2 Electronic structure theory

2.1 Generalities

2.1.1 Born-Oppenheimer approximation revisited

In Sec. 1.3 (lecture 3) the Born-Oppenheimer approximation was introduced (see also, for instance, [Tannor 12.1]). We are going to review this first. The context is this: the many body quantum Hamiltonian is too complicated to be solved directly. The Born-Oppenheimer approximation takes advantage of the time-scale separation between the nuclear and electronic dynamics to simplify the problem considerably. Further, if one manages to solve, or to approximate to some degree, the electronic problem, then one obtains a potential surface for the nuclear dynamics. With this one can study some fairly interesting features, like quite a bit of chemistry, which is mainly captured by the nuclear dynamics. This is what Ivan has been doing for the last few lectures. In the next few lectures we are going to review some of the most important methods used to approximate solutions to the electronic structure problem, from where one can obtain the potential surface for the nuclear dynamics.

Let’s remind ourselves of the complete non-relativistic Hamiltonian, in atomic units:

\[
H = -\sum_j \frac{1}{2M_j} \nabla^2_{N,j} - \sum_k \frac{1}{2} \nabla^2_{e,k} + \sum_{j<k} \frac{Z_j Z_k}{|R_j - R_k|} + \sum_{j<k} \frac{1}{r_j - r_k} - \sum_{j,k} \frac{Z_k}{|r_j - R_k|} = T_N + T_e + V_{NN} + V_{ee} + V_{Ne}.
\]

We want to get some back-of-the-envelope estimation for the time scale of the dynamics of electrons and nuclei. We can do this using one of the most important tools in the physics toolbox: dimensional analysis. We can get time scales from the natural frequencies, which we can get from the kinetic energy term. The units of this term are $M^{-1}L^{-2}$. Now, the lengths that we care about are bond lengths for nuclei and atomic size for electrons. Both are of the order of the Bohr radius (maybe a few times bigger) and, not accidentally, of comparable length. In atomic units, we just take them to be unity. So we conclude that the kinetic energy for electrons is of order unity (because their mass is unity) and for nuclei is $\sim 10^{-4}$ Hartrees. That is, we estimate $T \sim M^{-1}$. Now we get the frequency from the potential energy term

\[
M \omega^2 \sim T \sim M^{-1}
\]

\[
\omega \sim M^{-1}.
\]

That means that the nuclei frequency is $10^{-4}$ times the frequency of the electron, and then we can basically consider them to be static if we want to approximate the electronic structure.
Therefore, when considering the electronic structure we take $V_{NN}$ and $T_N$ to be constant (they depend on $R$, which we take itself to be a constant). As long as we are considering only the electronic structure, we can use the fact that a constant added to a Hamiltonian only "gauges" where we put the origin of the energy, but it does not change the stationary states or the dynamics. That is, the eigenvectors of $H + c \mathbb{I}$ are the same as those of $H$, and, for the dynamics,

$$\sum_j e^{-i(E_j+E_0)t} \alpha_j |\psi_j\rangle = e^{-iE_0t} \sum_j e^{-iE_jt} \alpha_j |\psi_j\rangle = \sum_j e^{-iE_jt} \alpha_j |\psi_j\rangle .$$

Ignoring then the nuclear part, we are left with the Hamiltonian

$$H_e = T_e + V_{ee} + V_{Ne} = -\sum_k \frac{1}{2} \nabla^2 e,k + \sum_{j<k} \frac{1}{|r_j - r_k|} - \sum_{j,k} \frac{Z_k}{|r_j - R_k|} .$$

We want to solve the problem

$$H_e |\psi\rangle = E_e |\psi\rangle .$$

From now on we drop the subscript $e$ of $H_e$.

