221B Lecture Notes
Many-Body Problems III
Molecular Physics

1 Molecules

In this lecture note, we discuss molecules. I cannot go into much details given I myself am not familiar enough with chemistry. But at least the notion of chemical covalence bonds which chemists had developed before the dawn of quantum mechanics is seen to emerge from the basic principles of quantum mechanics as an approximate concept. This point is certainly worth discussing.

1.1 Born–Oppenheimer Approximation

At the heart of most quantum-mechanical treatments of molecules is the Born–Oppenheimer Approximation. The discussion begins with an order-of-magnitude estimate of the time scales involved in various motions in a molecule. It turns out that the heaviness of nuclei compared to the electron $m_p/m \simeq 2000$ greatly helps us in developing an approximate treatment.

Imagine a diatomic molecule held together at a distance R between two atoms. We know typical orders of magntiude for exciting an electron in individual atmos:

$$\varepsilon_{elec} \sim \frac{e^2}{a_0} = \alpha^2 mc^2, \tag{1}$$

where m is the mass of the electron and $\alpha \simeq 1/137$ is the fine-structure constant. Here and below, we are concerned with outer shell electrons and hence most of the nuclear charge is screened by inner shell electrons. We regard the effective $Z \sim O(1)$. The typical velocity of the electron is αc, or the time scale for the electronic motion

$$t_{elec} \sim \frac{a_0}{\alpha c} = \frac{\hbar}{\alpha^2 mc^2}. \tag{2}$$

Now let us estimate the (almost) harmonic interatomic potential which stabilizes the distance between two atoms:

$$V(R) \simeq \frac{1}{2} M\omega^2 (R - R_0)^2. \tag{3}$$

We do not distinguish the nuclear mass M of two different atoms for the purpose of our order-of-magnitude estimates. We know that the stable distance between atoms R_0 is of the order of an Ångstrom, which is of the order of the Bohr radius $a_0 = \hbar^2/me^2 = \hbar c/(\alpha mc^2)$. When R approaches zero, electron wave functions of two atoms would significantly overlap and it is clear that it would cause disruption in electronic energies at the order of magnitude of Eq. (1). Therefore,

$$V(0) \simeq \frac{1}{2} M\omega^2 R_0^2 \sim \varepsilon_{elec}, \tag{4}$$

and hence we find

$$\begin{aligned} \varepsilon_{vib} = \hbar\omega \sim \hbar \left(\frac{\varepsilon_{elec}}{MR_0^2}\right)^{1/2} \\ \sim \hbar \left(\frac{Z^2\alpha^2 mc^2}{M\hbar^2c^2/(\alpha^2(mc^2)^2)}\right)^{1/2} = Z\alpha^2 mc^2 \left(\frac{m}{M}\right)^{1/2} \sim \varepsilon_{elec} \left(\frac{m}{Z^2M}\right)^{1/2} \end{aligned} \tag{5}$$

e Therefore the vibrational energy of atoms inside a molecule is suppressed by a factor of $(m/Z^2M)^{1/2} = 10^{-4}$–0.02 and is much smaller than the electronic energies. The time scale of the vibrational motion is

$$t_{rot} \sim \frac{1}{\omega} \sim \frac{\hbar}{Z\alpha^2 mc^2} \left(\frac{Z^2M}{m}\right)^{1/2} \tag{6}$$

which is much *slower* that the electronic motion Eq. (2).

Finally rotational energies are given by

$$\varepsilon_{rot} = \frac{\hbar^2}{MR_0^2} \simeq \frac{(\alpha mc^2)^2}{Mc^2} \sim \varepsilon_{elec} \frac{m}{Z^2M}. \tag{7}$$

Therefore rotational energies are further down by another factor of $(m/Z^2M)^{1/2}$ relative to the vibrational energies. The time scale for the rotation is

$$t_{rot} \simeq \frac{MR_0^2}{\hbar} \sim \frac{M\hbar^2c^2}{(\alpha mc^2)\hbar} = \frac{\hbar}{Z\alpha^2 mc^2} \frac{ZM}{m} \tag{8}$$

1.2 Hydrogen Molecule

Let us start with the simplest molecule we know of, the hydrogen molecule H_2. The way we discuss it is along the line of the original work by Heitler and London, where you use atomic orbitals of electrons attached to each of the protons.

The Hamiltonian of the sytem is

$$H = \frac{\vec{p}_A^2}{2M} + \frac{\vec{p}_B^2}{2M} + \frac{e^2}{r_{AB}} + H_e \tag{9}$$

with

$$H_e = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}} \tag{10}$$

Within the spirit of the Born–Oppenheimer approximation, we fix the distance between two protons for most of the discussions, evaluate the energy H_e as a function of the distance r_{AB}, and discuss the equilibrium distance as well as the vibrational excitation levels together with the remaining three terms in H.

The idea by Heitler–London is very simple. You start with the ground-state $1s$ wave functions for electrons attached to each of the proton. Let me write them as u_{1A}, u_{2B}, etc, which means that the electron 1 (or 2) is in the $1s$ state associated with the proton A (or B). The wave function of course consists of two electrons, and we put one electron for each proton. Therefore two possible wave functions are

$$N_\pm(u_A(\vec{x}_1)u_B(\vec{x}_2) \pm u_B(\vec{x}_1)u_A(\vec{x}_2)) \tag{11}$$

The wave function $u_A(\vec{x}) = (Za_0)^{-3/2}2e^{-|\vec{x}-\vec{x}_A|/Za_0}\frac{1}{\sqrt{4\pi}}$ depends on the distance between the electron and the proton A, and similarly for wave function $u_B(\vec{x})$ for the proton B, both for $1s$ states. The factor $N_\pm$ is there to normalize the wave function, and is different depending on the relative sign as we will see later.

