# Electronic Structure Theory

Dr. Patrick Rinke

Theory Department

Fritz Haber Institute of the Max Planck Society

Faraday Weg 4-6

Berlin

rinke@fhi-berlin.mpg.de

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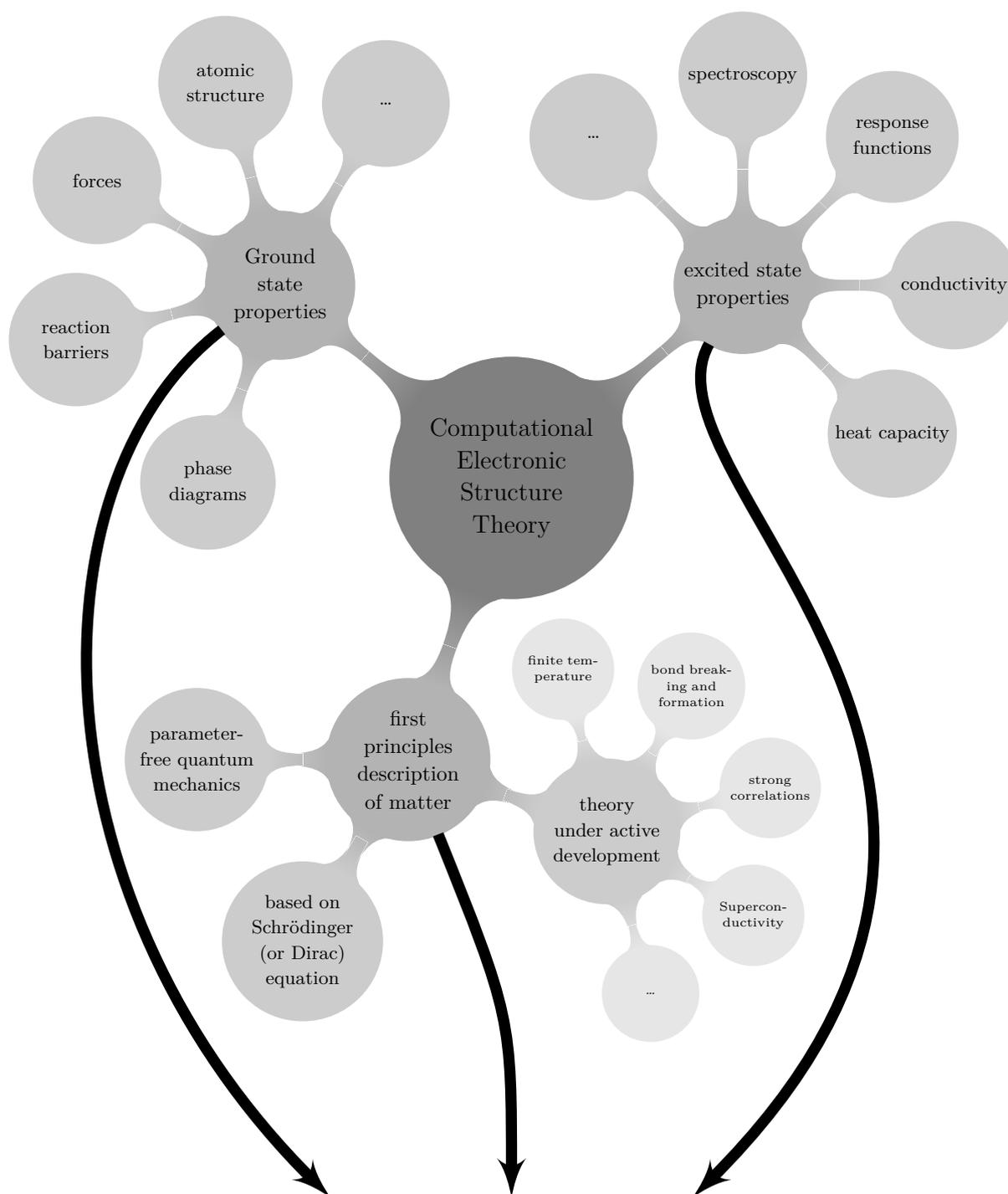
**The goal of electonic structure theory is to be predictive!**

Computational Electronic Structure Theory is an ever-growing field which combines theoretical physics and chemistry with computer science and math.

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# 1 The Schrödinger Equation

A system of electrons and nuclei is governed by the Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \tag{1.1}$$

where $\mathcal{H}$ is the Hamiltonian of the system, $E$ the energy and $\Psi$ the many-particle wave function. The dynamics of the system obey the time-dependent Schrödinger equation

$$\mathcal{H}\Psi(t) = \mathrm{i}\frac{\partial}{\partial t}\Psi(t) \tag{1.2}$$

Strictly speaking, we would have to solve the Dirac equation, but for now we are not interested in relativistic effects. We also do not include external fields. Throughout this lecture we will use atomic units, this means

$$m_e = e = \hbar = \frac{1}{4\pi\epsilon_0} = 1$$

and all energies are given in Hartree ($1Ha = 27.211eV$). Therefore, the general Hamiltonian in our systems is given by Equation 1.3.

$$
\begin{aligned}
\mathcal{H} = &\overbrace{-\sum_{I=1}^{N_n} \frac{\nabla_{\mathbf{R}_I}^2}{2M_I}}^{T^n} + \overbrace{\sum_{I=1}^{N_n}\sum_{J>I}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}^{V^{nn}} \\
&\underbrace{-\sum_{i=1}^{N_e} \frac{\nabla_{\mathbf{r}_i}^2}{2}}_{T^e} + \underbrace{\sum_{i=1}^{N_e}\sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V^{ee}} + \underbrace{\sum_{i=1}^{N_e}\sum_{J=1}^{N_n} \frac{-Z_J}{|\mathbf{r}_i - \mathbf{R}_J|}}_{V^{ne}}
\end{aligned}
\tag{1.3}
$$

$$
\begin{array}{llll}
\mathbf{R}: & \text{nuclear coordinate} & \mathbf{r}: & \text{electronic coordinate} \\
N_n: & \text{number of nuclei} & N_e: & \text{number of electrons} \\
M: & \text{nuclear mass} & Z: & \text{nuclear charge}
\end{array}
$$

Our Hamiltonian can be viewed as coupled nuclear and electronic problems. If the nuclei were fixed in space, $V^{ne}$ in Equation 1.3 would become an external potential and the problem we have to solve would become a purely electronic one:

$$\mathcal{H}^e \Phi^e = [T^e + V^{ee} + V^{ne}]\Phi^e \tag{1.4}$$

For a few special cases the electronic Schrödinger equation can be solved analytically:

> **particle in a box:** plane waves / sine and cosines

> **harmonic oscillator:** Hermite polynomials

> **hydrogen atom:** Laguerre polynomials

But in general, the interaction term $V^{ee}$ precludes any analytic solution. Since the Schrödinger equation is a differential equation where all terms are known to us, one could try to solve it numerically on a grid. But this naive approach fails because of $\Phi^e = \Phi(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_{N_e})$ is a high-dimensional object. Take a single Silicon atom as example: it has 14 electrons and therefore 42 electronic coordinates. Even if we would sample with only ten grid points per coordinate, we need a stack of DVDs from here to the moon just to store the wave function.

**To solve the Schrödinger equation we have to find suitable approximate ways!**
Different frameworks lead to different approach that lead themselves to different approximations, that in turn work for different systems and circumstances.

- **Wave function $\Phi^e(\{\mathbf{r}_i\})$ based methods**

    - **Quantum Chemistry**
      These methods rely on successively improving the accuracy of the approximated wave function in a hierarchical manner. So far, these methods are mostly applied to finite systems, e.g. molecules and clusters. Commonly used methods from this class are for example Hartree-Fock, Mjøller-Plesset perturbation theory and Coupled Cluster.

    - **Quantum Monte Carlo**
      QMC methods are based on a stochastic solution of the Schrödinger equation and representation of $\Phi^e$ and can be applied to finite as well as periodic systems. Popular variants are Variational and Diffusion Monte Carlo. These methods will not be covered in this lecture.

- **Density $n(\mathbf{r})$ based methods**
  Density Functional Theory reformulates the problem in terms of the electronic density and can be applied to finite and periodic systems. A wide range of different functionals exist an the challenge with these approaches is finding good and systematically improvable approximations for the functional.

- **Green's function $G(\mathbf{r}, \mathbf{r}', \omega)$ based methods**
  Many-body perturbation theory methods are often used in solid state physics and quantum chemistry and can be systematically improved. Well-known methods from this class are GW, T-Matrix, BSE and FLEX.

- **Density-matrix $n(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}, \mathbf{r}', t = 0)$ based methods**
  Density-matrix functional theory is one of the so far little explored methods and will not be covered in this lecture.

The important thing about the different frameworks is that all of them are in principle exact. Since they are based on different quantities and make different approximations, they give us a diverse set of tool to study a system.

## 1.1 The Born-Oppenheimer Approximation

The dynamics of a system are described by the time-dependent Schrödinger equation:

$$
\mathcal{H}\Psi(t) = \mathrm{i}\frac{\partial}{\partial t}\Psi(t)
$$
$$
\Rightarrow \Psi(t) = e^{-i\mathcal{H}(t-t_0)}\Psi(0)
$$

but how can we make this more tractable?

Nuclei are much heavier than electrons (e.g. $M_H/m_e = 1840$, $M_{Si}/m_e = 25760$ and $M_{Ag}/m_e = 86480$) and therefore react significantly slower to external perturbations than the electrons. As a first approximation electrons will therefore react instantaneously to nuclear motions and we can decouple the electronic and nuclear motion. Then we can treat the nuclei as clamped and solve the electronic problem from Equation 1.4.

