Lecture 33: Intermolecular Interactions

Recent Lectures

Non-degenerate Perturbation Theory vs. Variational Method

$$\text{For NDPT} \qquad \left| \frac{H_{ij}^{(1)}}{E_i^{(0)} - E_j^{(0)}} \right| \ll 1 \quad \text{for all } i, j$$

Basis Set is, in principle, Infinite

For exactly solved problems all basis states, zero-order energies, and matrix elements of $\mathbf{H}^{(1)}$ are known.

For $1/r_{ij}$ problems the matrix elements are too large and also difficult to evaluate.

It is important to choose an appropriate $\mathbf{H}^{(0)}$.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$
$$E_n^{(1)} = H_{nn}^{(1)}$$
$$E_n^{(2)} = \sum_{j \neq n} \frac{|H_{nj}|^2}{E_n^{(0)} - E_j^{(0)}}$$
$$\psi_n = \psi_n^{(0)} + \sum_{j \neq n} \frac{H_{nj}^{(1)}}{E_n^{(0)} - E_j^{(0)}} \psi_j^{(0)}$$

Non-Degenerate Perturbation Theory is good for:

- Local effects (accidental degeneracy): a "perturbation"

- Tunneling is encoded as an odd vs. even symmetry level shift

- Fitting formulas for energy levels sample $V(x)$

- Eigenvectors. Very important. Enable calculation of effects other than energy levels. Transition probabilities. R–dependence of many effects.

Variational Method

finite (small) basis set 〈 LCAO–MO

Hückel Theory
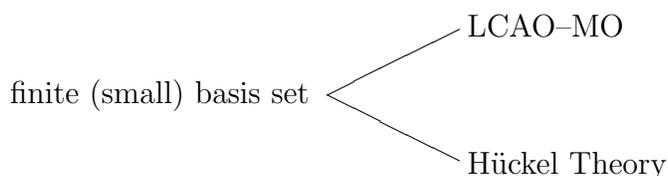
LCAO–MO: derive molecular properties from atomic properties, as understood in the Periodic Table. For H_2^+, got R_e. For A_2, got standard MO diagram. For AB, get polar bonding. Use Non-Degenerate Perturbation Theory to estimate fractional contribution from atom A vs. atom B in each MO.

Bonding/anti-bonding proportional to overlap $\mathbf{S}$, at small values of S_{ij}. Use AO ionization energy to estimate orbital size. Use orbital sizes to estimate S_{ij}.

Hückel Theory: Usually use fixed geometry. The key parameters are α, β. Know how α, β depend on orbital ionization energy and orbital size. Hückel Theory allows prediction of many properties and inter-molecule comparisons.

Eigenvectors are very important, especially in interpretation of reactivity properties via resonance structures.
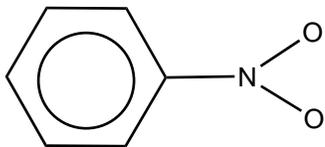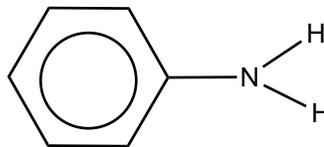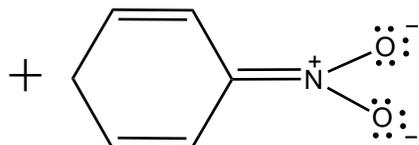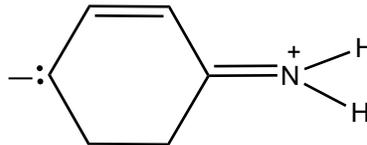
ortho, para activation

nucleophilic   electrophilic

(N lone pair donated to O atoms)   (N lone pair donated into ring)

Resonance Structures are expressed by special values of α (and β) for hetero-atoms [predicted by atomic orbital ionization energies] and are encoded in the eigenvectors for the lowest energy electronic state. Some amplitude of the resonance form is admixed into the electronic ground state and is evident in values of bond–order and atomic charge computed from the occupied molecular orbitals.

