv \infty$

Table 3.1: Dielectric constant for some materials.

The origin of the reduction of electric field due to the material placed inside the capacitor is in the fundamental stricture of matter. The fact that matter is composed of charges, arranged as electrons and nuclei, allows the electric field to *polarize* the material,i.e. to create within it a density of dipoles that are induced by the field. In the caption of Fig. 3.2 we explain how such a polarization effect can in principle affect the electric field. The connection between polarizability and dielectric constants is discussed in the next section.

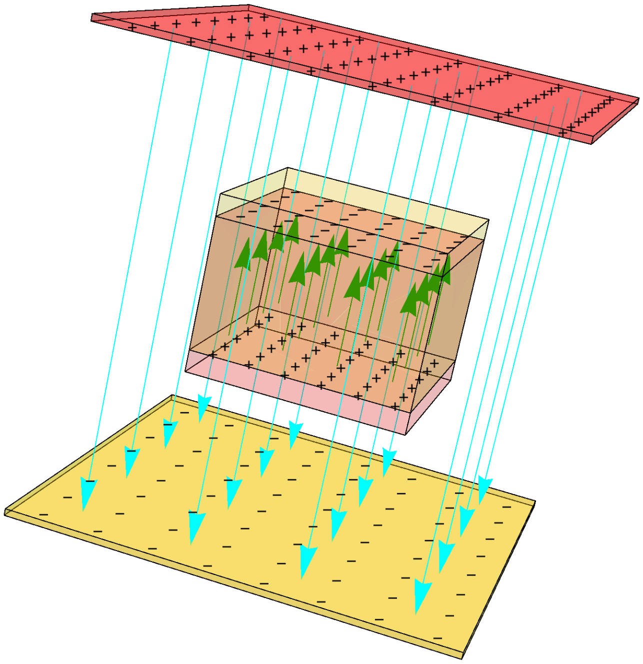


Figure 3.2: Positive (top, red) and negative (bottom, yellow) charged plates of a capacitor create an electric field E_{cap} (cyan arrows) pointing downwards. A slab of material with dielectric constant ϵ is inserted between the plates. The electric field E inside this material induces a proportionate density of dipoles $P = (\epsilon - 1)\,\epsilon_0 E$ and this relation serves as the exact definition of ϵ. Whenever a material is polarized uniformly there appears a thin layer of negative (positive) surface charge density $\sigma = P$ on the slab's top (bottom) face. By Gauss' law (Eq. 2.7), this creates an additional electric field $E_{pol} = -P/\epsilon_0$ (green arrows) pointing upwards forms inside the dielectric. In addition, The total field inside the slab is then $E = E_{cap} + E_{pol}$ from which $E = \epsilon^{-1} E_{cap}$ is deduced, showing that the electric field inside a dielectric is smaller than the field in its absence.

3.4 *Dielectric constant derived from molecular polarizability*

When a slab of material is placed in between two charged plates of a capacitor, the electric field inside the creates a net density of dipoles. This density is called *polarization* and it is described by a vector P_j which gives the number of dipoles in direction $j = x, y, z$ per unit volume. For weak fields P_j is proportional to E_j and the proportionality constant defines formally the *dielectric constant* of the material via the equation: $P_j = (\epsilon - 1)\,\epsilon_0 E_j$ (see Fig. 3.2).

If the material has a density of n molecules per unit volume then the polarizability is $P_j \equiv \langle \mu_j \rangle\, n$ where $\langle \mu_j \rangle$ is the average induced molecular dipole. It is natural to suppose that $\langle \mu_j \rangle$ is given by the molecular polarizability α times the polarizing field E_j. However, there is a subtle but important point here: a dipole cannot polarize itself! Thus

$\langle\mu_j\rangle = E_j^L\alpha$ where $E_j^L = E_j - \left(\overline{E_D}\right)_j$, called the Lorentz field, is the electric field after the average field created by μ_j has been subtracted. $\left(\overline{E_D}\right)_j = n\int\left(E_D\left(\mathbf{r}\right)\right)_j d^3r$ is the field created by the molecular dipole itself averaged over the molecular volume $v = n^{-1}$. From Eq. (2.24) we find $\left(\overline{E_D}\right)_j$ has 2 contributions: one, emanating from the integral $n\int\frac{\left(3r_ir_j-r^2\delta_{ij}\right)}{r^5}d^3r$, is easily shown to be equal to zero for random placement of the molecules (and also for most periodic structures of solids), leaving only the δ-function contribution: $\left(\overline{E_D}\right)_j = -\frac{n}{3\epsilon_0}\langle\mu_j\rangle = -\frac{P_j}{3\epsilon_0}$. We thus conclude that the Lorentz field is $E_j^L = E_j + \frac{P_j}{3\epsilon_0}$ and since