### 1.1.1 Formally Exact Decomposition

The electronic Hamiltonian $\mathcal{H}^e = T^e + V^{ee} + V^{ne}$ has the following eigenfunctions

$$
\mathcal{H}^e(\{\mathbf{R}_I\})\,\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_j\}) = E_\nu^e\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_j\}) \tag{1.5}
$$

which parametrically depend on the nuclear coordinates. These basis functions can be used to expand the full wave function.

$$
\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_j\}) = \sum_\nu \Lambda(\{\mathbf{R}_I\})\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_j\}) \tag{1.6}
$$

If we now insert this expansion into the full Schrödinger equation $\mathcal{H}\Psi = E\Psi$ and make use of the commutation rules, we find

$$
\mathcal{H}^e\Lambda_\nu\Phi_\nu = \Lambda_\nu\mathcal{H}^e\Phi_\nu = \Lambda_\nu E_\nu^e\Phi_\nu \tag{1.7}
$$

$$
V^{nn}\Lambda_\nu\Phi_\nu = \Lambda_\nu V^{nn}\Phi_\nu \tag{1.8}
$$

$$
T^n(\Lambda_\nu\Phi_\nu) = -\sum_{I=1}^{N_n}\frac{1}{2M_I}\left[\Lambda_\nu\nabla_{\mathbf{R}_I}^2\Phi_\nu + 2\nabla_{\mathbf{R}_I}\Lambda_\nu\nabla_{\mathbf{R}_I}\Phi_\nu + (\nabla_{\mathbf{R}_I}^2\Lambda_\nu)\Phi_\nu\right] \tag{1.9}
$$

By multiplying with an electronic state $\Phi_\mu$ from the left and integrate over all electronic coordinates, we then obtain for each state $\Phi_\mu$ the equation

$$
\begin{aligned}
\langle \Phi_\mu | \mathcal{H} | \Psi \rangle = E \left\langle \Phi_\mu \middle| \sum_\nu \Lambda_\nu \Phi_\nu \right\rangle &= E \Lambda_\mu \\
&= \left( E_\mu^e + T^e + V^{nn} \right) \Lambda_\mu \\
&- \sum_\nu \sum_{I=1}^{N_n} \frac{1}{M_I} \Big[ \underbrace{\langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\nu \rangle}_{} \Lambda_\nu + 2 \underbrace{\langle \Phi_\mu | \nabla_{\mathbf{R}_I} | \Phi_\nu \rangle}_{} \nabla_{\mathbf{R}_I} \Lambda_\nu \Big]
\end{aligned}
$$

$$\text{coupling of different electronic states}$$

The coupling term in the above equation arises from e.g. electron-lattice, electron-phonon or electron-vibron interactions. It is difficult to treat, but is of importance for a variety of interesting effects:

- Jahn-Teller and Peiers distortions

- superconductivity

- thermal conductivity

- phonon sidebands in spectroscopy

- polarons

- zero-point renormalizations

- …

## 1.1.2 The adiabatic approximation

*For each nuclear configuration $\{\mathbf{R}_I\}$ the electrons are in an eigenstate of $\mathcal{H}^e$, i.e. they react instantly and therefore do not "feel" the nuclear motion. As a consequence, the motion of the nuclei does not induce transitions between electronic states:*

$$
\langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\nu \rangle = \langle \Phi_\mu | \nabla_{\mathbf{R}_I} | \Phi_\nu \rangle = 0 \quad \forall \mu \neq \nu
$$

To judge the validity of this approximation and show that the diagonal elements can be neglected as well one can utilize first order perturbation theory to show that the first term gives no first-order contribution to the total energy. The second term has a non-vanishing contribution, but it scales with the mass ratio of the electrons and nuclei and is therefore several orders of magnitude smaller than the other terms and can be safely neglected. A detailed proof can be found in [1]. Neglecting the coupling terms, we arrive at

$$
\left( E_\mu^e + T^e + V^{nn} \right) \Lambda_\mu = E \Lambda_\mu \tag{1.10}
$$

which is the nuclear Schrödinger equation. Combining $T^e + V^{nn} = V_\mu^{BO}$ gives us the Born-Oppenheimer potential energy surface (PES) that the nuclei move in. To obtain the motion of the nuclei, we should solve their time-dependent Schrödinger equation

$$-i\frac{\partial \Lambda_\mu}{\partial t} \left(T^e + V_\mu^{BO}\right) \Lambda_\mu$$

but often it is sufficient to treat the nuclei classically and use Newton's equation of motion instead. In this approximation, the nuclei are always in their "ground state". Combining the nuclear ground state with the electronic one, we have

$$\Psi = \Psi^{BO} = \Lambda_0(\{\mathbf{R}_I\})\Phi_0(\{\mathbf{R}_I\}, \{\mathbf{r}_i\})$$

which yields the ground state energy:

$$E_0 = \left\langle \Psi^{BO}\big|\mathcal{H}\big|\Psi^{BO}\right\rangle = E_0^e + \left\langle \Lambda_0|T^n + V^{nn}|\Lambda_0\right\rangle$$

In general, the nuclear wave function is sharply peaked around the equilibrium position of the nuclei $\mathbf{R}_I^0$ and can be approximated by point charges.

$$E_0 = E_0^e + \underbrace{\sum_{I=1}^{N_n}\sum_{J>I}^{N_n}\frac{Z_I Z_J}{|\mathbf{R}_I^0 - \mathbf{R}_J^0|}}_{\text{classical electrostatic energy}} + \underbrace{\left\langle \Lambda_0\big|T^n + V^{nn}(\{\mathbf{R}_I^0 - \mathbf{R}_J^0\})\big|\Lambda_0\right\rangle}_{\text{quantum corrections}} \qquad (1.11)$$

The main aim of this lecture will be to find ways to calculate $E_0^e$.

## 1.2 What the electronic ground state energy reveals

Let us assume for a moment that we would know a reliable way to obtain $E_0^e$ in Equation 1.11, then what could we do with it?

### 1.2.1 Structure, lattice constant and elastic properties of perfect crystals

By computing $E_0^e$ for different polymorphs we can rank their stability by the energy per atom. By plotting the energy per atom as a function of the lattice constant (or volume for more complex structures), as done in Figure 1.1, we can determine several interesting properties of the crystal. First of all, we can determine the *equilibrium lattice constant* from the minimum of the so called equation of state. Another interesting property is the *cohesive energy* which is the difference between the equilibrium state and the dissociation limit and therefore measures how much energy can be released by the crystal formation. Also accessible from this curve is the *bulk modulus* $B_0$ which describes the dependence of the total energy as a function of the pressure.

$$B_0 = V \left.\frac{\partial^2 E(V)}{\partial V^2}\right|_{a=a_0} = \frac{1}{\kappa}$$
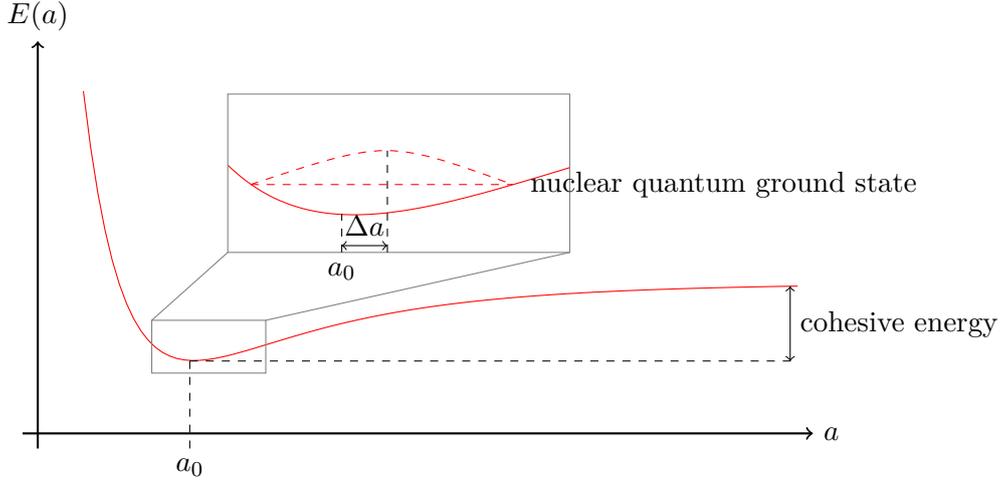
Figure 1.1: Equation of state for a simple cubic crystal

where $V$ is the volume and $\kappa$ denotes the compressibility. The quantum correction from Equation 1.11 gives rise to the *zero point energy*, which will correct the equilibrium lattice constant by an amount $\Delta a$, as shown in the inlay of the figure.

### 1.2.2 Forces, Equilibrium Geometries and Vibrations

Also if our system of interest is a molecule, small cluster or a more complicated crystal, we can determine its equilibrium geometry from electronic structure. Assuming a reasonable starting geometry, we can calculate the forces acting on the atoms as the negative gradient of the total energy with respect to the nuclear coordinates.

$$\mathbf{F}_I = -\frac{\partial}{\partial \mathbf{R}_I} E_0$$

$$\frac{\partial}{\partial \mathbf{R}_I} E_0 = \frac{\partial}{\partial \mathbf{R}_I} E_0^e + \frac{\partial}{\partial \mathbf{R}_I} \sum_{I=1}^{N_n} \sum_{J>I}^{N_n} \frac{Z_I Z_j}{\left| \mathbf{R}_I - \mathbf{R}'_J \right|} \tag{1.12}$$

The second term in Equation 1.12 can be solved analytically, but for the first term we in principle need gradients of the electronic structure. In practice, we can also approximate it using finite differences if analytic gradients are not available. By moving the atoms along their forces vectors and evaluating the new forces until they finally vanish and the structure converged to a stable state. From the equilibrium geometry we can also determine the (harmonic) vibrational frequencies by displacing the atoms by a small distance and computing the energy differences. These displacements correspond to snapshots of excited vibrational modes (or phonons in solids) and their energy follows from the energy difference relative to the starting point.

