INTERMOLECULAR INTERACTIONS

Consider the interaction between two stable molecules (e.g. water and ethanol) or equivalently between two noble atoms (e.g. helium and neon). Call the two species "A" and "B", and suppose they are oriented as

Now, according to our simple MO pictures, there will not be any chemical bonds between A and B; the MOs will be fairly localized either on A or on B and we should not have significant hybridization of the orbitals. Thus, according to the MO picture, these molecules will not interact. However, we know that they **do** interact. If they did not, we would never be able to form liquids or solids, as it is the attraction between molecules that holds such things together. Of course, our intuition also tells us that the interactions *between* molecules are much weaker than the forces that hold molecules together, and so we immediately guess that the intermolecular interactions can be treated as a perturbation.

Toward this end, we write the Hamiltonian for the A-B system as:

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}_{AB}$$

where $\hat{H}_A$ ($\hat{H}_B$) describes the isolated interactions within molecule A (B) and $\hat{V}_{AB}$ contains all the interaction terms between A and B. Now, $\hat{V}_{AB}$ is a fairly complicated object: it contains all the interactions between electrons and/or nuclei on A and electrons and/or nuclei on B. Rather than deal with the full $\hat{V}_{AB}$ (which would be very hard) we will note that as long as A and B are far apart (i.e. as long as R is large) we can approximate $\hat{V}_{AB}$ using a classical dipole-dipole interaction

$$\hat{V}_{AB} \approx \frac{R^2 \hat{\mu}_A \cdot \hat{\mu}_B - 3(\hat{\mu}_A \cdot \mathbf{R})(\mathbf{R} \cdot \hat{\mu}_B)}{4\pi\varepsilon_0 R^5} \qquad \text{Eq. 1}$$

Here, $\hat{\mu}_A$ ($\hat{\mu}_B$) is an operator that measures the dipole moment on molecule A (B). We won't particularly care about the form of this operator in this lecture, but we will use it quite a bit later on. For reference,

$$\hat{\mu}_A \equiv e(\hat{\mathbf{r}} - \mathbf{R}_A) - \mu_A^{Nuclear}$$

The first part measures the dipole moment of the electron charge distribution, while the second subtracts the dipole of the nuclear charges.

Now, Eq. 1 is still too complicated for us. The dipole is a vector quantity – it has a magnitude and a direction. As a result, the dipole-dipole interaction depends on the directions of the dipoles involved:
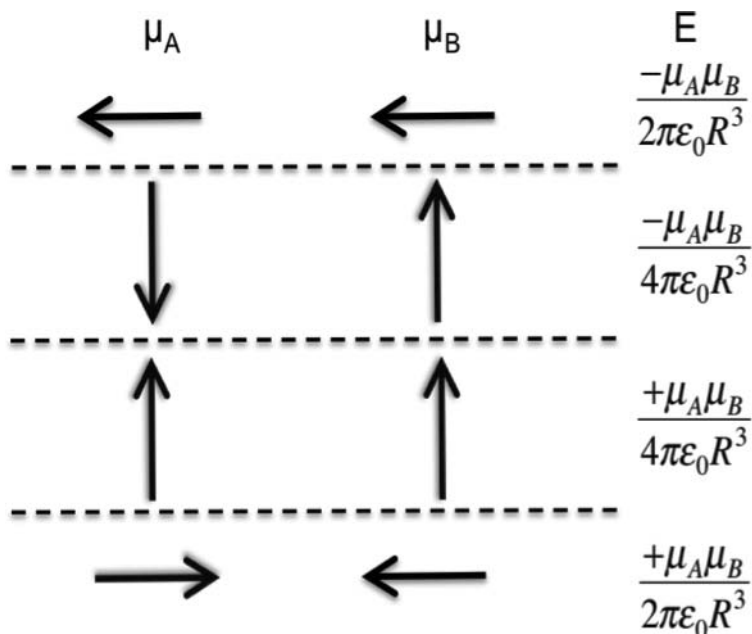
While the orientation dependence of the μ-μ interaction can be important in many situations, we will not be interested in this level of detail for now. Hence, we will assume that the molecular dipoles are oriented in their most favorable head-to-tail orientation (the first situation above) in which case

$$\hat{V}_{AB} \approx -\frac{\hat{\mu}_A \hat{\mu}_B}{2\pi\varepsilon_0 R^3}$$

where the non-boldface operator $\hat{\mu}_A (\hat{\mu}_B)$ returns the magnitude of the dipole moment on A(B). In practice, this will overestimate the true interactions, because sometimes the dipoles will be in less favorable orientations relative to one another, but it will suffice for qualitative purposes.