### 2.1.2 Molecular orbitals and the minimum basis for $H_2^+$

Let’s consider first the Hamiltonian for a single electron for $H_2^+$. It is:

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} .$$

We want to find solutions $\psi(r)$ for this Hamiltonian, the eigenstates. We are going to call these solutions molecular orbitals (MO). To approach the problem we use our knowledge of the solution of the Hydrogen atom

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r} .$$

We are going to build MOs out of approximate solutions $\phi(r)$ of this problem, which are called atomic orbitals (AO). We will consider AO for both atoms and we will try to express $\psi(r)$ as a linear combination of atomic orbitals (LCAO)

$$\psi(r) = \sum_{\mu} c_{\mu} \phi_{\mu}(r) .$$

For the solution to be exact, the basis set of AOs must be complete, but in general we will restrict ourselves to a sufficiently good approximation. Remember the form of the solutions of the Hydrogen atom

$$\psi_{n\ell m}(r, \theta, \varphi) = \sqrt{\left( \frac{2}{n a_0} \right)^3 (n - \ell - 1)!} e^{-\rho/2} \rho^{\ell + 1} L_{n-\ell-1}^\ell(\rho) \cdot Y_m^\ell(\theta, \varphi)$$

where
\( \rho = \frac{2r}{n a_0} \), \( a_0 \) is the Bohr radius,

- \( L_{n-l-1}^{2l+1}(\rho) \) are the generalized Laguerre polynomials of degree \( n - l - 1 \),
- \( Y^m_\ell(\theta, \phi) \) is a spherical harmonic function of degree \( l \) and order \( m \).

The most important feature is the \( e^{-\rho/2} \) exponential decay. Notice that from
the definition of \( \rho \) we get a decay length of the AO in the order of the Bohr
radius, consistent with our discussion of the Born-Oppenheimer approximation.

Inspired by this, a common choice for atomic orbitals are the so called Slater
orbitals

\[
\phi_\alpha(r) = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} e^{-\alpha |r - R_A|}
\]

![Figure 1: Slater AOs with \( \alpha = 1 \) (blue), \( \alpha = 4 \) (red) and \( \alpha = 1/4 \) (brown).](figure1.png)

We will say more about basis sets later...

We can now construct a very simple approximation to the \( H_2^+ \) ground state.
For some value of the exponent \( \alpha \), which we can optimize, we get, by symmetry, two possible MOs:

\[
\psi_+ = \frac{1}{\sqrt{2(1 + S_{12})}} (\phi_1 + \phi_2)
\]

\[
\psi_- = \frac{1}{\sqrt{2(1 - S_{12})}} (\phi_1 - \phi_2)
\]

where the normalization depends on the overlap

\[
S_{12} = \int d\mathbf{r} \phi_1(\mathbf{r}) \phi_2(\mathbf{r}) .
\]

At a first approximation we can take \( \alpha = 1 \) in a.u. The symmetric combination
\( \psi_+ \) turns out to lead to a bonding molecular orbital and has \textit{gerade} symmetry.
The antisymmetric combination leads to an antibonding MO and has *ungerade* symmetry. You can see how the wave functions look like in Figs. 2.1.2 and 2.1.2. As it turns out, the energy of the *gerade* wave function is lower than the atomic orbital energy, and the energy of the *ungerade* one is higher than the AO (see Fig. 2.1.2).

![Figure 2](image_url)

Figure 2: Amplitude for the *gerade* and *ungerade* MO wave functions. We take $\alpha = 1$, and a standard separation of $1.4a_0$ between the nuclei.

![Figure 3](image_url)

Figure 3: Density for the *gerade* and *ungerade* MO wave functions. Same parameters as the previous figure.

In general, we will consider some set of wave functions as possible solutions to the electronic structure problem, and then optimize the solution among this set, as in the $H_2^+$ case. Equivalently, we will try to solve the electronic structure Hamiltonian by writing it in some convenient basis. The wave functions of this basis which tend to look like wave functions for a single electron are called *molecular orbitals* (MO), $\phi(\mathbf{r})$. We will then combine molecular orbitals appropriately to get a solution to the many-electron problem. Usually, as in the $H_2^+$ case, the molecular orbitals are themselves expanded in a basis of *atomic orbitals* (AO), which are non-orthogonal wave-functions centered in the different atoms.
of the molecule. We normally restrict this combination to be linear and then \( \phi(r) \) is a linear combination of atomic orbitals (LCAO). For the solution to be exact, the basis set must be complete, but in general we will restrict ourselves to a sufficiently good approximation.