On top of assiging each electron to one of the protons, we also need to specify the spins of the electrons. In order to do so, we recall Fermi statistics and make sure that the whole wave function is anti-symmetric under the exchange of two electrons. Therefore allowed wave functions are

$$N_+(u_A(\vec{x}_1)u_B(\vec{x}_2) + u_B(\vec{x}_1)u_A(\vec{x}_2))\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \tag{12}$$

for $S = 0$ and

$$\begin{aligned} &N_-(u_A(\vec{x}_1)u_B(\vec{x}_2) - u_B(\vec{x}_1)u_A(\vec{x}_2))|\uparrow\uparrow\rangle \\ &N_-(u_A(\vec{x}_1)u_B(\vec{x}_2) - u_B(\vec{x}_1)u_A(\vec{x}_2))\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ &N_-(u_A(\vec{x}_1)u_B(\vec{x}_2) - u_B(\vec{x}_1)u_A(\vec{x}_2))|\downarrow\downarrow\rangle \end{aligned} \tag{13}$$

for $S=1$ spin wave function.

Then we evaluate the energy for fixed r_{AB}. First of all, the normalization factors $N_\pm$ need to be fixed

$$\begin{aligned} N_\pm^{-2} &= \int d\vec{x}_1 d\vec{x}_2 (u_A(\vec{x}_1)u_B(\vec{x}_2) \pm u_B(\vec{x}_1)u_A(\vec{x}_2))^2 \\ &= 2 \pm 2\int d\vec{x}_1 u_A(\vec{x}_1)u_B(\vec{x}_1) \int d\vec{x}_2 u_A(\vec{x}_2)u_B(\vec{x}_2) = 2 \pm 2\Delta^2, \end{aligned} \tag{14}$$

where

$$\Delta = e^{-D}\left(1 + D + \frac{1}{3}D^2\right), \qquad D = \frac{r_{AB}}{a_0}. \tag{15}$$

Once we know the normalization of the wave function, we can calculate the expectation value of the electron Hamiltonian H_e Eq. (10). For the term without the exchange,

$$\int d\vec{x}_1 d\vec{x}_2 u_A^2(\vec{x}_1)u_B^2(\vec{x}_2)\left(2E_{1s} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}}\right) = 2E_{1s} + 2J + J', \tag{16}$$

where we used the eigenequation for $1s$ states, and

$$J = \int d\vec{x}_i u_A^2(\vec{x}_i)\frac{-e^2}{r_{iB}} = \frac{e^2}{a_0}\left[-\frac{1}{D} + e^{-2D}\left(1 + \frac{1}{D}\right)\right], \tag{17}$$

$$\begin{aligned} J' &= \int d\vec{x}_1 d\vec{x}_2 u_A^2(\vec{x}_1)u_B^2(\vec{x}_2)\frac{e^2}{r_{12}} \\ &= \frac{e^2}{a_0}\left[\frac{1}{D} - e^{-2D}\left(\frac{1}{D} + \frac{11}{8} + \frac{3}{4}D + \frac{1}{6}D^2\right)\right]. \end{aligned} \tag{18}$$

The exchange integral is more complicated,

$$\begin{aligned} &\int d\vec{x}_1 d\vec{x}_2 u_A(\vec{x}_1)u_B(\vec{x}_2)u_B(\vec{x}_1)u_A(\vec{x}_2)\left(2E_{1s} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}}\right) \\ &= 2\Delta^2 E_{1s} + 2\Delta K + K', \end{aligned} \tag{19}$$

with

$$K = \int d\vec{x}_i u_A(\vec{x}_i)u_B(\vec{x}_i)\frac{-e^2}{r_{iB}} = -\frac{e^2}{a_0}e^{-D}(1+D), \tag{20}$$

$$\begin{aligned} K' &= \int d\vec{x}_1 d\vec{x}_2 u_A(\vec{x}_1)u_B(\vec{x}_2)u_B(\vec{x}_1)u_A(\vec{x}_2)\frac{e^2}{r_{12}} \\ &= \frac{e^2}{5a_0}\left[-e^{-2D}\left(-\frac{25}{8} + \frac{23}{4}D + 3D^2 + \frac{1}{3}D^3\right)\right. \\ &\qquad \left. + \frac{6}{D}\left\{\Delta^2(\gamma + \log D) + \Delta'^2 \mathrm{Ei}(-4D) - 2\Delta\Delta' \mathrm{Ei}(-2D)\right\}\right]. \end{aligned} \tag{21}$$

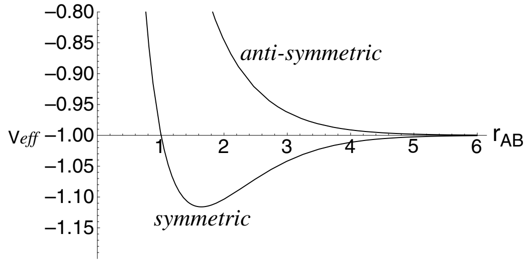

Figure 1: The energy of two electrons calculated using the perturbation theory for both symmetric and anti-symmetric spatial wavefunctions. The horizontal axis is the distance between two protons in the unit of Bohr radius a_0, and vertical axis total energy in the unit of e^2/a_0.