Next, we split the Hamiltonian into a zeroth order part and a perturbation in the logical way:

$$\hat{H}_0 = \hat{H}_A + \hat{H}_B \qquad \hat{V} = \hat{V}_{AB}$$

Because the zeroth order Hamiltonian is separable, we immediately recognize that the zeroth order eigenstates will factorize as products, and that the energies will add:

$$\hat{H}_0 \Psi_\alpha^A \Psi_\beta^B = \left(\hat{H}_A + \hat{H}_B\right)\Psi_\alpha^A \Psi_\beta^B = \left(E_\alpha^A + E_\beta^B\right)\Psi_\alpha^A \Psi_\beta^B$$

α and β are quantum numbers for A and B respectively. The reason we have two quantum numbers here instead of just one is exactly the same as why we had two quantum numbers (n_x and n_y) for the 2D harmonic oscillator: when we add degrees of freedom, we always introduce new quantum numbers. In the present case, when $\alpha=7$ and $\beta=3$, we are looking at an excited state where molecule A is in its seventh excited state and B is in its third excited state. It isn't enough to consider just excited states of A or B individually – one also has to allow for the possibility that both molecules might get excited at the same time. That being said, in chemistry we are usually interested in the **ground electronic state** of the system. For the A-B system, the ground state implies that both A and B are in their ground state, in which case

$$\Psi_0^{(0)} = \Psi_0^A \Psi_0^B \qquad E_0^{(0)} = E_0^A + E_0^B.$$

Now, as discussed above, this zeroth order energy does not contain any interactions between A and B. It is easy to see this in the equation because there are no terms that depend on A and B simultaneously. Thus A doesn't know that B exists, and vice versa. As a result, at zeroth order the molecules will never stick to one another.

To introduce interactions, we apply perturbation theory. At first order, we have:

$$E_0^{(1)} = \int\int \Psi_0^{A*}\Psi_0^{B*}\hat{V}_{AB}\Psi_0^A\Psi_0^B d\tau_A d\tau_B = \frac{-1}{2\pi\varepsilon_0 R^3}\int\int \Psi_0^{A*}\Psi_0^{B*}\hat{\mu}_A\hat{\mu}_B\Psi_0^A\Psi_0^B d\tau_A d\tau_B$$

$$= \frac{-1}{2\pi\varepsilon_0 R^3}\int \Psi_0^{A*}\hat{\mu}_A\Psi_0^A d\tau_A \int \Psi_0^{B*}\hat{\mu}_B\Psi_0^B d\tau_B$$

where on the second line we have grouped terms so that the integral clearly factorizes into a product of an integral over A and an integral over B. These two integrals have physical meaning:

$$\int \Psi_0^{A*}\hat{\mu}_A\Psi_0^A d\tau_A \equiv \langle\hat{\mu}_A\rangle \quad \text{(The ground state dipole of A)}$$

$$\int \Psi_0^{B*}\hat{\mu}_B\Psi_0^B d\tau_B \equiv \langle\hat{\mu}_B\rangle \quad \text{(The ground state dipole of B)}$$

Thus, the first order energy takes on an intuitive form:

$$E_0^{(1)} = \frac{-\langle\hat{\mu}_A\rangle\langle\hat{\mu}_B\rangle}{2\pi\varepsilon_0 R^3}.$$

This is just what we would expect. As in classical physics, the average dipole on A interacts with the average dipole on B. This interaction has a characteristic R^{-3} dependence, which will dominate at long range as all higher terms decay with R to some higher power (e.g R^{-6} below). At this point, we can make a physical connection with the abstract parameter λ used in

perturbation theory: here R^{-3} plays the role of λ. Thus, if we increase the separation between the fragments, the effective value of λ gets smaller and we expect perturbation theory to work perfectly for large enough R. Likewise, if we decrease R the strength of the perturbation gets stronger and we eventually expect perturbation theory to break down once the molecules get too close together.

