

From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

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Chapter III

Molecular Quantum Mechanics

The hydrogen atom

As the smallest “molecular” system we can take hydrogen-like atoms with the Hamiltonian

$$(1) \quad \hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

To make things easier, we define a new reference system, which is well-suited to describe atomic systems. We define the reference unit for distances as Bohr’s radius

$$(2) \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

and the reference unit for energy as the Hartree

$$(3) \quad E_h = \frac{\hbar^2}{m_e a_0^2}$$

This makes our Hamiltonian (1) appear much nicer, especially when defining the mass of an electron as our reference unit for mass and the charge of a proton as our reference unit for charges:

$$(4) \quad \hat{H} = -\frac{1}{2} \nabla^2 - \frac{Z}{r}$$

It is actually easiest to solve in spherical coordinates, hence

$$(5) \quad \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

The solution to this problem is a wavefunction

$$(6) \quad \psi_{nlm}(r, \theta, \phi) = N_{nl} e^{-\frac{\rho}{2}} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^m(\theta, \phi)$$

with

$$(7) \quad \rho = \frac{2r}{na_0}$$

The normalization of the wavefunction is

$$(8) \quad N_{nl} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

The terms $L_{n-l-1}^{2l+1}(\rho)$ and $Y_l^m(\theta, \phi)$ are generalized Laguerre polynomials and spherical harmonics, respectively.

With this wavefunction, the energies are

$$(9) \quad E_n = \frac{1}{n^2} \frac{Z^2}{2} E_h$$

As the wavefunctions are normalized, we obtain

$$(10) \quad \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \psi_{nlm}^*(r, \theta, \phi) \psi_{n'l'm'}(r, \theta, \phi) = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

These integrals are a little lengthy and we do not want to write them like this all the time. Instead, we use Dirac's notation and write

$$(11) \quad \int_0^{\infty} r^2 dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi \psi_{nlm}^*(r, \theta, \phi) \psi_{n'l'm'}(r, \theta, \phi) = \langle nlm | n'l'm' \rangle$$

This gives a bra-vector and a ket-vector, plus the opportunity to add an operator, i.e.

$$(12) \quad \langle bra | c | ket \rangle = \langle c \rangle$$

The complex conjugate of this integral is

$$(13) \quad \langle bra | c | ket \rangle^* = \langle ket | c | bra \rangle = \langle c \rangle$$

or, for a single vector:

$$(13) \quad |n\rangle^* = \langle n|$$

With this, our Schrödinger equation is

$$\begin{aligned}(14) \quad \langle nlm | \hat{H} | n'l'm' \rangle &= \langle nlm | -\frac{1}{2} \nabla^2 - \frac{Z}{r} | n'l'm' \rangle \\ &= -\frac{1}{2} \langle nlm | \nabla^2 | n'l'm' \rangle - Z \langle nlm | \frac{1}{r} | n'l'm' \rangle \\ &= \langle nlm | E_n | n'l'm' \rangle \\ &= \langle nlm | E_{n'} | n'l'm' \rangle \\ &= E_n \langle nlm | n'l'm' \rangle \\ &= E_n \delta_{nn'} \delta_{ll'} \delta_{mm'}\end{aligned}$$

The Molecular Hamiltonian

As soon as many electrons and many nuclei are in our system, our Hamiltonian gets more complicated:

$$(15) \quad \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_N \frac{Z_N}{r_{iN}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \frac{1}{2} \sum_N \frac{1}{m_N} \nabla_N^2 + \sum_N \sum_{M>N} \frac{Z_N Z_M}{r_{NM}}$$

According to Born and Oppenheimer, electrons are moving so much faster than nuclei, that one can consider the nuclear positions static with respect to the positions of the electrons. Thus, we can add the term $\sum_N \sum_{M>N} \frac{Z_N Z_M}{r_{NM}}$ parametrically to the electronic energies and neglect the term of kinetic energy for the nuclei $\frac{1}{2} \sum_N \frac{1}{m_N} \nabla_N^2$. This reduces the electronic Hamiltonian to

$$(16) \quad \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_N \frac{Z_N}{r_{iN}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + V_{nuc}$$