### 2.1.3 Spin orbitals

So far we have been writing spatial orbitals, wave functions describing the electron in real space, as:

\[
\psi(r) = \langle r | \psi \rangle
\]

That is, we write spatial coordinates like \( r \). Electrons also have spin, \( \pm 1/2 \), which we write \( |\alpha\rangle = |1/2\rangle \) and \( |\beta\rangle = |-1/2\rangle \). The complete wave function with spin is

\[
|\chi\rangle = |\psi^\alpha\rangle|\alpha\rangle + |\psi^\beta\rangle|\beta\rangle .
\]

Wave functions of multiple electrons can of course have higher total spin.

It is often convenient, to unify notation, to introduce a dummy variable \( \omega \) for spin, which can have values \( \omega = \pm 1/2 \), and to define the functions

\[
\alpha(\omega) = \langle \omega | \alpha \rangle = \delta_{\omega,1/2}
\]

\[
\beta(\omega) = \langle \omega | \beta \rangle = \delta_{\omega,-1/2} .
\]

Using standard quantum chemistry notation, we write \( x \) for spin orbital coordinates \( x = \{ r, \omega \} \). We can then write spin orbitals as functions

\[
\chi(x) = \psi^\alpha(r)\alpha(\omega) + \psi^\beta(r)\beta(\omega) .
\]

We also introduce a notation for simple spin orbitals

\[
|\psi\rangle \equiv |\psi\rangle|\alpha\rangle
\]

\[
|\tilde{\psi}\rangle \equiv |\psi\rangle|\beta\rangle .
\]
Although in this notation $|\psi\rangle$ can be both MO and a spin orbital, its meaning will be made clear by the context.

### 2.1.4 Pauli exclusion principle and Slater determinants

Consider a wave function for $N$ electrons, $\Phi(x_1, \ldots, x_N)$. Electrons are fermions, which implies that the Pauli exclusion principle applies. Explicitly, for any pair of indexes $j, k$ we have

$$\Psi(x_1, \ldots, x_j, \ldots, x_k, \ldots, x_N) = -\Psi(x_1, \ldots, x_k, \ldots, x_j, \ldots, x_N).$$

Consider a set of $N$ non-interacting electrons and atomic orbitals $\{\chi_j\}$. We can try to write the many body wave function as

$$\Psi(x_1, \ldots, x_N) = \chi_1(x_1) \cdots \chi_N(x_N).$$

A wave function like that is called a Hartree product. It describes uncorrelated quantum particles. A general many body wave function is a superposition of Hartree products, and, in general, cannot be written as a single Hartree product. This realization opens the fascinating subject of entanglement, which we are not going to discuss here.

The problem with this wave function is that it does not obey the Pauli Exclusion Principle. We need to anti-symmetrize the wave function. The simple case, with two electrons, becomes

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}(\chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)).$$

To write out a concrete case explicitly, if one AO is a Slater orbital centered at $R_1$ and decay $\alpha$, the other AO is also Slater at $R_2$ and also decay $\alpha$, and both have the same spin, the wave function is

$$\Psi(x_1, x_2) = \Psi(r_1, \omega_1, r_2, \omega_2) \propto (e^{-\alpha|r_1-R_1|} - e^{-\alpha|r_2-R_1|} - e^{-\alpha|r_2-R_2|} - e^{-\alpha|r_1-R_2|})\alpha(\omega_1)\alpha(\omega_2).$$

An interesting point is that all electrons are always indistinguishable in principle, and therefore the wave function should, in theory, be always antisymmetric. Nevertheless, if the wave functions do not have overlapping support, only one of the terms is not negligible. That is, for big $\alpha$ relative to $|R_1 - R_2|$ the second term of the previous equation is 0 for all practical purposes.

Notice that we can write the two-electron spin orbital as a determinant

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) \\ \chi_1(x_2) & \chi_2(x_2) \end{vmatrix}.$$ 

The general case can also be written as a determinant, called a *Slater determinant*

$$\Psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}.$$
Writing out Slater determinants and their superpositions is not very economical, so in practice one chooses an ordering for the electron labels and writes a Slater determinant like
\[ \Psi(x_1, x_2, \ldots, x_N) \equiv |\chi_1 \chi_2 \cdots \chi_N \rangle . \]
For the non-antisymmetrized version we will still use the notation
\[ |\chi_1 \rangle \cdots |\chi_N \rangle . \]

### 2.1.5 A little MO zoology

In reality, further restrictions are often imposed on the single determinant \( N \)-electron wave function when looking for solutions of the \( N \)-electron problem. Let’s review some of the more common types of determinants considered.