## 1.3 The Hydrogen Atom

The hydrogen atom is a special case of interest because it contains only one electron and has an analytic solution for the electronic problem. Since the solution of this problem is of relevance for us later on and we can use it to establish some notations, we will briefly review the problem here. The electronic Hamiltonian for the hydrogen atom is given in Equation 1.13, where we shifted the coordinate origin to the position of the nucleus and slightly generalized the problem by not fixing the nuclear charge $Z$ to 1.

$$\mathcal{H} = -\frac{\nabla_{\mathbf{r}}^2}{2} - \frac{Z}{|\mathbf{r}|} \tag{1.13}$$

Since this problem is spherically symmetric, we transform our coordinate system to spherical coordinates $x, y, z \to r, \varphi, \theta$. Under this transformation the Laplace operator transforms into

$$\nabla_{\mathbf{r}}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\underbrace{\left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \varphi^2}\right)}_{L^2} \tag{1.14}$$

In Equation 1.14 $L^2$ denotes the angular momentum operator, whose eigenfunctions are the well-known spherical harmonics $Y_{lm}(\varphi, \theta)$. Since the radial and the angular part in our Hamiltonian obviously separate under this transformation, we can now make the product ansatz $\Psi(r, \varphi, \theta) = R(r)Y_{lm}(\varphi, \theta)$ for our wave function. With $L^2 Y_{lm}(\varphi, \theta) = l(l+1)Y_{lm}(\varphi, \theta)$ our Schröedinger equation then has the form

$$\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} + \frac{Z}{r}\right]R(r) = ER(r) \tag{1.15}$$

To get rid of the linear derivative in Equation 1.15 we write $R(r) = \frac{1}{r}u(r)$ and obtain

$$\left[\frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2r^2} + \frac{Z}{r}\right]u(r) = Eu(r) \tag{1.16}$$

The solution to Equation 1.16 can be found in any basic textbook on quantum mechanics and because the derivation is rather tedious, we skip it here and simply present the result

$$R_{nl}(\mathbf{r}) = -\sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{Zr}{n}} \left(\frac{2Zr}{n}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{n}\right) \tag{1.17}$$

$$L_p^q(x) = \frac{d^q}{dx^q}L_p(x) \qquad\qquad L_p(x) = e^x \frac{d^p}{dx^p}e^{-x}x^p$$

where $L_p(x)$ are the *Laguerre Polynomials* and $L_p^q(x)$ are the *associated Laguerre Polynomials*. The energy eigenvalue is then given by $E_n = -\frac{Z}{2n^2}$. In Table 1.1 the functional shape of the radial component are shown for the lowest eigenstates of the hydrogen atom. Figure 1.2 shows the shape of the related spherical harmonics. In the case of the hydrogen atom, the total energy does not depend on the angular momentum quantum number $l, m$ and is therefore degenerate.

| $n$ | $l$ | $R_{nl}(r)$ |
|:---:|:---:|:---:|
| 1 "K-shell" | 0 "s-orbital" | $R_{10}(r)$ $r^2 R_{10}^2(r)$ $R_{10}(r) = 2Z^{\frac{3}{2}} e^{-Zr}$ 1.0 |
| 2 "L-shell" | 0 "s-orbital" | $R_{20}(r)$ $r^2 R_{20}^2(r)$ $R_{20}(r) = 2 \left(\frac{Z}{2}\right)^{\frac{3}{2}} \left(1 - \frac{Zr}{2}\right) e^{-\frac{Zr}{2}}$ 0.5 |
| 2 "L-shell" | 1 "p-orbital" | $R_{21}(r)$ $r^2 R_{21}(r)$ $R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2}\right)^{\frac{3}{2}} Zr e^{-Zr}$ 0.5 |
| 3 "M-shell" | 0 "s-orbital" | $R_{30}(r)$ $r^2 R_{30}^2(r)$ $R_{30}(r) = 2 \left(\frac{Z}{3}\right)^{\frac{3}{2}} \left(1 - \frac{2Zr}{3} + \frac{2(Zr)^2}{27}\right) e^{-\frac{Zr}{2}}$ 0.2 |
| 3 "M-shell" | 1 "p-orbital" | $R_{31}(r)$ $r^2 R_{31}^2(r)$ $R_{31}(r) = \frac{4\sqrt{2}}{3} \left(\frac{Z}{3}\right)^{\frac{3}{2}} Zr \left(1 - \frac{Zr}{6}\right) e^{-\frac{Zr}{3}}$ 0.2 |
| 3 "M-shell" | 2 "d-orbital" | $R_{32}(r)$ $r^2 R_{32}^2(r)$ $R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Z}{3}\right)^{\frac{3}{2}} (Zr)^2 e^{-\frac{Zr}{3}}$ 0.2 |
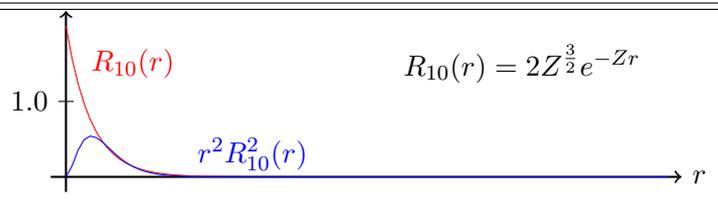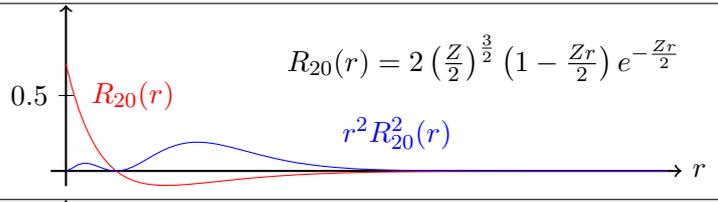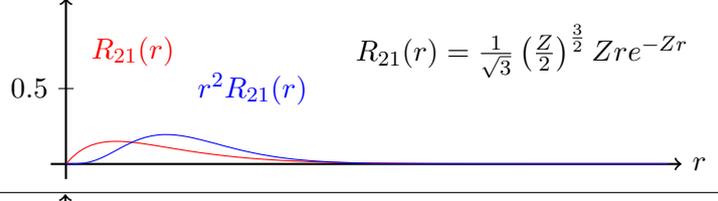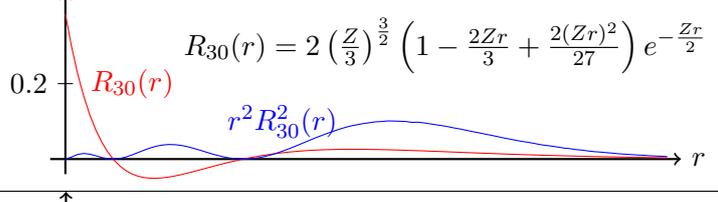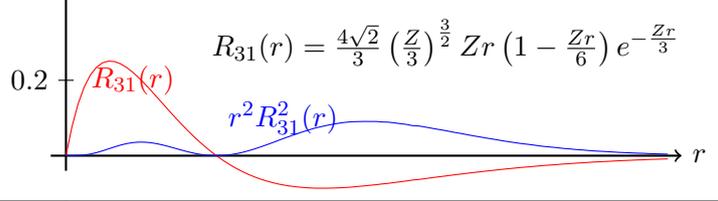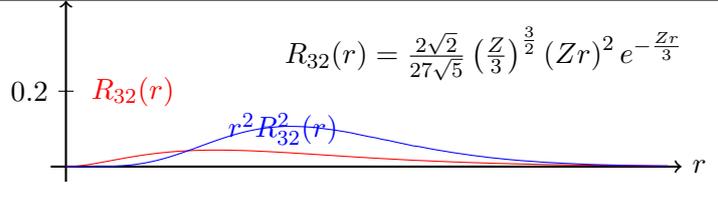
Table 1.1: Radial functions of hydrogen atom eigenstates
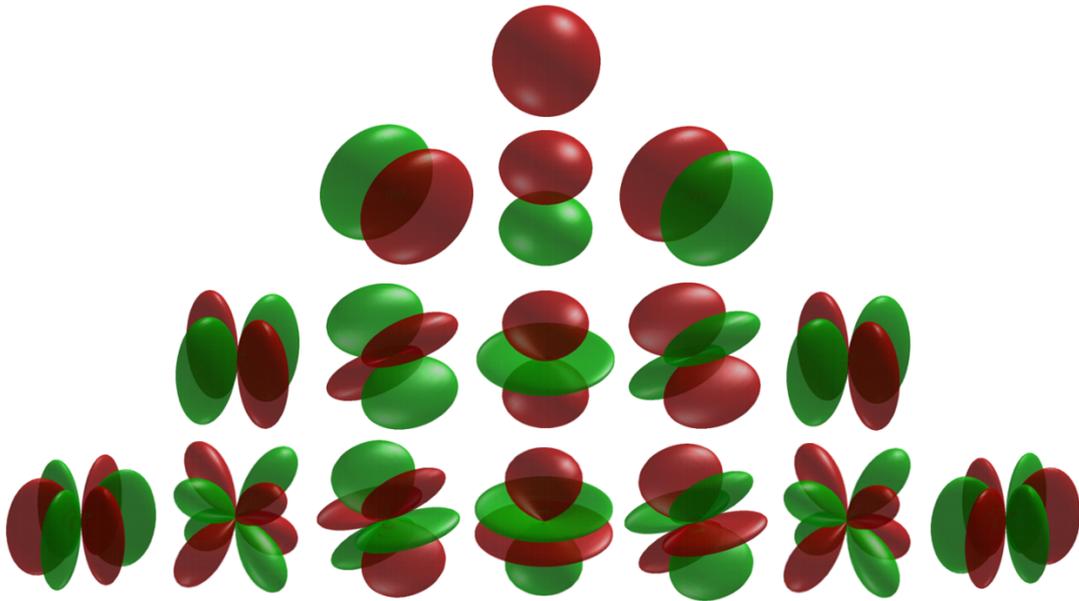
Figure 1.2: Shape of the spherical harmonics $Y_{lm}$, $l$ increases towards the bottom, and $m$ goes from $-l$ to $l$ from left to right. [2]
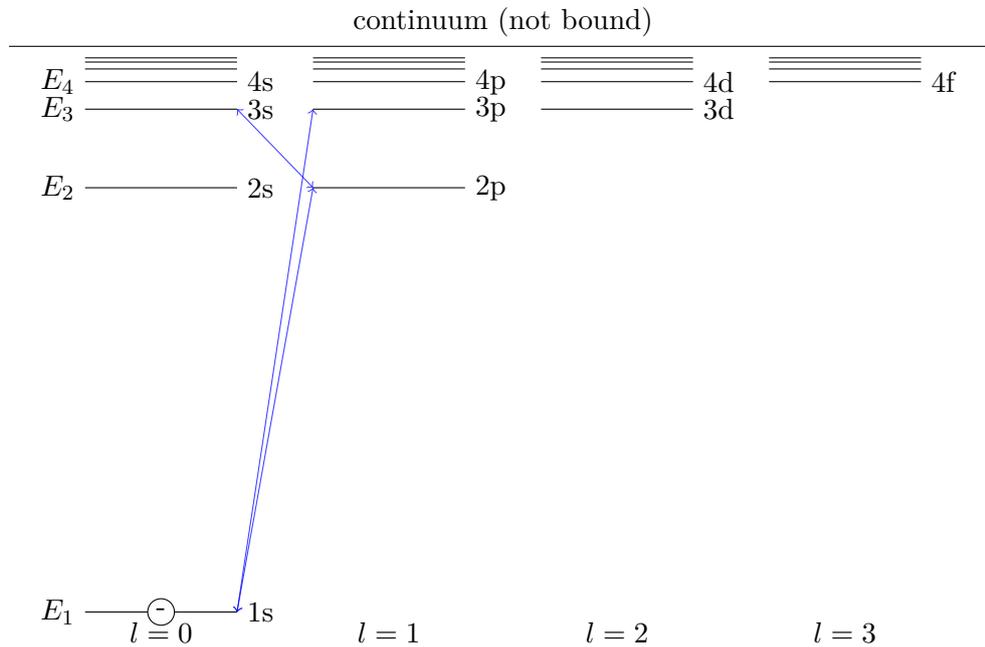