Large Basis Set Quantum Chemical Calculations

These give accurate results for almost any property. Often it is best to assemble insights from very low-level calculations (LCAO-MO or Hückel) and then test these using accurate Quantum Chemical calculations. Keep in mind that the numerical accuracy of Quantum Chemistry can be secondary to insight-generation. This is done by clever comparisons of systems.

Universal Theory of Intermolecular Interactions

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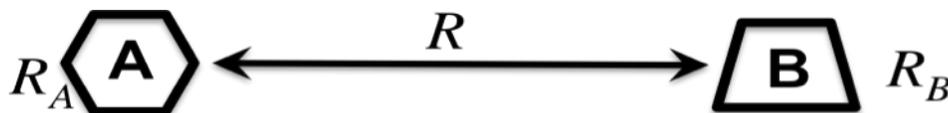
R_A, R_B are laboratory frame coordinates of molecule A and molecule B.

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 non-bonded 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 by perturbation theory.

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

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

where $\widehat{\mathbf{H}}_A$ ($\widehat{\mathbf{H}}_B$) describes the isolated interactions within molecule A (B) and $\widehat{V}_{AB}$ contains all the interaction terms between A and B. Now, $\widehat{V}_{AB}$ 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 $\widehat{V}_{AB}$ (which would be very difficult) we will note that as long as A and B are far apart (i.e. as long as R is large) we can approximate $\widehat{V}_{AB}$ using a classical dipole-dipole interaction

$$\widehat{V}_{AB} = \frac{R^2\hat{\boldsymbol{\mu}}_A \cdot \hat{\boldsymbol{\mu}}_B - 3(\hat{\boldsymbol{\mu}}_A \cdot \mathbf{R})(\mathbf{R} \cdot \hat{\boldsymbol{\mu}}_B)}{4\pi\varepsilon_0 R^5}. \tag{1}$$

Here, $\hat{\boldsymbol{\mu}}_A$ ($\hat{\boldsymbol{\mu}}_B$) is an operator that measures the electric 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,

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

The first part measures the dipole moment of the electron charge distribution, while the second subtracts the dipole moment 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 relative orientations of the dipoles involved:

μ_A	μ_B	E	
←	←	$\dfrac{-\mu_A\mu_B}{2\pi\varepsilon_0 R^3}$	attractive
↓	↑	$\dfrac{-\mu_A\mu_B}{4\pi\varepsilon_0 R^3}$	attractive
↑	↑	$\dfrac{+\mu_A\mu_B}{4\pi\varepsilon_0 R^3}$	repulsive
→	←	$\dfrac{+\mu_A\mu_B}{2\pi\varepsilon_0 R^3}$	repulsive

While the orientation dependence of the $\mu_A - \mu_B$ 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 energetically favorable head-to-tail orientation (the first situation above) in which case

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

where the non-boldface operator $\widehat{\mu}_A$ ($\widehat{\mu}_B$) 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 energetically favorable orientations relative to one another, but this will suffice for qualitative purposes.

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

$$\widehat{\mathbf{H}}^{(0)} = \widehat{\mathbf{H}}_A + \widehat{\mathbf{H}}_B, \qquad \widehat{\mathbf{H}}^{(1)} = \widehat{V} = \widehat{V}_{AB}.$$

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:

$$\widehat{\mathbf{H}}^{(0)}\Psi_\alpha^A\Psi_\beta^B = \left(\widehat{\mathbf{H}}_A + \widehat{\mathbf{H}}_B\right)\Psi_\alpha^A\Psi_\beta^B = \left(E_\alpha^A + E_\beta^B\right)\Psi_\alpha^A\Psi_\beta^B.$$

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 increase the number of 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 sufficient to consider only excited states of A or B individually — one also must 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, in zeroth-order the molecules will never stick to one another.