$$P_j = \langle\mu_j\rangle n = n\alpha E_j^L. \tag{3.12}$$

we find: $P_j = n\alpha\left(E_j + \frac{P_j}{3\epsilon_0}\right)$ which can be solved for P_j to give:

$$P_j = \frac{n\alpha}{1-\frac{n\alpha}{3\epsilon_0}}E_j. \tag{3.13}$$

This is called Debye's equation (1912). The dielectric constant ϵ is defined in the caption of Fig. 3.2 as the relation $P_j = (\epsilon-1)\,\epsilon_0 E_j$ and we conclude the following relation between the molecular polarizability and the dielectric constant:

$$\epsilon - 1 = \frac{3n\alpha}{3\epsilon_0 - n\alpha}, \tag{3.14}$$

$$\frac{\epsilon-1}{\epsilon+2} = \frac{n\alpha}{3\epsilon_0}. \tag{3.15}$$

The fact $\frac{\epsilon-1}{\epsilon+2}$ is proportional to the density n was noted already in 1850 by Ottaviano-Frabrizio Mossotti and the relation of Eq. 3.15 was noted by the famous physicist Rudolph Clausius somewhat later, hence this relation is named the Clausius-Mossotti equation. Note that when $n\alpha/3\epsilon_0 \ll 1$ i.e. the density or is very small one has:

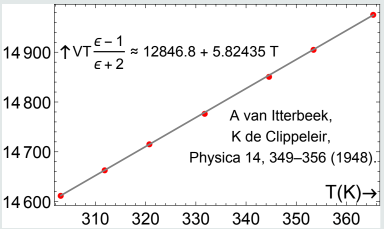
$$\epsilon \approx 1 + \frac{n\alpha}{\epsilon_0} \quad \text{(low density)} \tag{3.16}$$

We note that the concept of dielectric constant can be extended to the alternating current (AC) regime, where it becomes frequency dependent. In this case, the dielectric constant determines the refractive index of transparent material through: $N^2 = \epsilon$. The Lorentz-Lorenz relation for the refractive index:

$$\frac{N^2-1}{N^2+2} = \frac{n\alpha}{3\epsilon_0}. \tag{3.17}$$

follows from Eq. 3.15 extended to the AC regime.

Dipole moment and polarizability of gaseous Ammonia



In the figure, red circles are experimental results for $VT\frac{\epsilon-1}{\epsilon+2}$ vs. the temperature T where ϵ is the measured dielectric constant of gaseous ammonia at 1atm and V is its molar volume (in cm^3). The gray line is a best fit linear function with parameters shown in the figure. From the fit $N_A\frac{\alpha^{(e)}}{3\epsilon_0} = 5.82435cm^3$ and $N_A\frac{\mu^2}{9k_B\epsilon_0} = 12846.8cm^3K$ and thus $\alpha^{(e)} \approx 29.01\epsilon_0\mathring{A}^3$ and $\mu \approx 0.571ea_0$. A common unit for the dipole moment is the "Debye", denoted D (after the Dutch-American physicist Peter Debye), $1D = 0.3934ea_0$. **Conclusion**: The dipole moment is $\mu = 1.452D$; the electronic polarizability is $\alpha_{cgi}^{(e)} = 2.309\mathring{A}^3$ (in cgs units $\epsilon_0 = (4\pi)^{-1}$).

3.5 *The Born free energy and entropy of solvation*

The energy of solvation of an ion of "radius" r_i and charge Q_i is defined as the work required to move the ion from vacuum to deep inside a dielectric medium of constant ϵ.