The constant $\gamma = 0.5772\cdots$ is Euler's constant, and

$$\Delta' = e^D \left(1 - D + \frac{1}{3}D^2\right). \tag{22}$$

The integral using the exponential integral function

$$\text{Ei}(z) = -\int_{-z}^{\infty} e^{-t}\frac{dt}{t} \tag{23}$$

is due to Sugiura. Putting all the contributions together, we find the effective potential between two protons to be

$$V_{\textit{eff}}(r_{AB}) \equiv \langle H_e \rangle_\pm + \frac{e^2}{r_{AB}} = 2E_{1s} + \frac{e^2}{r_{AB}} + \frac{2J + J' \pm 2\Delta K \pm K'}{1 \pm \Delta^2}. \tag{24}$$

Fig. 1 plots this effective potential as a function of r_{AB} for both signs. The upper curve is for the anti-symmetric spatial wave function (or $S = 1$) while the lower curve for the symmetric spatial wave function (or $S = 0$).

It is clear from the plot that the anti-symmetric spatial wave function does not lead to a bound state of two atoms, while the symmetric one does. This simple treatment gives the equilibrium distance between two atoms to be 0.80Å, while the experimental value is 0.740Å. The dissociation energy of the molecule into two hydrogen atoms is 3.14 eV from this calculation, while the actual value is 4.72 eV. The vibrational frequency for protons is 4800 cm^{-1} from this calculation (**I get 3800 instead; maybe I copied it wrong from the book?**) while it is 4317.9 cm^{-1} from data. (All numbers from Pauling–Wilson.) Clearly this wave function is the zeroth order trial wave function which needs to be improved by further variation.

The primary reason why the symmetric one binds while the anti-symmetric one doesn't is in their kinetic energies. The symmetric one has slower spatial variation than the anti-symmetric one (which has to vanish when $\vec{x}_1 = \vec{x}_2$) and has a larger kinetic energy (because it is basically the derivative). (I thank Albert and Tony to clarify this point to me.) The potential energy is actually *lower* for the anti-symmetric one because the anti-symmetry minimizes the electron-electron repulsion. But the difference in the kinetic energies wins over the difference in the potential energies and the symmetric one binds. Given the above integrals, it is easy to verify these statements quantitatively.

Simple improvement by varying Z in the trial wave function improves the agreement with data, bringing the dissociation energy to 3.76 eV, but still not quite there. The effective Z comes out as 1.166 (anti-screened!). The anti-screening makes sense because the electron "sees" both protons at the equilibrium distance. The equilibrium distance is improved to 0.76Å. The variational wave function had been further improved by including the ionic term ($u_A(\vec{x}_1)u_A(\vec{x}_2)$ where both electrons are attached to only either of the protons) by Weinbaum and correlations which depend on the interelectronic distance r_{12} by James and Coolidge. The latter gives the dissociation energy of 4.722 eV, the internuclear separataion of 0.74Å (*cf.* the data 4.2 eV and 0.7395Å, respectively), in good agreement with data.

1.3 Morse Potential

Morse potential is an approximate form for the inter-atomic potential as obtained by Heitler–London calculation. It is given by

$$V(r) = V_0(e^{-2(r-r_0)/b} - 2e^{-(r-r_0)/b}). \tag{25}$$

By choosing the parameters V_0 and b appropriately, the Heitler–London potential Eq. (24) is well reproduced. In Fig. 2, I took $V_0 = 0.11597e^2/a_0$, $r_0 = 1.64254a_0$, $b = 0.917193a_0$.

The virtue of Morse potential is that the bound states can be solved analytically. Defining the parameter $K_0 = \sqrt{2mV_0}/\hbar$, the bound state energy levels are given by

$$E_n = -V_0\left(1 - \frac{n+\frac{1}{2}}{K_0 b}\right)^2, \qquad 0 \leq n \leq K_0 b - \frac{1}{2}. \tag{26}$$

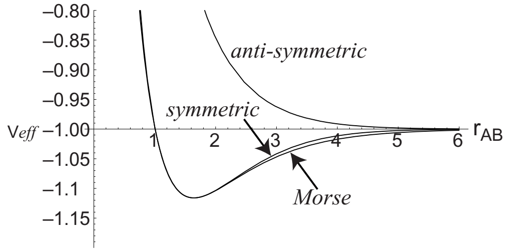

Figure 2: Comparison of potential energies in Fig. 1 to Morse potential.

For $n \ll K_0 b$, it behaves as the energy levels of a harmonic oscillator, while there are only a finite number of bound states.

1.4 Rotational Spectrum

Once the electronic energy is solved for each inter-proton distance, the Hamiltonian for two protons is

$$H = \frac{\vec{p}_A^2}{2M} + \frac{\vec{p}_B^2}{2M} + \frac{e^2}{r_{AB}} + \langle H_e \rangle = \frac{\vec{p}_A^2}{2M} + \frac{\vec{p}_B^2}{2M} + V_{\mathit{eff}}(r_{AB}). \tag{27}$$

The rest of the discussion is the standard one to separate the center-of-mass motion and the relative motion. Defining $\vec{P} = \vec{p}_A + \vec{p}_B$, $\vec{p} = (\vec{p}_A - \vec{p}_B)/2$, the Hamiltonian is

$$H = \frac{\vec{P}^2}{4M} + \frac{\vec{p}^2}{M} + V_{\mathit{eff}}(r_{AB}). \tag{28}$$

The first term is the center-of-mass motion and its wave function is given simply by plane waves. The second term is the relative motion, with the reduced mass $\mu = M/2$, together with the potential term V_{eff}. We write it in the spherical coordinates and find

$$H = \frac{\vec{P}^2}{4M} + \frac{\vec{L}^2}{M r_{AB}^2} + \frac{p_r^2}{M} + V_{\mathit{eff}}(r_{AB}). \tag{29}$$

Here, $p_r^2 = -\hbar^2 \frac{1}{r} \frac{d^2}{dr^2} r$ is a short-hand notation borrowed from classical mechanics.