Figure 1.3: Energy hierarchy of the hydrogen eigenstates. The blue lines are examples for allowed dipole transitions into excited states.

[Figure 1.3](#) shows the energy hierarchy of the different eigenstates in the hydrogen atom. At $T = 0$ and the absence of external fields our electron will always be in the $1s$, which is the *electronic ground state*. All other eigenvalues refer to states that are not occupied by any electrons, they are called *excited states*. With excited states we have to be careful, because they depend on how the system is excited. In the present example the Hamiltonian conserves the particle number and so do our excitations, which are therefore called neutral excitations. The neutral transitions in the hydrogen atom can be induced by an electric field, such as light and lift the electron into a higher state, leaving a *hole* in the original state. Since the absorption of a photon involves the absorption of its angular momentum, vertical transitions are not allowed. Furthermore, we can also directly extract the energy the photon must have to stimulate a transition as

$$\omega_{nm} = E_m - E_n = 1Ry\left(-\frac{1}{m^2} + \frac{1}{n^2}\right)$$

## 1.4 Pauli Exclusion Principle and Antisymmetry

Electrons are fermions and therefore carry a spin $\sigma = \pm\frac{1}{2}$, to fully describe an electron we need its position $\mathbf{R}$ and $\sigma$. The Schrödinger Equation itself does not contain any spin-dependency. To include the spin, we therefore define spin functions for up and down spins.

$$\uparrow: \quad \alpha(\sigma) \qquad\qquad \downarrow: \quad \beta(\sigma)$$

For convience we make these spin orbitals orthonormal:

$$\int \alpha^*(\sigma)\alpha(\sigma)\,\mathrm{d}\sigma = \int \beta^*(\sigma)\beta(\sigma)\,\mathrm{d}\sigma = 1$$
$$\int \alpha^*(\sigma)\beta(\sigma)\,\mathrm{d}\sigma = \int \beta^*(\sigma)\alpha(\sigma)\,\mathrm{d}\sigma = 0$$

We can now combine the position of the electron and its spin into a generalized coordinate $\mathbf{x} = (\mathbf{r}, \sigma)$ and introduce the Pauli Principle "*No two fermions can occupy the same quantum state*" in more general way, the *antisymmetry* of the wave function:
*A many-electron wave function must be antisymmetric with respect to the interchange of the coordinates $\mathbf{x}$ of any two electrons.*

$$\Phi^e(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_{N_e}) = -\Phi^e(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_{N_e}) \tag{1.18}$$

A proper many-electron wave function must satisfy both the Schrödinger Equation and the Antisymmetry principle.

# 2 Wave Function based approaches

In this chapter we will introduce wave-function based approaches to solve the electronic Schrödinger equation discussed in the previous chapter. Let us start with our electronic Hamiltonian[1] $\mathcal{H}$ from Equation 1.4 and split it into several contributions.

$$\mathcal{H} = \underbrace{-\sum_{i=1}^{N} \frac{\nabla_{\mathbf{r}_i}^2}{2} + \overbrace{\sum_{i=1}^{N}\sum_{J=1}^{N_n} \frac{-Z_J}{|\mathbf{r}_i - \mathbf{R}_J|}}^{=\sum_i^N v_{\text{ext}}(\mathbf{r}_i)}}_{\sum_i^N h(\mathbf{r}_i)} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2.1}$$

First of all, we realize that the sum over nuclei in the second term is identical for all atoms and we can treat it as an external potential. The first two terms of the Hamiltonian then constitute a sum over single-particle Hamiltonians. Only the last term, which couples all electrons with each other, remains to make our live difficult.

## 2.1 Hartree Theory

If the coupling term in Equation 2.1 would not be present, we could solve the $N$ single-particle problems right away. Although it is obviously a bad approximation to neglect this term, let us assume for the moment that we have a non-interacting (NI) system.

$$\mathcal{H}^{NI} = \sum_{i=1}^{N} h(\mathbf{r}_i) \tag{2.2}$$

For each electron we define the spin orbital $\varphi(\mathbf{x})$ to be an eigenstate of the single-particle Hamiltonian $h(\mathbf{r})$ and orthonormal to all other orbitals.

$$\varphi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\sigma) & \text{Since the spin states are orthonormal,} \\ \text{or} & \text{we can use the same spatial orbital for} \\ \psi(\mathbf{r})\beta(\sigma) & \text{two states.} \end{cases}$$

$$h(\mathbf{r})\varphi_j(\mathbf{x}) = \epsilon_j \varphi_j(\mathbf{x})$$

---

[1]Since we are interested in the electronic problem only, we will drop the electronic indexes from now on to simplify the notation.

$$\delta_{ij} = \int \varphi_i(\mathbf{x})\varphi_j(\mathbf{x}) \, \mathrm{d}\mathbf{x}$$

Since all the $h(\mathbf{x}_i)$ in $\mathcal{H}^{NI}$ act on the single orbital dependent on $\mathbf{x}_i$ only, the eigenfunction of $\mathcal{H}$ is the product of all the single-particle spin orbitals and the corresponding eigenvalue is just the sum of their eigenvalues.

$$\Phi^{HP}(\{\mathbf{x}_i\}) = \varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2)\dots\varphi_k(\mathbf{x}_N)$$
$$E^{HP} = \epsilon_i + \epsilon_j + \dots + \epsilon_k$$

The wave function $\Phi^{HP}$is also called the Hartree product and is an example for an uncorrelated wave function, because the probability of finding electron 1 in a volume element $\mathrm{d}\mathbf{x}_1$ and electron 2 in $\mathrm{d}\mathbf{x}_2$ is simply the product of the individual probabilities.

$$|\varphi_i(\mathbf{x}_1)|^2 \, \mathrm{d}\mathbf{x}_1 \, |\varphi_j(\mathbf{x}_2)|^2 \, \mathrm{d}\mathbf{x}_2 \dots |\varphi_k(\mathbf{x}_N)|^2 \, \mathrm{d}\mathbf{x}_N$$

In other words, we have factorized our wave function.