Born suggested the following 3-stage method for calculating this quantity:

1. We first neutralize the ion by coating it with a thin shell of charge $-Q_i$ at radius r_i. Since the coating is of opposite charge energy is emitted in the process and thus the work done on the system is negative and we call it the negative vacuum energy of the ion$-E_i$. In order to calculate it we gradually bring in the shell in N charge packets $\Delta q = -Q_i/N$. The first packet releases energy equal to Δq times the potential around the ion at $r = r_i$, which is $(4\pi\epsilon_0)^{-1}\frac{Q_i}{r_i}$. This process releases the energy $\Delta E_i(1) = (4\pi\epsilon_0)^{-1}\frac{Q_i}{r_i}\Delta q$. The second packet sees an ion of smaller charge, since the charge of the ion and the first packet is $Q_i - \Delta q$. Thus bringing the second packet releases an energy of amount $\Delta E_i(2) = (4\pi\epsilon_0)^{-1}\frac{(Q_i-\Delta q)}{r_i}\Delta q$. The energy released by the third packet is $\Delta E_i(3)=(4\pi\epsilon_0)^{-1}\frac{(Q_i-2\Delta q)}{r_i}\Delta q$ and so on. Summing up all such contributions yields a total vacuum energy of $E_{ion} = \sum_{n=1}^{N}(4\pi\epsilon_0)^{-1}\frac{(Q_i-(n-1)\Delta q)}{r_i}\Delta q$. The result depends on the number of packets N but in the limit $N \to \infty$ (and $\Delta q = Q_i/N \to 0$) it converges to the integral $E_i = \frac{1}{4\pi\epsilon_0}\int_0^{Q_i}\frac{(Q_i-q)}{r_i}dq$ which evaluates to:
$$E_i = \frac{1}{8\pi\epsilon_0}\frac{Q_i^2}{r_i}. \tag{3.18}$$
2. Next, we move the resulting *neutral* system from vacuum to deep inside an almost infinite dielectric slab. This process involves no electrostatic work by the system (we assume the dielectric has an empty pocket ready for the "coated ion"). If such a cavity needs to be "excavated" then this stage has an addition energy involved W_2
3. Finally, we remove the shell while the ion is in the dielectric medium. The calculation done at this stage is essentially identical to that done in vacuum with two differences: first the sign is reversed since now we are removing the shell and second the work is reduced by a factor ϵ^{-1} because the electric field doing the job is smaller by this factor. Thus the work consumed by this stage is $\frac{1}{\epsilon}E_i$.

The energies we computed are non-expansive work done by the system. These must equal the change in Gibbs energy upon solvation[1]. Neglecting W_2 have:
$$\Delta G^0_{solv} = E_i\left(\frac{1}{\epsilon}-1\right) \tag{3.19}$$

---

[1] The change in Gibbs energy in any reversible process is equal to the non-expansive work done on the system during that change.

The free energy of solvation is always negative (since $\epsilon \geq 1$) and insensitive to the *sign* of the ionic charge Q_i (this is squared in Eq. 3.18). This means that the ion is more stable in the solvated state and work $-\Delta G^0_{solv}$ must be done to bring the ion back to the vacuum.

Using the relation $S = -\left(\frac{\partial G}{\partial T}\right)_{p,N}$ we can compute the entropy of solvation $\Delta S^0_{solv} = -\left(\frac{\partial \Delta G^0_{solv}}{\partial T}\right)_{p,N}$ by differentiating Eq. (3.19) with respect to temperature:

$$\Delta S^0_{solv} = E_i \times \frac{\partial \epsilon^{-1}}{\partial T} \tag{3.20}$$

Assuming that the dielectric medium is a collection of non-interacting polar molecules as in the Langevin model of section 3.2 we can calculate from Eq. (3.14) it is possible to obtain $\frac{\partial \epsilon^{-1}}{\partial T} = -\frac{\epsilon_0}{n}\left(1 - \frac{1}{\epsilon}\right)^2 \frac{\partial \alpha^{-1}}{\partial T}$ so:

$$\Delta S^0_{solv} = -E_i \frac{\epsilon_0}{n}\left(1 - \frac{1}{\epsilon}\right)^2 \frac{\partial \alpha^{-1}}{\partial T}. \tag{3.21}$$

From Eq. (3.10) we have $\frac{\partial \alpha^{-1}}{\partial T} = \frac{3k_B}{\mu^2}$, so the entropy in this case is:

$$\Delta S^0_{solv} = -E_i \frac{3k_B \epsilon_0}{n\mu^2}\left(1 - \frac{1}{\epsilon}\right)^2. \tag{3.22}$$

We see that the entropy of solvation is negative. The reason is loss of orientational degrees of freedom as the solute dipoles align with the ion field.