We can further see that our Hamiltonian consists of a sum of one-electron terms and two-electron terms. If we define our (hydrogen-like) one-electron operator as

$$(17) \quad \hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_N \frac{Z_N}{r_{iN}}$$

our Hamiltonian re-writes to

$$(18) \quad \hat{H} = \sum_i \hat{h}_i + \sum_i \sum_{j>i} \frac{1}{r_{ij}}$$

Unfortunately, the energy of each electron depends on the positions of all other electrons. This yields a non-linear problem. But maybe we can try and solve the Schrödinger equation for one single electron and keep the positions of all other electrons constant. Let us consider further that each electron is described sufficiently by a single quantum number.

In this case we obtain

$$(19) \quad \langle n | \hat{H} | n \rangle = \langle n | \hat{h} | n \rangle + \left\langle n \left| \sum_{j \neq n} \frac{1}{r_{nj}} \right| n \right\rangle = \epsilon_n$$

Here we have assumed that the wavefunction is orthonormal.

Now, let us have a look what happens if we integrate over the entire system, i.e. all electrons

$$(20) \quad \sum_{ij} \langle ij | \hat{H} | ij \rangle = \sum_i \langle i | \hat{h} | i \rangle + \sum_{j>i} \left\langle ij \left| \frac{1}{r_{ij}} \right| ij \right\rangle = \sum_i \epsilon_i$$

The problem we are facing now is that we cannot distinguish between individual electrons. This means that, in principle, we have to solve the two-electron integral for both cases, one where electron i is the coordinates of i and one where it is in the coordinates of j , respectively (and the same for electron j).

We can describe this using a permutation operator. What we know about permutations is that we have to retain our system if we permute twice, hence

$$(21) \quad \hat{P}^2|ij\rangle = \hat{P}|ji\rangle = |ij\rangle$$

Now, this is fulfilled when

$$(22) \quad \hat{P}|ij\rangle = \pm|ji\rangle$$

The positive solutions are bosonic, and the negative solutions are fermionic. Unfortunately, electrons are fermions. This yields then for a single electron

$$(23) \quad \sum_{j \neq i} \left\langle ij \left| \frac{1}{r_{ij}} \right| ij \right\rangle = \sum_{j \neq i} \left\langle i \left| \left\langle j \left| \frac{1}{r_{ij}} \right| j \right\rangle \right| i \right\rangle - \sum_{j \neq i} \left\langle i \left| \left\langle j \left| \frac{1}{r_{ij}} \right| i \right\rangle \right| j \right\rangle$$

Obviously, we can define two operators out of this. The first one is the Coulomb operator, defined as

$$(24) \quad \hat{J}_{ij}|i\rangle = \sum_{j \neq i} \left\langle j \left| \frac{1}{r_{ij}} \right| j \right\rangle |i\rangle$$

And the second one is the exchange operator

$$(25) \quad \hat{K}_{ij}|i\rangle = \sum_{j \neq i} \left\langle j \left| \frac{1}{r_{ij}} \right| i \right\rangle |j\rangle$$

With these, our molecular Hamiltonian has the form

$$(26) \quad \hat{H} = \hat{h} + \hat{J} - \hat{K}$$

Now we have to find a solution to this problem. The problem is non-linear by nature, so we need to approach the solution iteratively. Let us consider that there exists a variational principle

$$(27) \quad \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} \geq \langle \psi | \hat{H} | \psi \rangle$$

We can always map this problem into a diagonalization problem if we construct a basis of trial functions. Let us consider that a hydrogen-like initial basis is not such a bad idea. Now if we take each atomic basis function to be hydrogen atom-like, we can construct our Hamiltonian as matrix with matrix elements

$$(28) \quad H_{ij} = \langle ij | \hat{h} + \hat{f} - \hat{K} | ij \rangle$$

Diagonalization of this matrix yields eigenvalues, which are orbital energies, and eigenvectors, which are our molecular orbitals.