At temperatures below the excitation energy for the vibrational motion, the distance between two protons is practically fixed at its equilibrium value. Then the second term in the Hamiltonian is that of a rigid rotator, $E_l = \hbar^2 l(l+1)/M r_{AB}^2$.

It is now time to compare different excitation energies of electronic, vibrational, and rotational components. To be definite, we compare energies to excite each motion to its first excited state. For the electronic excitation, it is given by the difference of $n = 2$ and $n = 1$ states, and hence

$$\varepsilon_{elec} = \frac{e^2}{2a_0}\left(1 - \frac{1}{2^2}\right) = 10.2 \text{ eV}. \tag{30}$$

For the vibrational motion, we can use the formula for excitation energies with Morse potential.

$$\varepsilon_{vib} = V_0 \frac{2}{K_0 b} = 0.50 \text{ eV}. \tag{31}$$

Finally, the excitation energy for the rotational motion is

$$\varepsilon_{rot} = \frac{\hbar^2}{M r_{AB}^2}(1(1+1) - 0) = 0.0110 \text{ eV}. \tag{32}$$

Their ratio is 930:45:1. Our rough estimate was 2000:$\sqrt{2000}$:1, which is not bad at all.

So far we have not included spin of the protons into account yet. The wave function of the molecule then is given by a product,

$$\psi = \psi_{elec}\psi_{vib}\psi_{rot}\psi_{spin}\psi_{CM}. \tag{33}$$

ψ_{elec} is a function of electron positions $\vec{x}_1$, $\vec{x}_2$, and their spins, for fixed proton positions $\vec{x}_A$, $\vec{x}_B$. Because of the form $(u_A(\vec{x}_1)u_B(\vec{x}_2) + u_B(\vec{x}_1)u_A(\vec{x}_2))/\sqrt{2}$, it does not change under the interchange of two protons. ψ_{vib} is a function of r_{AB}, and again does not change under the interchange of two protons. ψ_{CM} is just the center of mass motion given in terms of plane waves, $\psi_{CM} = e^{i\vec{P}\cdot\vec{X}/\hbar}$, with $\vec{P} = \vec{p}_A + \vec{p}_B$ and $\vec{X} = (\vec{x}_A + \vec{x}_B)/2$. Again it does not change under the interchange of two protons. On the other hand, ψ_{rot} is a function of (θ, ϕ) of the relative position $\vec{r}_{AB} = \vec{r}_A - \vec{r}_B$. In order to be eigenstates of $\vec{L}^2$, it is simply spherical harmonics,

$$\vec{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi). \tag{34}$$

Under the interchange of two protons, $\vec{r}_{AB} \to -\vec{r}$ flips, and hence $\theta \to \pi - \theta$, $\phi \to \phi + \pi$. Using the property of spherical harmonics

$$Y_l^m(\pi - \theta, \phi + \pi) = (-1)^l Y_l^m(\theta, \phi), \tag{35}$$

we find that ψ_{rot} gives a factor $(-1)^l$ under the interchange of two protons. Becaue the entire wave function must be anti-symmetric under the interchange of protons due to their Fermi-Dirac statistics, ψ_{spin} must be symmetric for odd l and anti-symmetric for even l. Adding two spin 1/2, we find total proton spin $S_p = 1$ (symmetric) or $S_p = 0$ (anti-symmetric). Therefore, the allowed combinations are odd l and $S_p = 1$ or even l and $S_p = 0$. Note that the multiplicities of states are different between $S_p = 1$ (3 states) and $S_p = 0$ (1 state).

In molecular band spectrum, you are looking at transitions between different rotational states by emission of photons. However, states with $S_p = 1$ and $S_p = 0$ can have transitions only when emission of a photon flips proton spin. Such a transition probability is proportional to the square of the magnetic moment of the proton and is very suppressed. In other words, such transitions do not occur within the duration of experiments in the lab. Therefore, the spectrum lines correspond to transitions among even l state, or odd l states, but not between them. This then gives 3 times stronger spectral lines for transitions among odd l states than those among even l states. This is the experimental way to determine proton spin. If the proton had obeyed Bose–Einstein statistics, the relative strengths would be the opposite.

For D_2 molecule, with two deuterium atoms, the relative strengths of spectral lines would be different. Deuterons, the nucleus of deterium atoms, have spin 1[1] and obey Bose–Einstein statistics. Therefore, even l rotational levels must be accompanied by symmetric spin wave functions, namely either $S = 0$ or $S = 2$, while odd l levels by anti-symmetric spin wave functions, namely $S = 1$. The multiplicities are then $5 + 1 = 6$ for even l and 3 for odd l. The transitions among odd l states produce twice as strong lines than those among even l states.

For DH molecules, there is no issue about interchanging two nuclei, and any combinations of rotational and spin wave functions are allowed.