4
The basic non-covalent intermolecular interactions

In this chapter we learn about molecule-molecule interactions. The level of this study is the quantum mechanical level. Using the interactions we study here we can also derive other types, more mean field interactions which will be discussed in the last chapter of this booklet.

4.1 The interaction energy between two distinct charge distributions

So far, we have considered the far field potential of a charge distribution and the interaction of a charge distribution with a slowly varying potential. We now combine the two theories by considering the electrostatic energy of two localized and distant charge distributions. We can consider charge distribution A around the origin and a distribution B centered on a point $\boldsymbol{r}_B$. Using Eq. (2.28) we write the interaction energy as:

$$W_{es}^{AB} = Q^B \varphi^A\left(\mathbf{r}_B\right) + \mu_i^B \varphi_i^A\left(\boldsymbol{r}_B\right) + \frac{1}{3}\Theta_{ij}^B \varphi_{ij}^A\left(\boldsymbol{r}_B\right) + \dots \tag{4.1}$$

The potential of A is (keeping terms to r^{-3})

$$\varphi^A\left(\mathbf{r}\right) = \frac{1}{4\pi\epsilon_0\epsilon}\left[\frac{Q^A}{r} + \frac{\mu_j^A r_j}{r^3} + \frac{\Theta_{jk}^A r_j r_k}{r^5} + \dots\right].$$

Using the first derivative $\left(\frac{1}{r}\right)_i = \frac{\partial}{\partial r_i}\left(\frac{1}{r}\right) = -\frac{r_i}{r^3}$, and the second derivative is: $\left(\frac{1}{r}\right)_{ij} = \frac{3r_ir_j - r^2\delta_{ij}}{r^5}$, we find:

$$\varphi_i^A\left(\mathbf{r}\right) = \frac{1}{4\pi\epsilon_0\epsilon}\left[-\frac{Q^A r_i}{r^3} - \frac{\mu_j^A\left(3r_jr_i - r^2\delta_{ij}\right)}{r^5} + \dots\right]$$

and:

$$\varphi_{ij}^A\left(\mathbf{r}\right) = \frac{1}{4\pi\epsilon_0\epsilon}\left[\frac{Q^A\left(3r_ir_j - r^2\delta_{ij}\right)}{r^5} + \dots\right]$$

Now let us specialize, without loss of generality to the case that B is on the x axis, namely that $\boldsymbol{r}_B = (r, 0, 0)$, or $r_i = r\delta_{i,x}$. Then

$$\varphi^A(\mathbf{r}_B) = \frac{1}{4\pi\epsilon_0\epsilon}\left[\frac{Q^A}{r} + \frac{\mu_x^A}{r^2} + \frac{\Theta_{xx}^A}{r^3}\right],$$

$$\varphi_i^A(\mathbf{r}) = \frac{1}{4\pi\epsilon_0\epsilon}\left[-\frac{Q^A\delta_{ix}}{r^2} - \frac{\mu_x^A(3\delta_{ix}-1)}{r^3} + \dots\right],$$

$$\varphi_{ij}^A(\mathbf{r}_B) = \frac{1}{4\pi\epsilon_0\epsilon}\frac{Q^A(3\delta_{ix}-1)}{r^3}\delta_{ij}$$

Plugging into Eq. 4.1, using $r_i = r\delta_{ix}$ and evaluating all the sums over i and j, and using $\Theta_{ij}^B\delta_{ij} = 0$, we find, after rearranging:

$$\begin{aligned} W_{es}^{AB} = \frac{1}{4\pi\epsilon_0\epsilon}&\left[\frac{Q^BQ^A}{r} + \frac{Q^B\mu_x^A - \mu_x^BQ^A}{r^2}\right. \\ &\left.+ \frac{\mu_i^B\mu_i^A(1-3\delta_{ix}) + Q^B\Theta_{xx}^A + \Theta_{xx}^BQ^A}{r^3}\right]. \end{aligned} \tag{4.2}$$

The derivation of this expression was tedious, yet straightforward. The energy of the non-covalent interaction between systems A and B, both on the x-axis at distance r exhibits one charge-charge interaction decaying as r^{-1}, two charge-dipole terms decaying as r^{-2}, a dipole-dipole term and two charge-quadrupole terms decaying as r^{-3} and finally, charge-dipole terms also decaying as r^{-3}. Neglected terms decay as r^{-4} or faster.