An example: Minimal basis H₂

We start with the known wavefunctions of the hydrogen atom. If we sum all constants into a new constant ζ the 1s function of hydrogen writes as

$$(29) \quad \phi_{1s}(r) = e^{-\zeta r}$$

As we have two hydrogen atoms, we center each of these at the respective hydrogen atom and we obtain the Hamiltonian

$$(30) \quad \begin{pmatrix} \langle 1s | \hat{h} | 1s \rangle + \langle 1s1s || 1s1s \rangle & \langle 1s1s || 1s1s \rangle \\ \langle 1s1s || 1s1s \rangle & \langle 1s | \hat{h} | 1s \rangle + \langle 1s1s || 1s1s \rangle \end{pmatrix} = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix}$$

Here, we abbreviated things a little and introduced

$$(31) \quad \langle ij || kl \rangle = \langle ij | \hat{f} | kl \rangle - \langle ij | \hat{K} | kl \rangle$$

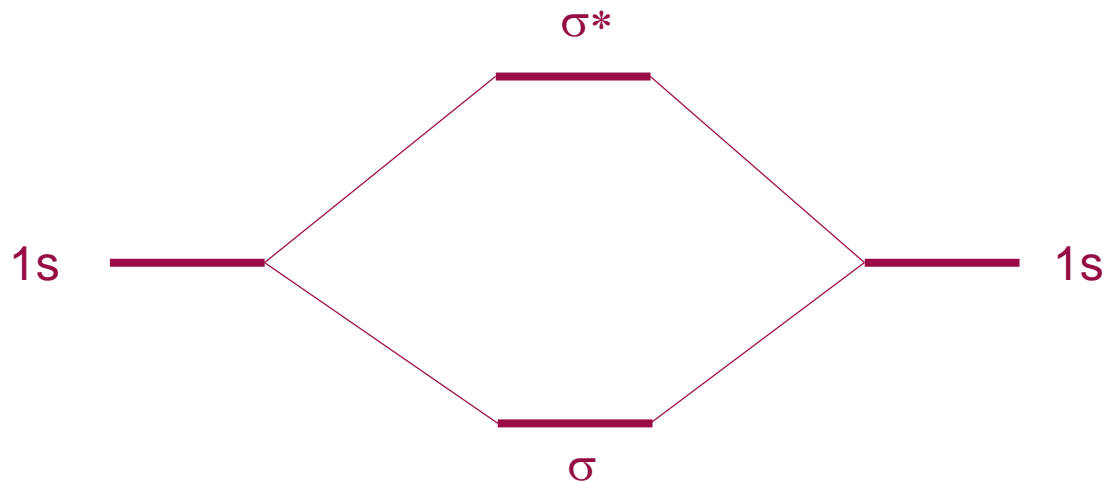
We obtain two solutions. The first one is a positive linear combination of wavefunctions:

$$(32) \quad \psi_{\sigma}(r) = \frac{1}{\sqrt{2}}(\phi_{1s}(r_1) + \phi_{1s}(r_2))$$