1.5 Covalence Bonds

The important lesson out of the example H_2 is the notion of the *covalence bonds*. We learn this concept a lot in chemistry classes as an empirical rule to build up molecules, and I never understood it. (But I'm quite impressed that chemists had all figured this out back in 19th century without knowing

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[1] We will discuss why deuteron has spin 1 in the next lecture note

quantum mechanics!) The idea based on the atomic orbital method, used here for the hydrogen molecule, is to put two electrons into the atomic orbitals for two nuclei in the symmetric spatial combination, as the zeroth order approximation to describe the electron wave function. Unlike the hydrogen molecule, two nuclei can be different, and the electrons may occupy different atomic orbitals for different nuclei. But the starting point is the same:

$$N_+(u_A(\vec{x}_1)u_B(\vec{x}_2) + u_B(\vec{x}_1)u_A(\vec{x}_2))\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \tag{36}$$

Because two electrons have the opposite spin, Pauli's exclusion principle allows the electrons to freely move between two nuclei, which is impossible for the paralell spins with anti-symmetric spatial wave function. This supports the intuitive picture of two electrons being "shared" between two atoms.

For instance, think about water molecule H_2O. Suppose you have filled $1s$ states, $2s$ states and $2p, m = 0$ states of the oxygen (six electrons so far). The remaining two electrons are "shared" with the hydrogen atoms with the single covalence-bonds. Of course hydrogen atoms contribute one electron each, and we use four electrons in total for the bonds. What it means is that you would put an electron in the $1s$ state of the hydrogen and another in the $2p_x$ state ($|x\rangle = (-|m = 1\rangle + |m = -1\rangle)/\sqrt{2}$) of the oxygen, in the symmetric spatial wave function. Do the same for the other hydrogen atom together with the $2p_y$ state of the oxygen ($|y\rangle = i(|m = 1\rangle + |m = -1\rangle)/\sqrt{2}$). You can easily write down the full electronic wave function given this configuration. Note that this wave function would have two hydrogen atoms located at 90° opening because they are attached along the p_x and p_y orbitals of the hydrogen, which doesn't quite agree with data (108° degrees). That is due to the Coulomb repulsion between electrons forcing the angle to widen up. In the end, a better approximation of the electronic wave function is given by the mixed orbitals discussed in the next section.

Nonetheless, the concept of covalence bonds is extremely useful, and it is quite nice that we can "derive" it in such a simple formulation.

1.6 Hybrid Orbitals

Once the molecules are more complicated, the Coulomb potentials from other nuclei become more important. If the effect of the Coulomb potentials from other nuclei is larger than the splitting between atomic levels, they start to *mix*, causing linear combination of $2s$ and $2p$ states, for instance. Note that states with different l never mix as long as the system is rotational invariant. However, the presence of other nuclei break rotational invariance explicitly, and hence states with different l mix.

In the example of the water molecules at the end of the previous section, the Coulomb potentials from hydrogen nuclei (protons) overcome the level splitting between the $2s$ and $2p$ states of oxygen and they form hybrid orbitals sp^3. We also had used p_x and p_y orbitals in the previous section which we don't normally use in quantum mechanics. What are they?

First of all, the p states come with the spherical harmonics

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}, \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta, \qquad Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}. \tag{37}$$

Because these states are degenerate (in the absence of external fields), we can free mix them as long as we keep the orthogonal to each other. It is instructive to rewrite Eq. (37) in terms of Cartesian coordinates

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \frac{x+iy}{r}, \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \frac{z}{r}, \qquad Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \frac{x-iy}{r}. \tag{38}$$

Inspired by this form, one interesting basis is

$$Y_1^x = \frac{1}{\sqrt{2}}(-Y_1^1 + Y_1^{-1}) = \sqrt{\frac{3}{4\pi}} \frac{x}{r}, \tag{39}$$

$$Y_1^y = \frac{i}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \sqrt{\frac{3}{4\pi}} \frac{y}{r}, \tag{40}$$

$$Y_1^z = Y_1^0 = \sqrt{\frac{3}{4\pi}} \frac{z}{r}. \tag{41}$$

This is clearly another orthonormal basis. The advantage of this basis is that it shows to which direction the wave function extends. For instance, by multiplying them with the radial wave function of the $2p$ states $re^{-r/2Za_0}$ (up to a normalization constant), exponential fall-off of the wave function is prolonged along the x-axis if the angular wave function is proportional to x/r while it does off quicker along the y and z axes.

The hybrid orbitals further mix different orbitals which would normally (*i.e.* in the absence of external field caused by other atoms) have different energy levels. The best example to discuss hybrid orbitals is the methane molecule CH_4. The carbon atom has six electrons, two for $1s$, two for $2s$ and two for $2p$ in the absence of hydrogen atoms. However, to build four covalence bonds, we need four unpaired electrons, and we cannot afford to use two electrons to fill $2s$ states. Instead, we distribute four electrons among one $2s$ and three $2p$ states. But all hydrogen atoms are equal, and we should also treat four electrons in $n = 2$ equally. The only way to do so is by taking linear combinations of $2s$ and $2p$ states to form four orthonormal states stretched along four axes of a tetrahedron. We can choose the vertices of the tetrahedron to be

$$(0, 0, \frac{\sqrt{3}}{2}), \quad (\sqrt{\frac{2}{3}}, 0, -\frac{1}{2\sqrt{3}}), \quad (-\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{2}}, -\frac{1}{2\sqrt{3}}), \quad (-\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{2}}, -\frac{1}{2\sqrt{3}}). \tag{42}$$