4.2 The interaction energy of distinct molecules

Consider two molecules, A and B, which are sufficiently distant that we can think of their electron clouds as non-overlapping. We ask how the energy of this system changes as these molecules change position with respect to each other. The question is formulated within the Born Oppenheimer approximation (BOA) as we control the nuclear degrees of freedom and bring them from far apart to proximity. The energy of the system is the groundstate energy of the Hamiltonian:

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B + \hat{W}_{es}^{AB} \tag{4.3}$$

where $\hat{H}_A$ is the Hamiltonian of electrons of molecule A given that its nuclei are at positions $\{\mathbf{R}_A\}$ and a similar definition for molecule B. The interaction between the two molecules is designated by $\hat{W}_{es}^{AB}$, which is the sum of the Coulomb interaction between pairs of particles, one from each molecule:

$$\begin{aligned}\hat{W}_{es}^{AB} = \frac{e^2}{4\pi\epsilon_0\epsilon}\Bigg[\sum_{A,B}\frac{Z_A Z_B}{|\mathbf{R}_A-\mathbf{R}_B|} - \sum_{A,b}\frac{Z_A}{|\mathbf{R}_A-\mathbf{r}_b|} + \\ -\sum_{B,a}\frac{Z_B}{|\mathbf{R}_B-\mathbf{r}_a|} + \sum_{ab}\frac{1}{|\mathbf{r}_a-\mathbf{r}_b|}\Bigg],\end{aligned} \tag{4.4}$$

where we designate the electrons of molecule A positions by index a and those of molecule B by b despite this, all electrons interact with all nuclei in the same way, so they are essentially indistinguishable.

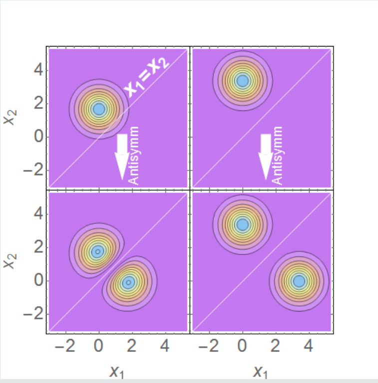
We view $\hat{H}_{eA} + \hat{H}_{eB}$ in Eq. (4.3) as the unperturbed (zero order) part while the intermolecular part is a first order perturbation. The unperturbed wave functions are then simply the product

$$\Psi_{nm}^{(0)}\left(\mathbf{r}_1 \ldots \mathbf{r}_{N_A+N_B}\right) = \Psi_n^{(A)}\left(\mathbf{r}_1, \ldots, \mathbf{r}_{N_A}\right)\Psi_m^{(B)}\left(\mathbf{r}_1, \ldots, \mathbf{r}_{N_B}\right). \tag{4.5}$$

The zeroth order ground-state is $\Psi_{00}^{(0)}$, the product of the two ground state wave functions $\Psi_0^{(A)}$ and $\Psi_0^{(B)}$. At first sight this wave function seems to violate the Pauli principle is problematic since it treats electrons $1, \ldots, N_A$ differently from electrons $1, \ldots, N_B$. In particular, the Pauli principle, by which antisymmetry should be imposed on the wave function, is not taken into account. We show in the discussion on the margin that as long as the two fragments are non-overlapping, there is no need to impose antisymmetry: the wave function will not change.

Pauli exclusion irrelevant for "well-separated" electrons

We show that when two electrons are held apart we do not need to impose the Pauli principle. Consider a probability density for two one-dimensional electrons $\Psi\left(x_1, x_2\right)^2$, where x_1 is the coordinate of the first electron and x_2 of the second. In the top left panel of the figure below we show a "touching" pair of electrons while in the top right we show "well-separated" electrons. Pauli's exclusion principle requires that we consider the density of either the symmetrized (singlet) or antisymmetrized (triplet) wave function. Assuming the latter, we plot the antisymmetrized density in the lower panels. We see that unlike "touching" electrons the distribution of "well-separated" electrons is unaffected.