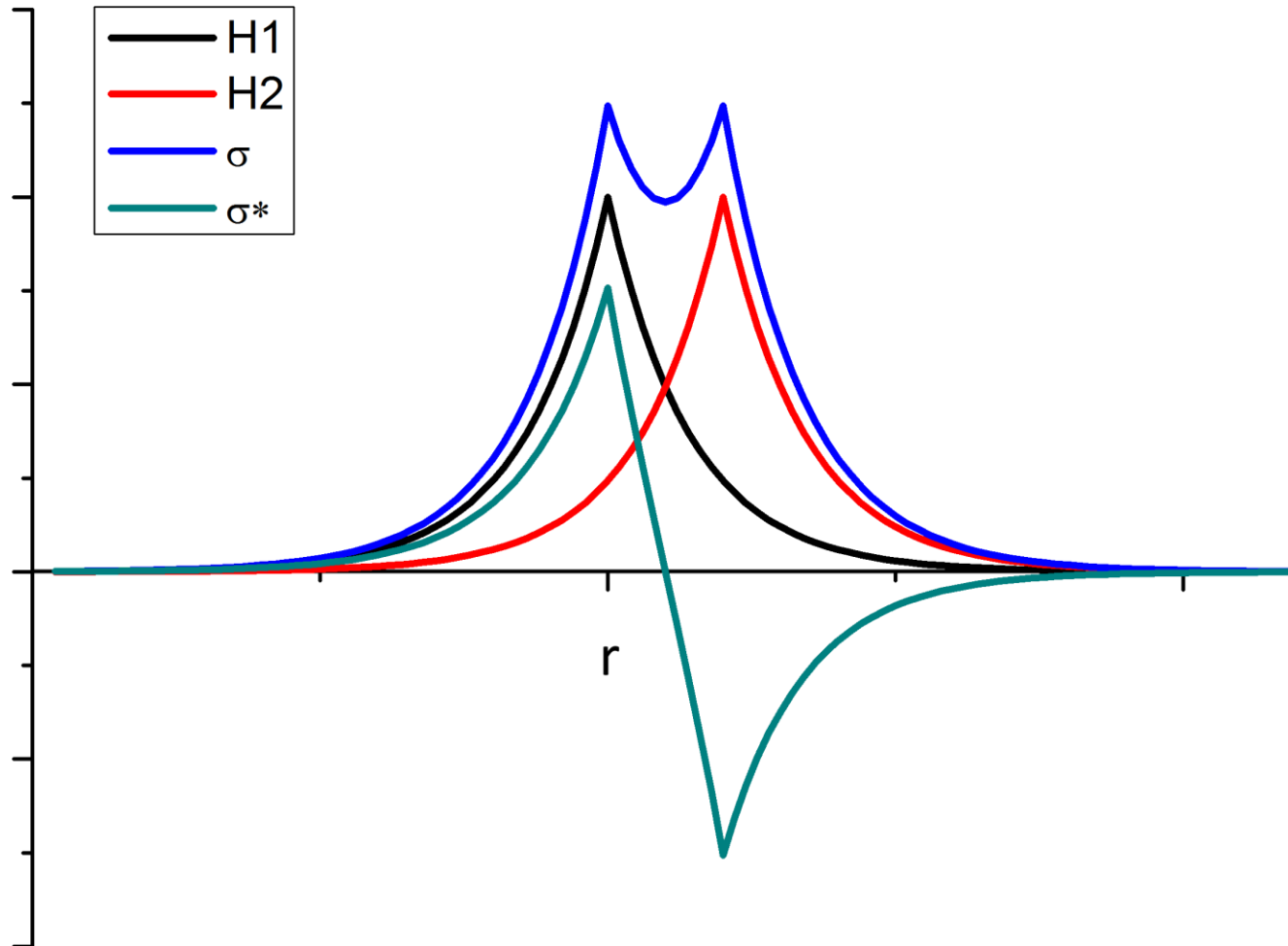
And the second one is the negative linear combination

$$(33) \quad \psi_{\sigma^*}(r) = \frac{1}{\sqrt{2}}(\phi_{1s}(r_1) - \phi_{1s}(r_2))$$

The energies are splitting up when a bond is formed:



Our wavefunctions are looking like this



From here we can conclude that a positive overlap of atomic functions yields a chemical bond, whereas a negative overlap (+1 node wrt HOMO) yields a anti-bonding orbital. As anti-bonding orbitals are higher in energy than the atomic orbitals, it is thermodynamically unfavorable to occupy them. Furthermore, if there is no overlap at all, we obtain a non-bonding orbital. Such orbital do not contribute directly to bonding, but their Coulomb and exchange interactions may stabilize or destabilize neighboring bonds.