$\Phi^{HP}$violates the antisymmetry principle, because it is obviously symmetric when we interchange any two electronic coordinates. For now, we will ignore this fact and use the Hartree product ansatz to solve the full electronic Schrödinger equation.

$$\mathcal{H}\Phi^{HP} = E\Phi^{HP}$$

As we will see, $\Phi^{HP}$is also an eigenstate of $\mathcal{H}$. We can now ask which functions $\varphi_i(\mathbf{x})$ minimize our energy $E$ and thus give us the ground state. Since we not only want to find the orbitals $\varphi_i(\mathbf{x})$ that minimize the energy, but also preserve their orthonormality, we need to perform a constrained minimization with a Lagrangian:

$$\mathcal{L}[\Phi] = E[\Phi] - \sum_{i=1}^{N}\sum_{j=1}^{N}\lambda_{ij}\left[\int \varphi_i^*(\mathbf{x})\varphi_j(\mathbf{x}) \, \mathrm{d}\mathbf{x} - \delta_{ij}\right] \tag{2.3}$$

$$= \frac{\langle\Phi|\mathcal{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} - \sum_{i=1}^{N}\sum_{j=1}^{N}\lambda_{ij}\left[\int \varphi_i^*(\mathbf{x})\varphi_j(\mathbf{x}) \, \mathrm{d}\mathbf{x} - \delta_{ij}\right] \tag{2.4}$$

where $\lambda_{ij}$ are the Lagrange multipliers. Since our orbitals are orthonormal by condition, we can also further simplify the energy term to $\langle\Phi|\mathcal{H}|\Phi\rangle$. We also know already that

$$\langle\Phi^{HP}|h(\mathbf{r}_i)|\Phi^{HP}\rangle = \langle\varphi_i|h(\mathbf{r}_i)|\varphi_i\rangle \tag{2.5}$$

and for the coulomb potential we find

$$\left\langle\Phi^{HP}\left|\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right|\Phi^{HP}\right\rangle = \int\dots\int \varphi_n^*(\mathbf{x}_1)\dots\varphi_k^*(\mathbf{x}_N)$$
$$\times \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\varphi_n(\mathbf{x}_1)\dots\varphi_k(\mathbf{x}_N) \, \mathrm{d}\mathbf{x}_1\dots\,\mathrm{d}\mathbf{x}_N$$

$$= \iint \frac{\varphi_l^*(\mathbf{x}_i)\varphi_m^*(\mathbf{x}_j)\varphi_l(\mathbf{x}_i)\varphi_m(\mathbf{x}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} \, \mathrm{d}\mathbf{x}_i \, \mathrm{d}\mathbf{x}_j$$

where integrated out all other electronic coordinates and only the orbitals $l$ and $m$ occupied by the $i$th and $j$th atom remain. With this knowledge, we can now rewrite our Lagrangian as

$$\mathcal{L}[\Phi] = \sum_{i=1}^{N} \int \varphi_i^*(\mathbf{x})h(\mathbf{x})\varphi_i(\mathbf{x}) \, \mathrm{d}\mathbf{x} + \sum_{i=1}^{N}\sum_{j>i}^{N} \iint \frac{\varphi_i^*(\mathbf{x})\varphi_j^*(\mathbf{x}')\varphi_i(\mathbf{x})\varphi_j(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{x}'$$

$$- \sum_{i=1}^{N}\sum_{j=1}^{N} \lambda_{ij} \left[ \int \varphi_i^*(\mathbf{x})\varphi_j(\mathbf{x}) \, \mathrm{d}\mathbf{x} - \delta_{ij} \right] \tag{2.6}$$

where we changed the notation such, that $\varphi_i(\mathbf{x})$ now denotes the orbital of the $i$th electron. In the next step, we can now perform the variation with respect to $\varphi_i^*$. In principle, we also need to vary with respect to the Lagrange multipliers $\lambda_{ij}$, but we will skip this part.

$$\frac{\delta\mathcal{L}}{\delta\varphi_i^*} = 0 \quad \forall i \in [1 \ldots N]$$

$$= h(\mathbf{x})\varphi_i(\mathbf{x}) + \underbrace{\sum_{j\neq i}^{N} \int \frac{\varphi_j^*(\mathbf{x}')\varphi_j(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{x} \, \varphi_i(\mathbf{x})}_{\parallel} - \sum_{j=1}^{N} \lambda_{ij}\varphi_j(\mathbf{x})$$

$$\sum_{j=1}^{N} \int \frac{\varphi_j^*(\mathbf{x}')\varphi_j(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{x} \, \varphi_i(\mathbf{x}) - \int \frac{\varphi_i^*(\mathbf{x}')\varphi_i(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{x} \, \varphi_i(\mathbf{x})$$

By introducing the density of non-interacting electrons $n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi(\mathbf{r})|^2$ and integrating out the spin variables, we can rewrite the integral term as

$$\underbrace{\int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}}_{=V_H(\mathbf{r})} \varphi_i(\mathbf{r}) - \int \frac{\varphi_i^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \varphi_i(\mathbf{r}) \tag{2.7}$$

where $V_H(\mathbf{r})$ denotes the Hartree potential, which is simply the electrostatic potential generated by a charge distribution. Putting all together, the minimization of the Lagrangian finally yields the following set of equations

$$[h(\mathbf{r}) + V_H(\mathbf{r})]\varphi_i(\mathbf{x}) - \int \frac{|\varphi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \varphi_i(\mathbf{r}) = \sum_{j=1}^{N} \lambda_{ij}\varphi_j(\mathbf{x}) \tag{2.8}$$

which are known as the Hartree equations. It should be noted that although we included the spin in our considerations, nothing in the equation depends on the spin. Since each

$$V_H(\mathbf{r}) = \frac{1}{r}\left(1 - (1 + r)e^{(} - 2r)\right)$$
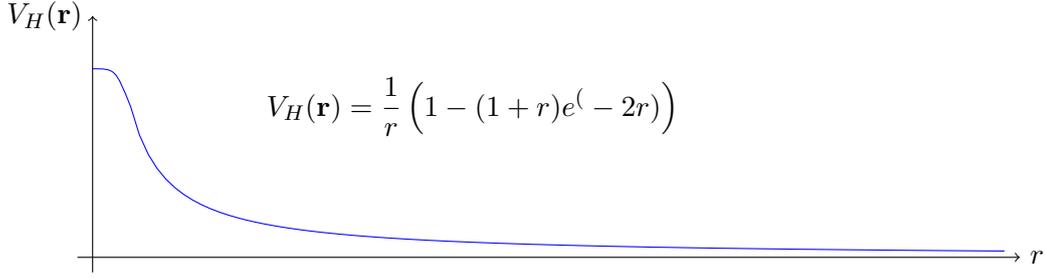
Figure 2.1: Hartree potential for the hydrogen 1s orbital

$\varphi_i(\mathbf{r})$ holds one electron, these equations are also called single particle equations. In the presented form all equations are directly coupled, but this problem can be solved by a suitable orbital transformation which diagonalizes the matrix defined by the $\lambda_i j$, as shown in [3].

One important thing to note is that the Hartree potential appearing in the equations depends on the orbitals via the electron density. Therefore, the Hartree equations need to be solved self-consistently. Also, the Hartree-term induces a self-interaction error because it includes a sum over all electrons. This error is canceled exactly by the orbital dependent term.

The Hartree potential is the classic electrostatic potential of a charge distribution. It is positive and therefore repulsive, keeping the electrons apart from each other, as one would expect. For the hydrogen $\varphi_{1s}(\mathbf{r})$ orbital, the Hartree potential is depicted in Figure 2.1. The Hartree potential largely counteracts the external potential:

$$-\sum_{i=1}^{N}\sum_{J=1}^{N_n}\frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} = -\sum_{i=1}^{N}\int\frac{n_n(\mathbf{R})}{|\mathbf{r}_i - \mathbf{R}|}\,\mathrm{d}\mathbf{R} \tag{2.9}$$

If we now relabel the integration variable, we can merge the external and the Hartree-potential into one term, denoting the total charge density as $\Delta n(\mathbf{r})$.

$$V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) = \int\frac{n(\mathbf{r}) - n_n(\mathbf{r})}{|\mathbf{r}_i - \mathbf{r}|}\,\mathrm{d}\mathbf{r} = \int\frac{\Delta n(\mathbf{r})}{|\mathbf{r}_i - \mathbf{r}|}\,\mathrm{d}\mathbf{r} \tag{2.10}$$

Finally, we can compute the total energy of the Hartree-Product.

$$
\begin{aligned}
E^{HP} &= \left\langle \Phi^{HP}\middle|\mathcal{H}\middle|\Phi^{HP}\right\rangle \\
&= \sum_{i=1}^{N}\int\varphi_i^*(\mathbf{x})h(\mathbf{x})\varphi_i(\mathbf{x})\,\mathrm{d}\mathbf{x} + \frac{1}{2}\sum_{i,j=1}^{N}\iint\frac{\varphi_i^*(\mathbf{x}')\varphi_j^*(\mathbf{x}')\varphi_i(\mathbf{x})\varphi_j(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}' \\
&= \underbrace{\sum_{i=1}^{N}\int\varphi_i^*(\mathbf{x})\nabla_i^2\varphi_i(\mathbf{x})\,\mathrm{d}\mathbf{x}}_{\text{kinetic energy of the electrons}} + \underbrace{\frac{1}{2}\iint\frac{\Delta n(\mathbf{r})\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'}_{\text{electrostatic energy of charge distribution}} \tag{2.11}
\end{aligned}
$$

As it can be seen from the total energy given in Equation 2.11, the only quantum contribution is the kinetic energy of the electrons, more complex electron-electron interactions are not included.