4.3 *Perturbation theory*

Perturbation theory is a technique for obtaining approximate solutions to a Schrodinger equation in which the Hamiltonian is a sum of a solvable Hamiltonian and a small perturbation. In out case, that of the Hamiltonian in Eq. (4.3), when the distance between A and B is large $\hat{W}_{es}^{AB}$ is only a slight perturbation to $\hat{H}_A + \hat{H}_B$, which has eigenstates $\mathcal{E}_{nm}^{(0)} = \mathcal{E}_n^A + \mathcal{E}_m^B$ and the eigenfunctions of Eq. (4.5). The first order correction to the energy of the ground state is given by the expectation value of the perturbation:

$$\delta\mathcal{E}_{00}^{(1)} = \left\langle \Psi_{00}^{(0)} \middle| \hat{W}_{es}^{AB} \middle| \Psi_{00}^{(0)} \right\rangle \tag{4.6}$$

The first order correction to the ground state wave function is

$$\delta\Psi_{00}^{(1)}(x) = \sum_{nm\neq 00}\Psi_{nm}(x)\frac{\left\langle \Psi_{nm}^{(0)} \middle| \hat{W}_{es}^{AB} \middle| \Psi_{00}^{(0)} \right\rangle}{\mathcal{E}_{00}^{(0)} - \mathcal{E}_{nm}^{(0)}} \tag{4.7}$$

Finally, the second order correction to the energy is given by:

$$\delta\mathcal{E}_{00}^{(2)} = -\sum_{nm\neq 00}\frac{\left|\left\langle \Psi_{nm}^{(0)} \middle| \hat{W}_{es}^{AB} \middle| \Psi_{00}^{(0)} \right\rangle\right|^2}{\mathcal{E}_{nm}^{(0)} - \mathcal{E}_{00}^{(0)}} \tag{4.8}$$

Note that the second order correction for the ground state, is always negative!

4.4 *Classical electrostatic interactions molecules*

Applying Eq. 4.6 to the electrostatic energy of two molecules (Eq. (4.2)) we find (all expectation values are made with respect to the ground state of the relevant molecule):

$$\delta\mathcal{E}_{00}^{(1)} = \delta\mathcal{E}_{\text{ion-ion}}^{(1)} + \delta\mathcal{E}_{\text{ion-dipole}}^{(1)} + \delta\mathcal{E}_{\text{dipole-dipole}}^{(1)} \tag{4.9}$$

There are several types of interactions appearing here.

Fundamental Ion-ion interaction

The strongest interaction is when both molecules are ions. Then the interaction is predominately the coulomb interaction of two charges decaying as the inverse of the distance between them:

$$\delta\mathcal{E}_{\text{ion-ion}}^{(1)} = \frac{1}{4\pi\epsilon_0\epsilon}Q^AQ^B\frac{1}{r} \tag{4.10}$$

One noteworthy issue is that this interaction is proportional to ϵ^{-1} and so can be reduced considerably in a polar solution, such as water where $\epsilon \approx 80$.

Fundamental Ion-dipole interactions

Next we have the case of an ion interacting with a polar molecule having a dipole moment component in the x direction:

$$\delta\mathcal{E}_{\text{ion-dipole}}^{(1)} = \frac{1}{4\pi\epsilon_0\epsilon}\frac{\left\langle\mu_x^A\right\rangle Q^B - Q^A\left\langle\mu_x^B\right\rangle}{r^2}. \tag{4.11}$$

This interaction decays as the square of the inverse distance and it too is sensitive to the dielectric constant.

Fundamental Dipole-dipole interactions

$$\delta\mathcal{E}_{\text{dipole-dipole}}^{(1)} = -\frac{1}{4\pi\epsilon_0\epsilon}\frac{\left\langle\mu_i^B\right\rangle\left\langle\mu_i^A\right\rangle - 3\left\langle\mu_x^B\right\rangle\left\langle\mu_x^A\right\rangle}{r^3}. \tag{4.12}$$

This interaction decays as r^{-3} and has an interesting dependence on the direction of the dipoles. If both dipoles are in the x direction then the interaction is attractive while when they are both in the y (or z) direction it is repulsive. The following figure explains this behavior qualitatively.

4.5 Inductive molecular interactions

2nd order PT gives further types of interaction, called "induction" which are weaker than the zeroth order and first order terms unless the latter are extremely small or zero. The dielectric constant will be entering the interaction as ϵ^{-2}, thus the induction interactions are especially small when the electronic dielectric constant of the medium is much greater than 1. We will keep only terms up to r^{-6}.