1. The first restriction is that we work with LCAO, and the set of AOs is not a complete basis, but some convenient basis set.

2. Another common approximation is to impose that the MOs are the same for all spins. That is, we choose a set of MOs \( \{\psi_j\} \) and then work with the spin orbitals \( \psi_j^\alpha \equiv \psi_j \) and \( \psi_j^\beta \equiv \bar{\psi}_j \). This is called restricted Hartree-Fock, while the more general case is called unrestricted Hartree-Fock. In the minimal basis \( H_2 \) case, one has the spin orbitals \( \psi_\pm \) and \( \bar{\psi}_\pm \).

   This is not always the best choice. Consider, for instance, the case of Lithium \([Szabo 2.5.3]\). A restricted HF ground state would look like
   \[ |\psi_1 \bar{\psi}_1 \psi_2 \rangle . \]
   Both \( \psi_1 \) and \( \bar{\psi}_1 \) have the same MOs spatial wave function, but \( \psi_1 \) interacts with \( \psi_2 \) while \( \bar{\psi}_1 \) does not. This is because the spin contraction between the later two wave functions is zero, and cancels any spatial interaction
   \[ \langle \bar{\psi}_1 | f(\mathbf{r}) | \psi_2 \rangle = 0 . \]
   Therefore, the energy can be lowered if different spins can have different MOs in this case.

3. Restricted Slater determinants are not, in general, eigenfunction of the total spin operator. This is the case, for instance, of \( |\psi_+ \bar{\psi}_- \rangle \). Nevertheless, one can form linear combinations which are appropriate spin eigenstates, called spin adapted configurations \([Szabo 2.5]\) or configuration state functions \([Helgaker 2.5]\). For example
   \[
   \frac{1}{\sqrt{2}} (|\psi_+ \bar{\psi}_- \rangle - |\bar{\psi}_+ \psi_- \rangle )
   = \frac{1}{\sqrt{2}} (|\phi_1 \rangle |\phi_2 \rangle + |\phi_2 \rangle |\phi_1 \rangle ) \frac{1}{\sqrt{2}} (|\alpha \rangle |\beta \rangle - |\beta \rangle |\alpha \rangle ) .
   \]

4. A determinant in which each spatial orbital is double occupied is called closed shell. An open shell orbital is a spatial orbital with a single electron. A restricted close shell orbital is spin adapted already.
2.1.6 Exchange term

Let’s consider the effect of the Coulomb electron repulsion term for two electrons

\[ V_{ee} = \frac{1}{|\mathbf{r}_1\mathbf{r}_2|} = \frac{1}{r_{12}}. \]

In particular, let’s work out the expectation value for the state \(|\psi_1\psi_2\rangle\), that is

\[ \langle \psi_1\psi_2| \frac{1}{r_{12}} |\psi_1\psi_2\rangle. \]

We get

\[ \frac{1}{2} \left( \langle \psi_1|\psi_2\rangle - \frac{1}{r_{12}} \langle \psi_1|\psi_2\rangle \right) \frac{1}{r_{12}} \left( |\psi_1\rangle|\psi_2\rangle - |\psi_2\rangle|\psi_1\rangle \right) \]

\[ = \frac{1}{2} \left( \langle \psi_1|\psi_2\rangle \frac{1}{r_{12}} |\psi_1\rangle - \frac{1}{r_{12}} |\psi_2\rangle \right) + \langle \psi_2|\psi_1\rangle \frac{1}{r_{12}} |\psi_1\rangle \]

\[ - \langle \psi_1|\psi_2\rangle + \langle \psi_1|\psi_2\rangle \frac{1}{r_{12}} - \langle \psi_2|\psi_1\rangle \frac{1}{r_{12}}. \]