(The vectors are intentially normalized to 3/4 rather than 1 for later conveniences.) The angles between axes is $\arccos -\frac{1}{3} = 109.5^\circ$. Correspondingly, we form four linear combinations

$$\frac{1}{2}|s\rangle \qquad\qquad\qquad\qquad + \frac{\sqrt{3}}{2}|p_z\rangle, \tag{43}$$

$$\frac{1}{2}|s\rangle + \sqrt{\frac{2}{3}}|p_x\rangle \qquad\qquad - \frac{1}{2\sqrt{3}}|p_z\rangle, \tag{44}$$

$$\frac{1}{2}|s\rangle - \frac{1}{\sqrt{6}}|p_x\rangle + \frac{1}{\sqrt{2}}|p_y\rangle - \frac{1}{2\sqrt{3}}|p_z\rangle, \tag{45}$$

$$\frac{1}{2}|s\rangle - \frac{1}{\sqrt{6}}|p_x\rangle - \frac{1}{\sqrt{2}}|p_y\rangle - \frac{1}{2\sqrt{3}}|p_z\rangle. \tag{46}$$

It is easy to check that they indeed form an orthonormal set with the wave functions stretched along the axes of the tetrahedron. Once you have explicit forms of the orbitals, you can form the covalence-bond wave function for electrons shared between the carbon and one of the hydrogen atoms easily. This way, you build up the methane molecule with the tetrahedral structure.

Similar molecules such as ammonia NH_3 and water H_2O are also well approximated by the sp^3 hybrid orbitals where one (two) of them have electrons only from the nitrogen (oxygen) which are not shared with the hydrogen. However, the opening angles are not exactly 109.5° but somewhat smaller, interpolating between the situations with Cartesian combinations (as discussed in the previous section) and the tetrahedral ones (as discussed here).

There are also other kinds of hybrid orbitals. The relevant ones for ethylene C_2H_4 are sp^2 hybrid orbitals, arranged as a unilateral triangle on a plane. For both carbon atoms, $1s$ states are filled, using two electrons already. For the remaining four electrons, we put three of them into sp^2 hybrid orbitals and the remaining one into $2p_z$ orbital. The one in the $2p_z$ is shared between two carbon atoms, forming one covalence bond between two carbons. The sp^2 orbitals are given by

$$\frac{1}{\sqrt{3}}|s\rangle + \sqrt{\frac{2}{3}}|p_x\rangle, \tag{47}$$

$$\frac{1}{\sqrt{3}}|s\rangle - \frac{1}{\sqrt{6}}|p_x\rangle + \frac{1}{\sqrt{2}}|p_y\rangle, \tag{48}$$

$$\frac{1}{\sqrt{3}}|s\rangle - \frac{1}{\sqrt{6}}|p_x\rangle - \frac{1}{\sqrt{2}}|p_y\rangle. \tag{49}$$

The first orbital along the x-axis can be shared between two carbon atoms, giving the second covalence bond. Therefore two carbon atoms are bonded with a double bond. Other two sp^2 orbitals are shared with $1s$ orbitals of hydrogen atoms. This way, you build up the ethylene molecule with a planar structure.

1.7 Molecular Orbitals

So far we had discussed building up molecules using the atomic orbitals, *i.e.*, by attaching electrons to one of the nuclei and forming covalence bonds. Even though this method nicely matches with the chemical formulae and give simple intuition behind the molecular structure, it is quantiatively not as good zeroth-order approximation compared to the molecular orbital method. With the molecular orbitals, you situate nuclei at certain fixed locations, and solve the Schrödinger equation for a single electron in the presence of multiple Coulomb sources (nuclei). Clearly this can be done only numerically, and we do not go into details. Once you find the molecular orbitals, you start filling them up from the bottom, in the same way we did with the multi-electron atoms. Of course the Coulomb repulsion among the electrons again complicates the problem and you further need to rely on approximation methods such as Hartree–Fock to build up the complete multi-electron wave function based on molecular orbitals. But quantitatively this method is much more successful that starting with atomic orbitals (thanks to Tony again).

The molecular orbital method is the literal application of the Born–Oppenheimer approximation. Take hydrogen molecule as an example. In the spirit of Born–Oppenhemier, we fix the positions of two protons, and solve for the electronic wave functions. In the Heitler–London treatment we discussed above, we used atomic orbitals for each electron associated with either of the protons as the starting point of the discussion. The electrons move around in the Coulomb potential from two protons. The first task is to solve for single-particle electron wave functions in the presence of two Coulomb sources. This has to be done numerically. However, some simple consideratios help us to understand numerical results. First of all, the system has an axial symmetry. If you choose the positions of two protons to be on the z-axis, J_z is hence a good quantum numbers. All single-electron states can be labeled by the eigenvalues of J_z. If you look at the single-electron energy levels as a function of the distance between two protons R, we at least know two limits: $R \to 0$ where the problem reduces to the single-electron levels for Helium, and $R \to \infty$ where you have two independent hydrogen levels. For a finite d, the levels interpolate between these two limits.