Fundamental Ion-Atom interaction

Consider first the interaction between an ion B of charge $Q^B \neq 0$ and a neutral atom A ($Q^A = 0$, $\mu^A = 0$,...). Clearly, there is no interaction in the zeroth order since all moments of A are zero. The second order induction which falls off slowest is the interaction between an ion and a molecule:

$$\delta\mathcal{E}_{00}^{(2)}\left(r^{-4}\,\text{term}\right) = -\left(\frac{1}{4\pi\epsilon_0\epsilon}\right)^2 \frac{\left(Q^B\right)^2}{r^4} \sum_{n\neq 0} \frac{\left|\langle\mu_x^A\rangle_{00,n0}\right|^2}{\mathcal{E}_{n0}^{(0)} - \mathcal{E}_{00}^{(0)}} \tag{4.13}$$

which upon developing the expression and, using the definition of polarizability Eq. (3.5) we find :

$$\delta\mathcal{E}_{Ion-Mol}^{(2)} = -\left(\frac{1}{4\pi\epsilon_0\epsilon}\right)^2 \frac{\alpha_{xx}^{(A)}\left(Q^B\right)^2}{2r^4}. \tag{4.14}$$

When B, say is the ion and A is the molecule, we find that the inductive interactions decay as $\frac{1}{r^4}$ and are proportional to the charge of the ion squared and the molecular polarizability.

Debye interactions: inductive permanent-dipole – molecule interaction

Next consider two neutral molecules, B with a permanent dipole $\langle\mu^B\rangle = 0$ and A with a dipole $\langle\mu^A\rangle = 0$. Then
$\frac{\mu_i^B\mu_i^A - 3\mu_x^B\mu_x^A + Q^B\Theta_{xx}^A + \Theta_{xx}^B Q^A}{r^3}$

$$\delta\mathcal{E}_{00}^{(2)}\left(r^{-6}\,\text{term}\right) = -\left(\frac{1}{4\pi\epsilon_0\epsilon}\right)^2 \frac{1}{r^6} \sum_{n\neq 0} \frac{\left|\langle\mu_i^B\rangle_{00}\langle\mu_i^A\rangle_{0,n} - 3\langle\mu_x^B\rangle_{00}\langle\mu_x^A\rangle_{0,n}\right|^2}{\mathcal{E}_{n0}^{(0)} - \mathcal{E}_{00}^{(0)}} \tag{4.15}$$

$$= -\left(\frac{1}{4\pi\epsilon_0\epsilon}\right)^2 \frac{1}{2r^6}\mu_i^B\mu_j^B\left(1 + 9\delta_{ix}\delta_{jx} - 3\left(\delta_{ix} + \delta_{jx}\right)\right)\alpha_{ij}^A \tag{4.16}$$

When A is a spherically symmetric system $\alpha_{ij} = \alpha\delta_{ij}$ we find:

$$\delta\mathcal{E}^{(2)}_{dip-Atom}=-\left(\frac{1}{4\pi\epsilon_0\epsilon}\right)^2\frac{\left(\mu^B\right)^2+3\left(\mu^B_x\right)^2}{2r^6}\alpha^A. \tag{4.17}$$

London dispersion interactions

Next, we consider the only term that survives even when $Q^A=Q^B=0$ and $\mu^A=\mu^B=0$. This is the so-called London dispersion interaction (note that it exists also when the molecules are ions but then it might be of lesser importance) and from Eq. (4.2) can be written as:

$$\delta\mathcal{E}^{(2)}_{vdW}=-\frac{1}{\epsilon^2}\frac{C_{AB}}{r^6}, \tag{4.18}$$

with:

$$C_{AB}=\left(\frac{1}{4\pi\epsilon_0}\right)^2\sum_{nm\neq 00}\frac{\left|\left\langle\Psi^{(0)}_{00}\left|\mu^B_i\mu^A_i\left(3\delta_{ix}-1\right)\right|\Psi^{(0)}_{nm}\right\rangle\right|^2}{\mathcal{E}^{(0)}_{nm}-\mathcal{E}^{(0)}_{00}}$$

the C_6 energy constant, as it is often called, since the interaction goes as r^{-6} and has an angular dependence:

$$C_{AB}=\left(\frac{1}{4\pi\epsilon_0}\right)^2\left(3\delta_{ix}-1\right)^2\sum_{nm\neq 00}\frac{\left|\left(\mu^A_i\right)_{n0}\left(\mu^B_i\right)_{m0}\right|^2}{\mathcal{E}^A_{n0}+\mathcal{E}^B_{m0}}.$$