## 2.2 Hartree-Fock Theory

In the previous section we showed that the Hartree-product $\Phi^{HP}$ is not a good approximation to the real wave function because it violates the antisymmetry principle. We will now show how we can construct a wave function which obeys this principle based on the Hartree-product.

Consider (for simplicity) a two electron system, like the hydrogen molecule, where we have two possible $\Phi^{HP}$:

$$\Phi^{HP}_{12}(\mathbf{x}_1, \mathbf{x}_2) = \varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2)$$
$$\Phi^{HP}_{21}(\mathbf{x}_1, \mathbf{x}_2) = \varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1)$$

These two products can be combined into a new wave function, which obeys the antisymmetry principle.

$$\Phi = \frac{1}{\sqrt{2}}\left[\Phi^{HP}_{12} - \Phi^{HP}_{21}\right] = \frac{1}{\sqrt{2}}\left[\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2) - \varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1)\right] \tag{2.12}$$

This wave function can also be written as a determinant:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_i(\mathbf{x}_1) & \varphi_j(\mathbf{x}_1) \\ \varphi_i(\mathbf{x}_2) & \varphi_j(\mathbf{x}_2) \end{vmatrix} \downarrow \text{electrons} \tag{2.13}$$
$$\longrightarrow \text{orbitals}$$

The determinant Equation 2.13 is called "Slater determinant" $\Phi^{SD}$ and can be generalized to an arbitrary number of electrons.

$$\Phi^{SD}(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N) = \frac{1}{\sqrt{N}}\begin{vmatrix} \varphi_i(\mathbf{x}_1) & \varphi_j(\mathbf{x}_1) & \cdots & \varphi_k(\mathbf{x}_1) \\ \varphi_i(\mathbf{x}_2) & \varphi_j(\mathbf{x}_2) & \cdots & \varphi_k(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_i(\mathbf{x}_N) & \varphi_j(\mathbf{x}_N) & \cdots & \varphi_k(\mathbf{x}_N) \end{vmatrix} \downarrow \text{electrons}$$
$$\longrightarrow \text{orbitals}$$

We can now approximate our real wave function by a single Slater determinant and use the variational principle to determine the spin orbitals that minimize the ground state energy. For the construction of the Lagrangian we first need the energy of a $\Phi^{SD}$:

$$E^{SD} = \frac{\langle\Phi^{SD}|\mathcal{H}|\Phi^{SD}\rangle}{\langle\Phi^{SD}|\Phi^{SD}\rangle} \tag{2.14}$$

which reduces to $\langle\Phi^{SD}|\mathcal{H}|\Phi^{SD}\rangle$ because we normalize our wave function. Again we can split the energy in two contributions $T^e + V^{en}$ and $V^{ee}$. The following derivation can be generalized to an arbitrary number of electrons, but for simplicity we will consider only two electrons.

$$
\begin{aligned}
\langle\Phi^{SD}|h(\mathbf{r}_1)|\Phi^{SD}\rangle &= \iint \left[\varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2) - \varphi_i^*(\mathbf{x}_2)\varphi_j^*(\mathbf{x}_1)\right]h(\mathbf{r}_1) \\
&\quad \times \left[\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2) - \varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1)\right] \, \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \qquad (2.15)
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}\iint \Big[\varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2)h(\mathbf{r}_1)\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2) \\
&\quad - \varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2)h(\mathbf{r}_1)\varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1) \\
&\quad - \varphi_i^*(\mathbf{x}_2)\varphi_j^*(\mathbf{x}_1)h(\mathbf{r}_1)\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2) \\
&\quad + \varphi_i^*(\mathbf{x}_2)\varphi_j^*(\mathbf{x}_1)h(\mathbf{r}_1)\varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1)\Big] \, \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \qquad (2.16)
\end{aligned}
$$

In Equation 2.16 we have the single-particle Hamiltonian $h(\mathbf{r}_1)$ which only depends on the first electron's position. Therefore, we can directly integrate over the second electronic coordinate $\mathbf{x}_2$. If we impose orthonormality as we did before for the Hartree-theory, the negative terms in the equation reduce to zero.

$$
\langle\Phi^{SD}|h(\mathbf{r}_1)|\Phi^{SD}\rangle = \frac{1}{2}\int \left[\varphi_i^*(\mathbf{x}_1)h(\mathbf{r}_1)\varphi_i(\mathbf{x}_1) + \varphi_j^*(\mathbf{x}_1)h(\mathbf{r}_1)\varphi_j(\mathbf{x}_1)\right] \, \mathrm{d}\mathbf{x}_1 \qquad (2.17)
$$

For $h(\mathbf{r}_2)$ we obtain an identical result and therefore we can write the final result as (generalized to N particles):

$$
\left\langle\Phi^{SD}\left|\sum_{i=1}^{N} h(\mathbf{r}_i)\right|\Phi^{SD}\right\rangle = \sum_{i=1}^{N} \langle\varphi_i|h(\mathbf{r})|\varphi_i\rangle \qquad (2.18)
$$

This is the same result as we obtained in the Hartree theory, as can be seen from a comparison with Equation 2.6. Let us continue with the evaluation of the Coulomb operator in the two-electron case:

$$
\begin{aligned}
\left\langle\Phi^{SD}\left|\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right|\Phi^{SD}\right\rangle &= \frac{1}{2}\iint \Big[\varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2) \\
&\quad - \varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1) \\
&\quad - \varphi_i^*(\mathbf{x}_2)\varphi_j^*(\mathbf{x}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2) \\
&\quad + \varphi_i^*(\mathbf{x}_2)\varphi_j^*(\mathbf{x}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1)\Big] \, \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 \qquad (2.19)
\end{aligned}
$$

Equation 2.19 has the same structure as the single-particle contribution, but because the Coulomb operator depends on both electronic coordinates we cannot integrate out

anything in this case. To shorten the notation, we now introduce the two-electron or Coulomb integrals:

$$\langle ij|kl\rangle = \iint \varphi_i^*(\mathbf{x})\varphi_j^*(\mathbf{x})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\varphi_k(\mathbf{x})\varphi_l(\mathbf{x}') \tag{2.20}$$

With Equation 2.20 we can rewrite the Coulomb matrix element as

$$\left\langle \Phi^{SD}\left|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right|\Phi^{SD}\right\rangle = \frac{1}{2}\Big[\langle ij|ij\rangle + \langle ij|ji\rangle\Big] - \frac{1}{2}\Big[\langle ji|ji\rangle + \langle ji|ij\rangle\Big]$$
$$= \langle ij|ij\rangle - \langle ij|ji\rangle \tag{2.21}$$

For the general N-electron case we have:

$$V^{ee} = \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} \tag{2.22}$$

Each term in this sum will pick out the two orbitals that these two electrons are occupying, let us call them $m$ and $n$.

$$\left\langle \Phi^{SD}\big|V^{ee}\big|\Phi^{SD}\right\rangle = \frac{1}{2}\sum_{m}^{N}\sum_{n\neq m}^{N}\langle mn|mn\rangle - \langle mn|nm\rangle \tag{2.23}$$

As we will see, the first term in Equation 2.23 will again give rise to the Hartree potential energy. The second term however is new. We can now write down the total energy of a single Slater determinant:

$$\left\langle \Phi^{SD}\big|\mathcal{H}\big|\Phi^{SD}\right\rangle = \sum_{n}^{N}\langle n|h|n\rangle + \frac{1}{2}\sum_{n}^{N}\sum_{m\neq n}^{N}\langle mn|mn\rangle - \langle mn|nm\rangle \tag{2.24}$$

From Equation 2.24 we can make an important observation: Although we have a many-electron wave function and a many-electron Hamiltonian, we can write the energy of $\Phi^{SD}$in terms of one- and two-electrons integrals only! This is of course a consequence of the fact that the Hamiltonian is composed from one- and two-electron operators. The fact that such a "complicated" wave function gives a relatively simple energy expression is one of the foundations of Quantum chemistry.

Now we can finally write down our Lagrangian and minimize it to obtain the ground state orbitals.

$$\mathcal{L}[\Phi^{SD}] = E[\Phi^{SD}] - \sum_{n}^{N}\sum_{m}^{N}\lambda_{nm}\left[\int \varphi_n^*(\mathbf{x})\varphi_m(\mathbf{x})\,\mathrm{d}\mathbf{x} - \delta_{nm}\right] \tag{2.25}$$

$$= \sum_{n}^{N}\int \varphi_n^*(\mathbf{x})h(\mathbf{r})\varphi_n(\mathbf{x}) - \sum_{n}^{N}\sum_{m}^{N}\lambda_{nm}\left[\int \varphi_n^*(\mathbf{x})\varphi_m(\mathbf{x})\,\mathrm{d}\mathbf{x} - \delta_{nm}\right] \tag{2.26}$$

$$+ \frac{1}{2} \sum_n^N \sum_{m \neq n}^N \iint \left[ \frac{\varphi_m^*(\mathbf{x})\varphi_n^*(\mathbf{x})\varphi_m(\mathbf{x})\varphi_n(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \right.$$
$$\left. - \frac{\varphi_m^*(\mathbf{x})\varphi_n^*(\mathbf{x})\varphi_n(\mathbf{x})\varphi_m(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \right] \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{x}' \tag{2.27}$$