Nonetheless, we have arrived at what we sought: an expression for the interaction between two molecules. This dipole-dipole interaction will typically dominate the intermolecular attraction at long range, except in one circumstance: if either A or B has a dipole moment of zero, the first order term vanishes identically and we are left once again with no intermolecular attraction. Thus, we would still have no interaction between methane and water, because methane has no dipole. To rectify this, we must go to second order in the expansion:

$$E_0^{(2)} = \sum_{m \neq (0,0)} \frac{\left| \int \Psi_m^{(0)*} \hat{V}_{AB} \Psi_0^{(0)} d\tau \right|^2}{E_0^{(0)} - E_m^{(0)}} = \sum_{(\alpha,\beta) \neq (0,0)} \frac{\left| \int\int \Psi_\alpha^{A*} \Psi_\beta^{B*} \hat{V}_{AB} \Psi_0^A \Psi_0^B d\tau_A d\tau_B \right|^2}{E_0^A + E_0^B - E_\alpha^A - E_\beta^B}$$

Here we clarify that in this expression the single index m always specifies all of the quantum numbers for the system. Thus, in this case $m=(\alpha,\beta)$, contains two quantum numbers. The exemption $m \neq (0,0)$ that restricts the sum eliminates only one term: the case were both $\alpha=0$ and $\beta=0$. It does not remove terms where only $\alpha=0$ or only $\beta=0$. We can rationalize this by recalling that only the state whose eigenvalue we are computing (in this case the AB ground state) is eliminated from the sum. All other terms are to be included. Since the state with $\alpha=0$ and $\beta=1$ is not the ground state (because molecule B is excited) it is allowed in the sum.

As a result, we can break down the sum into three pieces. If $\alpha=0$ we get

$$E_{B,ind}^{(2)} = \sum_{\beta \neq 0} \frac{\left| \int\int \Psi_0^{A*} \Psi_\beta^{B*} \hat{V}_{AB} \Psi_0^A \Psi_0^B d\tau_A d\tau_B \right|^2}{E_0^A + E_0^B - E_0^A - E_\beta^B} = \frac{1}{4\pi^2\varepsilon_0^2 R^6} \sum_{\beta \neq 0} \frac{\left| \int\int \Psi_0^{A*} \Psi_\beta^{B*} \hat{\mu}_A \hat{\mu}_B \Psi_0^A \Psi_0^B d\tau_A d\tau_B \right|^2}{\cancel{E_0^A} + E_0^B - \cancel{E_0^A} - E_\beta^B}$$

$$= \frac{1}{4\pi^2\varepsilon_0^2 R^6} \sum_{\beta \neq 0} \frac{\left| \int \Psi_0^{A*} \hat{\mu}_A \Psi_0^A d\tau_A \int \Psi_\beta^{B*} \hat{\mu}_B \Psi_0^B d\tau_B \right|^2}{E_0^B - E_\beta^B}$$

where on the second line we have again rearranged things so that it is clear we have a product of an A integral times a B integral. The A integral does not depend on β, so we can move it outside the sum:

$$E_{B,ind}^{(2)} = \frac{\left|\langle\hat{\mu}_A\rangle\right|^2}{4\pi^2\varepsilon_0^2 R^6} \sum_{\beta\neq 0} \frac{\left|\int \Psi_\beta^{B*}\hat{\mu}_B\Psi_0^B d\tau_B\right|^2}{E_0^B - E_\beta^B} = \frac{\left|\langle\hat{\mu}_A\rangle\right|^2}{4\pi^2\varepsilon_0^2 R^6} \sum_{\beta\neq 0} \frac{\left|\hat{\mu}_B^{0\to\beta}\right|^2}{E_0^B - E_\beta^B} \qquad \textbf{Eq. 2}$$

where we have defined the **transition dipole** by
$$\hat{\mu}_B^{0\to\beta} = \int \Psi_\beta^{B*}\hat{\mu}_B\Psi_0^B d\tau_B.$$

The interpretaion of this integral is a bit challenging at first. There are a number of ways to understand it: 1) If we put B in an electric field, $\hat{\mu}_B^{0\to\beta}$ reflects the importance of the state β in the new ground state of the system 2) In matrix language, $\hat{\mu}_B^{0\to\beta}$ is the off-diagonal coupling between state 0 and state β produced by the dipole operator 3) In spectroscopy, we will find that $\hat{\mu}_B^{0\to\beta}$ relates to the intensity of the optical transition between 0 and β. However you slice it, the important point is that $\hat{\mu}_B^{0\to\beta}$ **need not be zero even if** $\langle\hat{\mu}_B\rangle$ **vanishes**. Thus the second order term we have labeled $E_{B,ind}^{(2)}$ will typically give a non-zero contribution as long as A has a dipole moment. The contribution will be attractive, because the numerator in Eq. 2 is positive and the denominator is negative. Further, $E_{B,ind}^{(2)}$ has a characteristic R^{-6} dependence on the A-B separation. If both molecules have a dipole, this contribution will be totally swamped by the dipole-dipole contribution (which only decays as R^{-3}), and so $E_{B,ind}^{(2)}$ only really becomes important in cases where B has no dipole.