It is possible to convert the two fragment sum into a product of single fragment sums. For example. when $\mathcal{E}>0$ we can use the identity:

$$\frac{1}{\mathcal{E}}=\int_0^\infty e^{-\mathcal{E}t}dt \tag{4.19}$$

and then we define “time-dependent” polarizabilities:

$$\alpha^X_i\left(t\right)=\sum_{n\neq 00}\left|\left(\mu^X_i\right)_{n0}\right|^2e^{-\mathcal{E}^X_{m0}t},\ X=A,B \tag{4.20}$$

so with these definitions the dispersion coefficient becomes:

$$C_{AB}=\left(\frac{1}{4\pi\epsilon_0}\right)^2\left(3\delta_{ix}-1\right)^2\int_0^\infty\alpha^A_i\left(t\right)\alpha^B_i\left(t\right)dt. \tag{4.21}$$

This formula is very useful, as it involves just one function from each species. So if we have $\alpha^A_i\left(t\right)$ for each molecule in nature, we would be able to easily assemble all the dispersion coefficients. One can also use the experimental absorption spectrum of species $X$to determine $\alpha^A_i\left(t\right)$ and thus connect the optical absorption properties of a molecule with its dispersion interaction.

London discovered a neat approximation, simplifying the expression for C_{AB}, by writing the sum as $\sum_{nm\neq 00} \frac{|(\mu_i^A)_{n0}|^2 |(\mu_i^B)_{m0}|^2}{\mathcal{E}_{n0}^A \mathcal{E}_{m0}^B} \frac{\mathcal{E}_{n0}^A \mathcal{E}_{m0}^B}{\mathcal{E}_{n0}^A + \mathcal{E}_{m0}^B}$ and assuming :

$$\frac{\mathcal{E}_{n0}^A \mathcal{E}_{m0}^B}{\mathcal{E}_{n0}^A + \mathcal{E}_{m0}^B} \approx \frac{I^A I^B}{I^A + I^B},$$

i.e. that the n^{th} excitation energy of atom A, $\mathcal{E}_{n0}^A$, can be approximated by its ionization energy I^A (similar consideration holds for B). The remaining sum now factorizes into a product of two atomic contributions:

$$\sum_{nm\neq 00} \frac{|(d_i^A)_{n0} (d_i^B)_{m0}|^2}{\mathcal{E}_{n0}^A + \mathcal{E}_{m0}^B} = \sum_{n\neq 0} \frac{|(d_i^A)_{n0}|^2}{\mathcal{E}_{n0}^A} \sum_{m} \frac{|(d_i^B)_{m0}|^2}{\mathcal{E}_{m0}^B},$$

each is half of the atomic polarizability (see Eq. (3.5)). Thus the C_6 for atoms in this London approximation is:

$$C_{AB} = \frac{1}{4} \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{I^A I^B}{I^A + I^B} (3\delta_{ix} - 1)^2 \alpha_{ii}^A \alpha_{ii}^B \tag{4.22}$$

For atoms, we can assume α_{ii}^A is independent of i, and thus:

$$\sum_{i=x,y,z} (3\delta_{ix} - 1)^2 \alpha_{ii}^A \alpha_{ii}^B = \alpha^A \alpha^B \sum_{i=x,y,z} (3\delta_{ix} - 1)^2 = 6\alpha^A \alpha^B$$

Thus, the London approximation is:

$$C_{AB} = \frac{3}{2} \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{I^A I^B}{I^A + I^B} \alpha^A \alpha^B \tag{4.23}$$

5

Mean-field non-covalent interactions

In the previous chapter we studied the basic forces between molecules, finding a certain heirarchy. These microscopic interactions are not always the apparent forces seen in systems containing many molecules. The reason for this is the thermal fluctuations which average out some forces, leaving only special correlated motions as significant. We study some of these effects in this chapter.

5.1 Exercises

1. Between two positive charges we install a spring of force constant $k > 0$. The spring exerts a force on particle 1 equal to $k\left(\mathbf{r}_1 - \mathbf{r}_2\right)$ and an opposite force on particle 2. What is the equilibrium distance between the two charges?

2. Prove that the electric potential charge e_a at the origin is given by Eq. (2.11).

3. Prove Laplace Equation, Eq. (**??**)) when $\varphi\left(\mathbf{r}\right)$ is given as the potential of a single particle in the origin (Eq. (2.11)).