In analogy to the Hartree theory, we now require $\frac{\delta \mathcal{L}}{\delta \varphi_n^*} = 0 \quad \forall m$ and find:

$$\sum_m^N \lambda_{nm} \varphi_m(\mathbf{x}) = h(\mathbf{r})\varphi_n(\mathbf{x}) + \sum_{m \neq n}^N \int \left[ \frac{\varphi_m^*(\mathbf{x}')\varphi_m(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_n(\mathbf{x}) - \frac{\varphi_m^*(\mathbf{x}')\varphi_m(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} \varphi_n(\mathbf{x}') \right] \, \mathrm{d}\mathbf{x}'$$

The first term in the right hand side sum is exactly equal to the one from Hartree theory (see Equation 2.7), so we can rewrite it in terms of the Hartree potential and the self-interaction correction.

$$\sum_m^N \lambda_{nm} \varphi_m(\mathbf{x}) = \left[ h(\mathbf{r}) + V_H(\mathbf{r}) \right] \varphi_n(\mathbf{x}) - \sum_m^N \int \frac{\varphi_m^*(\mathbf{x}')\varphi_m(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} \varphi_n(\mathbf{x}') \, \mathrm{d}\mathbf{x}'$$

By defining the density matrix as Equation 2.28, we can rewrite the last sum as a nonlocal potential $\Sigma^{HF}(\mathbf{x}, \mathbf{x}')$.

$$n(\mathbf{x}, \mathbf{x}') = \sum_n^N \varphi_n(\mathbf{x})\varphi_n^*(\mathbf{x}') \tag{2.28}$$

$$\Sigma^{HF}(\mathbf{x}, \mathbf{x}') = \frac{n(\mathbf{x}, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \tag{2.29}$$

Now, we can finally write the obtained set of equations as

$$\left[ h(\mathbf{r}) + V_H(\mathbf{r}) \right] \varphi_n(\mathbf{x}) - \int \Sigma^{HF}(\mathbf{x}, \mathbf{x}')\varphi_n(\mathbf{x}') \, \mathrm{d}\mathbf{x}' = \sum_m^N \lambda_{nm} \varphi_m(\mathbf{x})$$

$$h(\mathbf{r})\varphi_n(\mathbf{x}) - \int \underbrace{V^{HF}(\mathbf{x}, \mathbf{x}')}_{=V_H(\mathbf{r})+\Sigma^{HF}} \varphi_n(\mathbf{x}') \, \mathrm{d}\mathbf{x}' = \sum_m^N \lambda_{nm} \varphi_m(\mathbf{x})$$

By transforming the orbitals, as described in [3], we reach the canonical form:

$$h(\mathbf{r})\varphi_n(\mathbf{x}) - \int \underbrace{V^{HF}(\mathbf{x}, \mathbf{x}')}_{=V_H(\mathbf{r})+\Sigma^{HF}} \varphi_n(\mathbf{x}') \, \mathrm{d}\mathbf{x}' = \lambda_n \varphi_n(\mathbf{x}) \tag{2.30}$$

In Equation 2.30, $h(\mathbf{r})$ is the orbital-independent part, while $V^{HF}$ depends on the orbitals. As for the Hartree theory, we therefore need to solve these equations self-consistently.
$\hat{f} = \hat{h} + \hat{V}^{HF}$ is then called the Fock operator and is an effective one-particle operator.
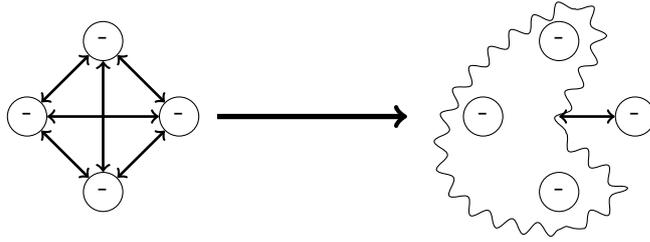
Figure 2.2: schematic representation of the mean-field approach

It replaces the many-body Schrödinger equation by a set of one-particle equations, in which each electron moves in an effective field, often also called mean-field. The mean-field is the same for all electrons. It is an important concept, because it allows us to separate the many-body problem into one-electron problems, as depicted in Figure 2.2. The mean-field also introduces the concept of one-electron wave functions or orbitals $\varphi_n(\mathbf{x})$. In the many-body wave function $\Phi(\{\mathbf{x}_i\})$ we cannot identify a single electron. In the mean-field formulation the wave function of a given electron has no explicit dependence on the position of all other electrons. The dependence is only implicit via the $V^{HF}$ and the complexity of the problem therefore reduces to finding the mean-field potential.

## 2.3 Closed-Shell Hartree-Fock and the meaning of exchange

Let us consider a system with an even number of electrons and the following scenario:



The spatial orbitals $\Psi_i$ are restricted to be the same same for spin $\uparrow$ and $\downarrow$. This is called "Restricted Hartree-Fock". As a consequence of this assumption we can pair up orbitals:

$$\varphi_1(\mathbf{x}) = \Psi_1(\mathbf{r})\alpha(\sigma) = \Psi_1(\mathbf{x})$$
$$\varphi_2(\mathbf{x}) = \Psi_1(\mathbf{r})\beta(\sigma) = \bar{\Psi}_1(\mathbf{x})$$

Our Slater determinant, initially a function of $\varphi_1, \varphi_2, \ldots \varphi_N$, now is a Slater determinant of the functions $\Psi_1, \bar{\Psi}_1, \Psi_2, \bar{\Psi}_2, \ldots, \Psi_{N/2}, \bar{\Psi}_{N/2}$ and the energy expression (Equation 2.24) becomes:

$$E[\Phi^{SD}] = \sum_n^{N/2} \langle n|h|n \rangle + \sum_n^{N/2} \langle \bar{n}|h|\bar{n} \rangle + \frac{1}{2}\sum_n^{N}\sum_m^{N} \langle mn|mn \rangle - \langle mn|nm \rangle \qquad (2.31)$$

If we write out the summands in the two single-particle sums, we find that the spin variable integrates out and they are equal.

$$\langle n|h|n\rangle \overset{?}{=} \langle \bar{n}|h|\bar{n}\rangle$$

$$\iint \Psi_n^*(\mathbf{r})\alpha(\sigma)h(\mathbf{r})\Psi_n(\mathbf{r})\alpha(\sigma)\,\mathrm{d}\mathbf{r}\,\mathrm{d}\sigma \overset{?}{=} \iint \Psi_n^*(\mathbf{r})\beta(\sigma)h(\mathbf{r})\Psi_n(\mathbf{r})\beta(\sigma)\,\mathrm{d}\mathbf{r}\,\mathrm{d}\sigma$$

$$\int \Psi_n^*(\mathbf{r})h(\mathbf{r})\Psi_n(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int \Psi_n^*(\mathbf{r})h(\mathbf{r})\Psi_n(\mathbf{r})\,\mathrm{d}\mathbf{r} = (n|h|n)$$

To rewrite the double sum in terms of these orbitals as well, we first need to rewrite the orbital products.

$$\sum_{nm}^{N} = \varphi_n\varphi_m = \sum_n^{N/2}(\varphi_n + \bar{\varphi}_n)\sum_m^{N/2}(\varphi_m + \bar{\varphi}_m)$$

$$= \sum_{nm}^{N/2}(\varphi_n\varphi_m + \varphi_n\bar{\varphi}_m + \bar{\varphi}_n\varphi_m + \bar{\varphi}_n\bar{\varphi}_m)$$

This will yield a total of 16 different terms in the two-electron integrals. Fortunately, we know that the coulomb-operator is spin-independent and we can integrate out the spin. As a consequence, only those product terms will be non-zero where the spin functions for $\mathbf{x}$ and $\mathbf{x}'$ are the same.

$$\Rightarrow E[\Phi^{SD}] = 2\sum_n^{N/2}(n|h|n) + \frac{1}{2}\sum_{nm}^{N/2}\bigg[\langle mn|mn\rangle - \langle nm|mn\rangle$$

$$+ \langle n\bar{m}|n\bar{m}\rangle + \langle \bar{n}m|\bar{n}m\rangle + \langle \bar{n}\bar{m}|\bar{n}\bar{m}\rangle - \langle \bar{n}\bar{m}|\bar{m}\bar{n}\rangle\bigg]$$

$$= 2\sum_n^{N/2}(n|h|n) + \sum_{nm}^{N/2}\bigg[2\underbrace{(mn|mn)}_{=J_{nm}} - \underbrace{(nm|mn)}_{=K_{nm}}\bigg] \tag{2.32}$$

$$(mn|kl) = \iint \frac{\Psi_m^*(\mathbf{r})\Psi_n^*(\mathbf{r}')\Psi_k(\mathbf{r})\Psi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

As one can see from the definition of the spatial two-electron integrals $(mn|mn)$, the $J_{nm}$ in Equation 2.32 is nothing else than the classic coulomb repulsion between the two charge distributions $|\Psi_n(\mathbf{r})|^2$ and $|\Psi_m(\mathbf{r})|^2$. The exchange integral $K_{nm}$ on the other hand has no classical analog! It arises from the antisymmetry principle requirement on the wave function, the fact that we can exchange two particles in the wave function and only change the sign. That is why this term is called *exchange*.