In Fig. 3, you can see how the energy levels move around as you change the inter-nuclear distance. When $R = 0$, what you see is the energy levels of He^+. The ground state is $1s$, with $m = 0$. The next level is either $2s$ or $2p$, and hence there are two $m = 0$ states and two $m = \pm 1$ states. When you separate two protons $R \neq 0$, there is no longer conserved l, but only m is converved. The $1s$ state still has $m = 0$, and is now called $1\sigma_g$. The symbol σ is the Greek version of the atomic specroscopic symbol s, representing $m = 0$ (not l). The subscript g means *gerade*, which is even in German. The opposite is u meaning *ungerade*, odd. Even or odd is the change of the sign in the wave function when you interchange two protons. Actually, to be more precise, it is the sign under the reflection with respect to the plane half way between two protons. From the $2s$ state, we again obtain $2\sigma_g$. But the $2p$ states split into $1\sigma_u$ (for $m = 0$) and $1\pi_u$ (for $m = \pm 1$). They are "1" rather than "2" states because this is the first occurance of σ_u and π_u. Both of these states are odd under the interchange of two protons. In general, even l states in the $R = 0$ limit lead to *gerade* states for finite R, and odd l states to *ungerade* states. In the limit of infinite R, each proton can have $1s$ states, both $m = 0$, and hence there must be two independent σ states. This is the limit where atomic orbitals can be used to label states. There must be symmetric and anti-symmetric states, corresponding to $1\sigma_g$ and $1\sigma_u$. This way, we know (without doing any calculations) that $m = 0$

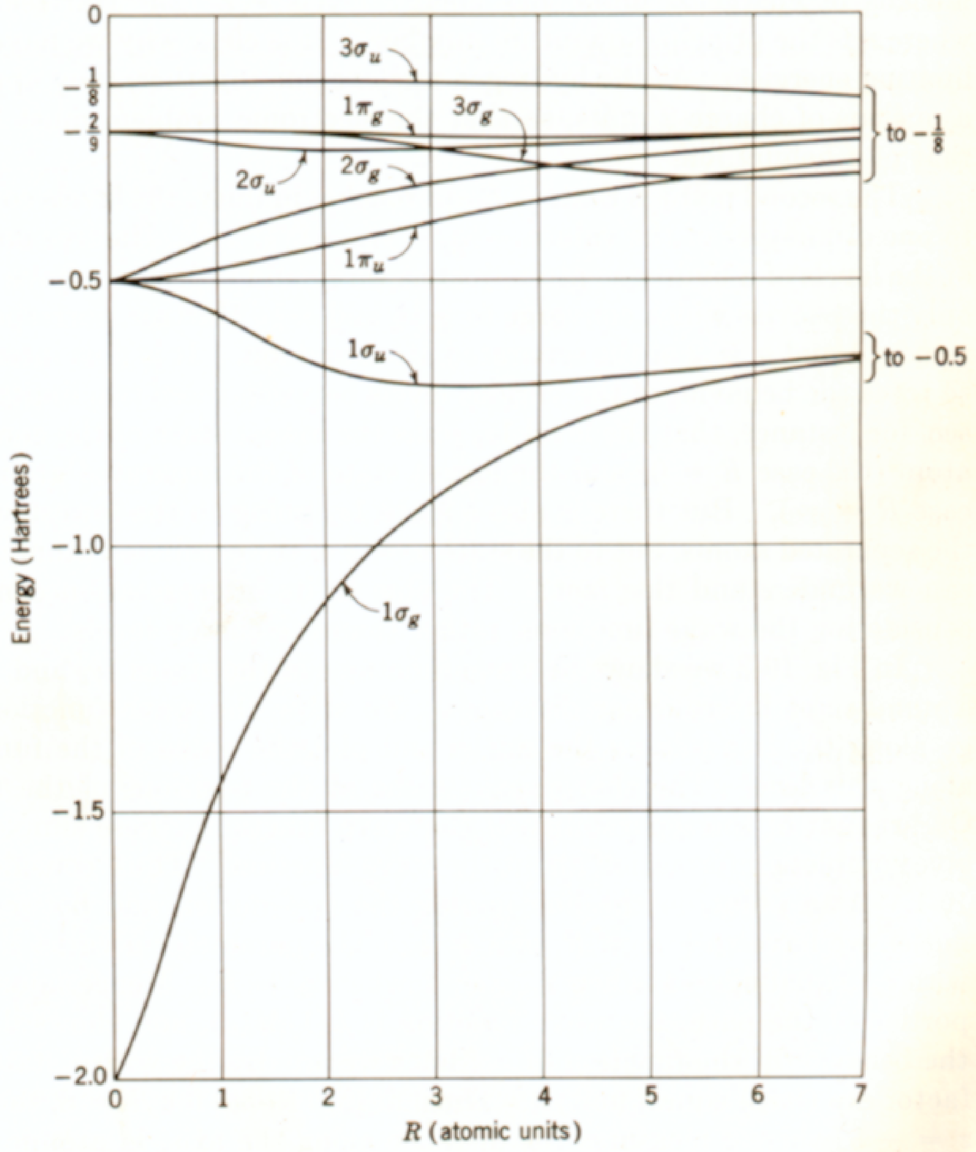

Fig. 19-2. Lowest energy levels of $H_2{}^+$ as function of internuclear distance. Internuclear repulsive energy not included.