Using the symmetry of the potential, we see that

\[ \langle \psi_1|\psi_2\rangle \frac{1}{r_{12}} |\psi_1\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_1^*(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \frac{1}{r_{12}} \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) \]

\[ = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_1^*(\mathbf{r}_2) \psi_2(\mathbf{r}_1) \frac{1}{r_{12}} \psi(\mathbf{r}_2) \psi(\mathbf{r}_1) \]

\[ = \langle \psi_1|\psi_2\rangle \frac{1}{r_{12}} |\psi_1\rangle. \]

A similar equivalence holds for the negative terms. We have

\[ \frac{1}{2} \left( \langle \psi_1|\psi_2\rangle + \frac{1}{r_{12}} \langle \psi_1|\psi_2\rangle \right) \frac{1}{r_{12}} \left( |\psi_1\rangle|\psi_2\rangle + |\psi_2\rangle|\psi_1\rangle \right) \]

\[ = \frac{1}{2} \left( \langle \psi_1|\psi_2\rangle + \frac{1}{r_{12}} |\psi_1\rangle \right) + \langle \psi_2|\psi_1\rangle \frac{1}{r_{12}} |\psi_1\rangle \]

\[ - \langle \psi_1|\psi_2\rangle + \langle \psi_1|\psi_2\rangle \frac{1}{r_{12}} - \langle \psi_2|\psi_1\rangle \frac{1}{r_{12}}. \]

According to the first equation, this term is just the Coulomb energy of the classical probability distribution corresponding to the given wave functions. Looking at the second equation, we see that we can also write this term as a Coulomb operator \(J_2\) acting on \(|\psi_1\rangle\),

\[ J_2(\mathbf{r}_1) = \int d\mathbf{r}_2 |\psi_j(\mathbf{r}_2)|^2 \frac{1}{r_{12}}. \]
This is the Coulomb field due to the second wave function. In general, for the N-body problem, this term generalizes to a Coulomb operator due to all particles, which acts on particle \( j \). That is, we get something like

\[
\langle \psi_j | \sum_{k \neq j}^N \mathcal{J}_k | \psi_j \rangle.
\]

In essence, we can see how one will get an effective Hamiltonian which contains an operator \( \sum_{k \neq j}^N \mathcal{J}_k \).

Finally, we look at the negative term of the electron repulsion. Notice that this term comes from the anti-symmetry of the wave function, that is, the wave function must get negative sign when we “exchange” two electrons. This introduces an exchange correlation between the electrons, and its effect in the Coulomb interaction is called the exchange term. If we write this term explicitly we get

\[
\langle \psi_1 | \langle \psi_2 | \frac{1}{r_{12}} | \psi_2 \rangle | \psi_1 \rangle = \int d\mathbf{r}_1 \psi_1^\ast \langle \mathbf{r}_1 | \int d\mathbf{r}_2 \psi_2^\ast \langle \mathbf{r}_2 | \frac{1}{r_{12}} \psi_2 \langle \mathbf{r}_1 | \psi_1 \rangle .
\]

If we write an effective operator, as we did for the Coulomb term, we find out that the exchange term is not a local potential

\[
\mathcal{K}_2(\mathbf{r}_1) \psi_1(\mathbf{r}_1) = \left[ \int d\mathbf{r}_2 \psi_2^\ast \langle \mathbf{r}_2 | \frac{1}{r_{12}} \psi_1 \langle \mathbf{r}_2 | \right] \psi_2(\mathbf{r}_1) .
\]

The exchange term is not a local potential because to find the effect of the effective exchange operator on \( \psi_1(\mathbf{r}_1) \), we actually need to integrate over all \( \psi_1(\mathbf{r}_2) \). This is a purely quantum effect which arises from the indistinguishability of the electrons and the Pauli exclusion Principle. Of course, a relativistic treatment will restore causality, but it will still not give a local potential.

In general, for the N-body problem, this term generalizes in a similar way as the Coulomb operator, giving a exchange term due to all particles, which acts on particle \( j \). That is, we get something like

\[
\langle \psi_j | \sum_{k \neq j}^N \mathcal{K}_k | \psi_j \rangle.
\]

Again, we can see how one will get an effective Hamiltonian which contains an operator \( \sum_{k \neq j}^N \mathcal{K}_k \).