Physically, we can interpret $E_{B,ind}^{(2)}$ as an induction effect (hence the subscript "ind"). If molecule A has a permanent dipole, this dipole exerts a field on B and **induces a dipole** there because the electrons on B can polarize in the presence of the field. If we instead have the scenario where B has a permanent dipole but A does not, we still get a contribution from the β=0 terms in the sum where the roles of A and B are interchanged

$$E_{A,ind}^{(2)} = \frac{\left|\langle\hat{\mu}_B\rangle\right|^2}{4\pi^2\varepsilon_0^2 R^6} \sum_{\alpha\neq 0} \frac{\left|\int \Psi_\alpha^{A*}\hat{\mu}_A\Psi_0^A d\tau_A\right|^2}{E_0^A - E_\alpha^A} = \frac{\left|\langle\hat{\mu}_B\rangle\right|^2}{4\pi^2\varepsilon_0^2 R^6} \sum_{\alpha\neq 0} \frac{\left|\hat{\mu}_A^{0\to\alpha}\right|^2}{E_0^A - E_\alpha^A}$$

This term describes induction where the dipole moment on B induces a dipole on A.

However, in the case where neither A nor B has a dipole, we appear to still be out of luck. How do non-polar molecules stick to one another? The final piece to the puzzle is provided by the terms in the second order energy where neither α nor β is zero. In this case

$$E_{disp}^{(2)} = \frac{1}{4\pi^2\varepsilon_0^2 R^6} \sum_{\alpha,\beta=1} \frac{\left|\int\int \Psi_\alpha^{A*}\Psi_\beta^{B*}\hat{\mu}_A\hat{\mu}_B\Psi_0^A\Psi_0^B d\tau_A d\tau_B\right|^2}{E_0^A + E_0^B - E_\alpha^A - E_\beta^B}$$

$$= \frac{1}{4\pi^2\varepsilon_0^2 R^6} \sum_{\alpha,\beta=1} \frac{\left|\int \Psi_\alpha^{A*}\hat{\mu}_A\Psi_0^A d\tau_A \int \Psi_\beta^{B*}\hat{\mu}_B\Psi_0^B d\tau_B\right|^2}{E_0^A + E_0^B - E_\alpha^A - E_\beta^B}$$

Using our definitions of transition dipoles, this reduces to

$$E_{disp}^{(2)} = \frac{1}{4\pi^2\varepsilon_0^2 R^6} \sum_{\alpha,\beta=1} \frac{\left|\mu_A^{0\to\alpha}\right|^2\left|\mu_B^{0\to\beta}\right|^2}{E_0^A + E_0^B - E_\alpha^A - E_\beta^B}. \qquad\qquad \textbf{Eq. 3}$$

In general the summand will be a small number, because the denominator involves an energy difference between electronic states and we have seen that electronic energy differences are big numbers. However, **it need not be zero even if neither molecule has a permanent dipole**. The only thing involved are the transition dipoles, and we have seen that in general these need not be zero. We have thus discovered a universal force between molecules. It is attractive, because the numerator in Eq. 3 is positive, while the denominator is negative. Further, it has no classical counterpart – it only exists because of quantum interactions. This attractive force was discovered by Frtiz London and is called the London dispersion force in his honor. In physics, the analogous interaction between two uncharged plates is called the Casimir force. In either situation, one typically rationalizes the interaction using the following quantum logic: "While neither molecule has a dipole **on average**, the two molecules can still cooperate so that half the time molecule A will have a + dipole while B will have a – dipole (creating an attractive interaction) while the other half the time A is – and B is + (also attractive. On average, the dipoles are still zero, but there is still a net interaction."

The dispersion interaction has a characteristic R^{-6} dependence on distance, and the coefficient is typically much smaller than that for dipole-induced dipole forces. Thus, it is most important in systems with no dipole moment. An important example of this is graphite, where the graphene sheets are held together solely by the dispersion interaction between the layers.

Putting everything together, perturbation theory gives us a physical hierarchy of intermolecular forces and also justifies why all kinds of molecules tend to stick together.

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