Figure 3: The single-electron energy levels of hydrogen molecule as a function of the distance between two protons. Taken from "Quantum Theory of Matter," John C. Slater, McGraw-Hill, 1968.

state out of the $2p$ states come down and join with $1s$ state to become two $1\sigma_{u,g}$ states. Similarly, the $2s$ and $2p$ states in the $R \to \infty$ limit are either symmetric or antisymmetric, with four $m = 0$, two $m = +1$ and two $m = -1$ states. Therefore there must be $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $3\sigma_u$, $1\pi_g$, $1\pi_u$ states. On the other hand, in the $R \to 0$ limit, we indeed have $1\pi_u$ states from $2p$ and $2\sigma_g$ from $2s$, but we are missing $1\pi_g$, $2\sigma_u$, and $3\sigma_g$, $3\sigma_u$. $1\pi_g$ comes from $3d$, $2\sigma_u$ from $3p$, $3\sigma_g$ from a linear combination of $3s$ or $3d$, and finally $3\sigma_u$ from a linear combination of $4p$ and $4f$. This way, you can systematically interpolate states between $R = 0$ and ∞. Of course, the energy levels must be worked out numerically. As for the hydrogen molecule, clearly the ground state is to put two electrons in $1\sigma_g$ state. Because you put two electrons in the same orbital, clearly the spin wave function is anti-symmetric. This is consistent with our discussion using the atomic orbitals.

Fig. 3 shows that structure of diatomic molecules is much richer than that of hydrogen molecule. For instance, oxygen molecule O_2 is in spin-triplet state of electrons. To fill up 16 electrons in an oxygen molecule, you need to fill up electrons in $1\sigma_g$ (2), $1\sigma_u$ (2), $1\pi_u$ (4), $2\sigma_g$ (2), $3\sigma_g$ (2), $2\sigma_u$ (2), 14 electrons so far. Note that π states can have either $m = \pm 1$ and hence accommodates four electrons in total. The remaining two electrons go into $1\pi_g$ states, occupying only two out of four states. To minimize Coulomb repulsion between two electrons, you would use two different spatial wave functions, one with $m = +1$ and the other with $m = -1$, anti-symmetric under the interchange. Because the electronic wave function must be anti-symmetric, the spin part must be symmetric, and hence $S = 1$.

In molecules with more than two atoms, the single-electron levels are much more complicated. For instance, consider methane. You fix a cabon and four hydrogen nuclei at some locations, and solve for the electronic wave functions. You keep doing it for different configurations of the nuclei, and look for the minimum for the sum of the electronic and inter-nuclear repulsive Coulomb energies. This is the molecular orbital method. Once single-electron wave functions are obtained, you can further improve them by the variational method or Hartree–Fock approach. Mother Nature does all this calculation instantaneously!

2 Van der Waals Interaction

We had discussed the potential between two atoms as a function of the distance, using the first-order perturbation theory and atomic orbitals. Do we then know the force between two neutral atoms? Look at the long-range behavior of the potential we had calculated. It actually goes to zero at large distances *exponentially*. This is because the potential comes from the expectation values of the Coulomb potential with the exponentially decaying wave functions.

It turns out that the dominant potential between two neutral atoms at long distances is not given by the expectation value of the Coulomb interactions, but rather at the *second order*, which gives a power-law dependence than an exponential. Clearly, a power-law decays much slower than the exponential and dominates at long distances. This power-law potential between two neutral atoms is van der Waals interaction.

Here is a general argument that says that van der Waals potential decays as $1/R^6$ at large R. Consider again two hydrogen atoms. Suppose R is large enough $R \gg a_0$ so that we can consider the electron 1 to be attached to the proton A and the electron 2 to the proton B. The interaction Hamiltonian is then

$$H_I = -\frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} + \frac{e^2}{r_{AB}} + \frac{e^2}{r_{12}}. \tag{50}$$

Now we start making approximations. First fix two protons A and B along the z-axis, say at $z = -R/2$ and $z = R/2$. Because $r_{1A} \sim r_{2B} \sim a_0 \ll R$, we can expand in them. More precisely, the electron 1 is at $(x_1, y_1, -R/2 + z_1)$, and the electron 2 at $(x_2, y_2, R/2 + z_2)$. Clearly in the limit where x, y, z vanish, the potential also vanishes. In other words, the atoms are neutral and there is no "monopole" component $1/R$ in the potential. By expanding it up to $1/R^3$, we find

$$H_I = \frac{e^2}{R^3}(x_1x_2 + y_1y_2 - 2z_1z_2) + O(R^{-4}). \tag{51}$$

This is a dipole-dipole interaction. Now the important point is that when you evaluate the expectation value of this term with the $1s$ states for each atoms, the operator is basically x, y, or z, and the expectation values vanish identically:

$$\Delta E_1 = \langle H_A H_B | H_I | H_A H_B \rangle = 0. \tag{52}$$

Therefore the dipole-dipole interaction does not lead to a potential between the atoms at the first-order in perturbation theory. In other words, there is no dipole moment in neither atom, and there is no *classical* dipole-dipole interaction between atoms. However, x, y, or z have matrix elements between $1s$ and, say, $2p$. Therefore there is a contribution at the second-order in perturbation theory

$$\Delta E_2 = \sum_i \frac{\langle H_A H_B | H_I | i \rangle \langle i | H_I | H_A H_B \rangle}{E_0 - E_i}. \tag{53}$$

This does not vanish in general. Because it uses H_I twice, each giving $1/R^3$ behavior, we learn that the van der Waals potential behaves as $1/R^6$ at large R. This is an interaction between induced dipoles or quantum polarizabilities. The van der Waals force is a genuinely quantum effect.[2]

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[2] Actually, at large distances, one also needs to take the retardation effects into account, modifying the van der Waals potential to $1/R^7$ rather. There is also an interesting connection to the Casimir effect, which we discuss when we quantize the radiation field. See Milonni, P. W., and Shih, M. L., 1992, *Contemp. Phys.* **33**, 313.