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

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

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

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:

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

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

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

$$E_0^{(1)} = \frac{-\langle\widehat{\boldsymbol{\mu}}_A\rangle\langle\widehat{\boldsymbol{\mu}}_B\rangle}{2\pi_0\varepsilon_0 R^3}.$$

This is exactly 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 at some higher power of R (e.g R^{-6}, see below).

Non-Lecture

We have derived a first–order perturbation correction to the energy. This correction term is $\propto R^{-3}$. Non-degenerate perturbation theory provides no explicit guidance as to when the perturbation term becomes so large at small–R that perturbation theory becomes invalid. However, it is reasonable to exercise caution when this dipole–dipole term becomes comparable to differences between zero–order energies. It is also necessary to be cautious at very small–R when the dipole–quadrupole term $(1/R^5)$ becomes larger than the dipole–dipole $(1/R^3)$ term.

We have arrived at what we sought: an expression for the energy of 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. For example, we would still have no interaction between methane and water, because methane has zero electric dipole moment. To rectify this, we must go to second-order in the expansion:

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

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 exclusion $m \neq (0,0)$ that restricts the sum eliminates only one term: the case where *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 perturbed eigenvalue we are computing (in this case the AB ground state) is excluded from the sum. All other terms must be included. Since the state with $\alpha = 0$ and $\beta = 1$ is not the ground state (because molecule B is excited) it is included in the sum.

As a result, we can break down the sum into three pieces.

(i) If $\alpha = 0$ we get

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

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

(a sum over all $\beta \neq 0$ excited states of 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:

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

where we have defined the **transition dipole** by

$$\widehat{\mu}_B^{0 \to \beta} = \int \Psi_\beta^{B*} \widehat{\mu}_B \Psi_0^B d\tau_B.$$

The interpretation of this integral seems a bit challenging. There are several ways to understand it:

1) If we put B in an electric field, $\widehat{\mu}_B^{0 \to \beta}$ reflects the importance of the excited state $\beta \neq 0$ in the new ground state of the system;

2) in matrix language, $\widehat{\mu}_B^{0 \to \beta}$ is the off-diagonal interaction between state 0 of B and state β of B produced by the dipole operator;

3) in spectroscopy, we will find that $\widehat{\mu}_B^{0 \to \beta}$ is related to the intensity of the optical transition between states 0 and β.

However you slice it, the important point is that $\widehat{\mu}_B^{0 \to \beta}$ **need not be zero even if** $\langle \widehat{\mu}_B \rangle$ **vanishes**. Thus, the second-order term we have labeled $E_{B,\text{ind}}^{(2)}$ 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, $E_{B,\text{ind}}^{(2)}$ 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 decays only as R^{-3}), and so $E_{B,\text{ind}}^{(2)}$ only really becomes important in cases where B has no dipole.

Physically, we can interpret $E_{B,\text{ind}}^{(2)}$ as an induction effect (hence the subscript "ind"). If molecule A has a permanent dipole, this $\widehat{\mu}_A$ dipole generates an electric field on B and **induces a dipole** on B because the electrons on B can *polarize* in the presence of the field.

(ii) If we instead have the scenario where B has a permanent dipole but A does not, we get a contribution from the $\beta = 0, \alpha \neq 0$ terms in the sum, where the roles of A and B are interchanged

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

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

(iii) Finally, in the case where neither A nor B has a dipole, we appear to 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 that case

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

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

Inserting our definitions of transition dipoles, this reduces to

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

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 things involved are the non–zero transition dipole moments, 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 necessarily positive, while the denominator is necessarily negative. Further, this *dispersion* term has no classical counterpart — it only exists because of quantum interactions. This attractive force was discovered by Fritz 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 (resulting in 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 attractive 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 important in systems where both interacting particles have zero dipole moments. An important example of a material that exhibits this effect 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.

Polarizability

Once you understand how to use NDPT to compute induced-dipole effects, you know something about polarizability. Suitable topics for consideration include:

- electric dipole transition moments

- energy denominators

He–He vs. Xe–Xe

Large molecules vs. small molecules. Vibrational transition contribution toward polarizability.

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