## 2.4 Hartree-Fock in a basis

If we consider a closed-shell system and integrate out the spin dependence in Equation 2.30, we obtain

$$\hat{f}(\mathbf{r})\Psi_m(\mathbf{r}) = \epsilon_m \Psi_m(\mathbf{r})$$

$$\hat{f} = h(\mathbf{r}) + V_H(\mathbf{r}) + \int \mathrm{d}\mathbf{r}' \Sigma^{HF}(\mathbf{r}, \mathbf{r}')$$

where we relabeled our $\lambda_m$ as $\epsilon_m$. The kinetic energy operator can be written as a high order finite difference expansion on a grid.
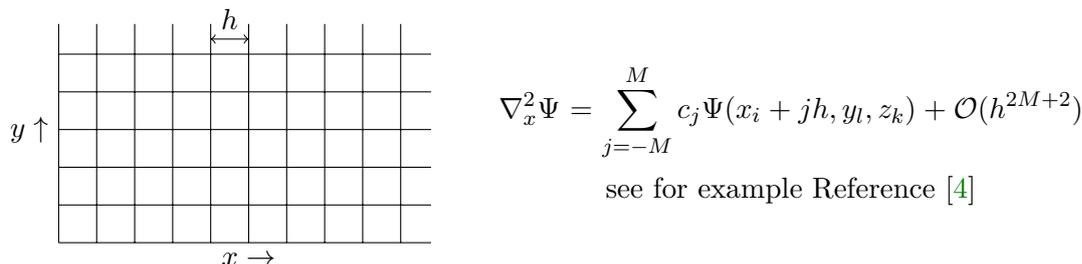


$$\nabla_x^2 \Psi = \sum_{j=-M}^{M} c_j \Psi(x_i + jh, y_l, z_k) + \mathcal{O}(h^{2M+2})$$

see for example Reference [4]

For the other terms a suitable quadrature can be found. This ansatz then allows to solve the HF equations on a grid. However, the problem are the core states, as depicted in Figure 2.3. To represent these states and their rapid decay/oscillations accurately we
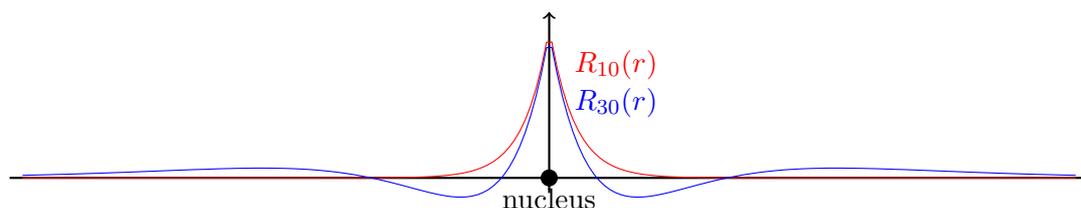


Figure 2.3: Wave function shape near the nucleus.

need a high grid point density close to the nuclei. To describe a molecule, we cannot afford the density of points near the nuclei throughout all space. There are several possible solutions to this problem:

**Adaptive Grids** : These grids have different spacings in different regions. While this approach is in principle feasible, it is quite cumbersome to implement.

**Pseudopotentials** : For many applications the valence electrons are the important part of the system, while the core electrons only have a minor impact on the property of interest. The core electrons are then no longer considered explicitly, but instead they form a pseudo-core with the nucleus, which gives rise to the pseudopotential. This potential is smooth and finite at the nucles and therefore generates a smooth

pseudo-wavefunction. This approach is very popular, but more often than not the core region is important.

**Basis Sets** : Introduce a basis that builds rapid oscillations into the basis functions, e.g. orbitals of free atoms.

We will only discuss the third approach in detail. Without specifying the type of basis functions yet, we introduce a set of $K$-many basis functions $\{\phi_m u(\mathbf{r}), mu = 1, \ldots K\}$. The Hartree-Fock can then be expanded in this basis:

$$\Psi_i(\mathbf{r}) = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu(\mathbf{r}) \tag{2.33}$$

If we would use a complete basis for this expansion, this expression would be exact. However, in practice the basis is usually not complete. By inserting the expansion into the HF equations, we obtain:

$$\int F(\mathbf{r}, \mathbf{r}') \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu(\mathbf{r}') \, \mathrm{d}\mathbf{r}' = \epsilon_i \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu(\mathbf{r}) \tag{2.34}$$

Now we multiply this equation with $\phi_\nu(\mathbf{r})$ from the left and integrate over $\mathbf{r}$.

$$\sum_{\mu=1}^{K} C_{\mu i} \underbrace{\iint \phi_\nu(\mathbf{r}) F(\mathbf{r}, \mathbf{r}') \phi_\mu(\mathbf{r}') \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'}_{=F_{\nu,\mu}} = \epsilon_i \sum_{\mu=1}^{K} C_{\mu i} \underbrace{\int \phi_\nu(\mathbf{r}) \phi_\mu(\mathbf{r}) \, \mathrm{d}\mathbf{r}}_{=S_{\nu,\mu}} \tag{2.35}$$

$F_{\nu,\mu}$ here denotes a matrix element of the "Fock matrix" and $S_{\nu,\mu}$ are the elements of the of the "overlap matrix". With this expansion in a basis set we have transformed the HF equation for a single particle state into a set of equations for the expansions coefficients. This can be written in a compact matrix form

$$\mathbf{FC} = \mathbf{SCE} \tag{2.36}$$

where all matrices have dimension $K \times K$ and and $\mathbf{E}$ is a diagonal matrix containing the HF eigenvalues. Note that this equation will only gives us as many eigenvalues as we have basis functions in our expansion. Therefore, $K$-many basis functions can expand at most $K$-many single particle states. Equation 2.36 is called the Roothaan-equation and a central quantity for quantum chemistry. To solve it, all that is left to do is to express $F_{\nu,\mu}$ explicitly in our basis.

$$F(\mathbf{r}, \mathbf{r}') = \left[ h(\mathbf{r}) + V_H(\mathbf{r}) \right] \delta(\mathbf{r} - \mathbf{r}') + \Sigma(\mathbf{r}, \mathbf{r}')$$

We do not want to set up $F(\mathbf{r}, \mathbf{r}')$ on a grid first to obtain the matrix elements from integration. To express the Fock matrix elements in terms of the basis functions, let us start with the electronic density:

$$
\begin{aligned}
n(\mathbf{r}) &= 2\sum_{i=1}^{N/2} |\Psi_i(\mathbf{r})|^2 = 2\sum_{i=1}^{N/2} \Psi_i(\mathbf{r})^* \Psi_i(\mathbf{r}) \\
&= 2\sum_{i=1}^{N/2} \left(\sum_{\nu=1}^{K} C_{\nu i}^* \phi_\nu^*(\mathbf{r})\right) \left(\sum_{\mu=1}^{K} C_{\mu i} \phi_\mu(\mathbf{r})\right) \\
&= \sum_{\nu,\mu=1}^{K} 2\underbrace{\sum_{i=1}^{N/2} C_{\nu i}^* C_{\mu i}}_{=P_{\mu,\nu}} \phi_\nu^*(\mathbf{r})\phi_\mu^*(\mathbf{r}) \\
&= \sum_{\nu,\mu=1}^{K} 2P_{\mu,\nu}\phi_\nu^*(\mathbf{r})\phi_\mu^*(\mathbf{r}) \tag{2.37}
\end{aligned}
$$

With the expansion in Equation 2.37 and the density matrix elements $P_{\mu,\nu}$ we can easily determine the matrix elements of the Hartree-potential.

$$
\begin{aligned}
V_{\nu,\mu}^H &= \int \phi_\nu^*(\mathbf{r})V_H(\mathbf{r})\phi_\mu(\mathbf{r})\,\mathrm{d}\mathbf{r} = \iint \phi_\nu^*(\mathbf{r})\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_\mu(\mathbf{r})\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \\
&= \sum_{\lambda,\tau} P_{\lambda,\tau} \iint \frac{\phi_\nu^*(\mathbf{r})\phi_\tau^*(\mathbf{r}')\phi_\lambda(\mathbf{r}')\phi_\mu(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \\
&= \sum_{\lambda,\tau} P_{\lambda,\tau}\,(\nu\tau|\mu\lambda)
\end{aligned}
$$

The representation of the exchange operator follows analogously:

$$
\begin{aligned}
\Sigma_{\nu,\mu} &= \iint \phi_\nu^*(\mathbf{r})\Sigma(\mathbf{r},\mathbf{r}')\phi_\mu(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' = -\iint \phi_\nu^*(\mathbf{r})\sum_{i=1}^{N/2}\frac{\Psi_i(\mathbf{r})\Psi_i^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_\mu(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \\
&= -\iint \phi_\nu^*(\mathbf{r})\sum_{i=1}^{N/2}\sum_{\lambda,\tau} C_{\lambda i}C_{\tau i}^* \frac{\phi_\lambda(\mathbf{r})\phi_\tau^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_\mu(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \\
&= -\frac{1}{2}\sum_{\lambda,\tau} P_{\lambda,\tau}\,(\nu\tau|\lambda\mu)
\end{aligned}
$$

$$
\Rightarrow F_{\nu,\mu} = h_{\nu,\mu} + \sum_{\lambda,\tau} P_{\lambda,\tau}\left[(\nu\tau|\mu\lambda) - \frac{1}{2}(\nu\tau|\lambda\mu)\right]
$$

Since the density matrix elements depend on the expansion coefficients, the Fock matrix is also dependent on them and the Roothaan equations are nonlinear. To solve them, we again need a self-consistent approach:

1. choose the basis to expand in

2. calculate the integrals $S_{\mu,\nu}$, $h_{\mu,\nu}$ and $(\nu\lambda|\tau\mu)$

3. initialize $P_{\mu,\nu}$

4. compute $F_{\mu,\nu}$

5. solve the Roothan equations to obtain new expansion coefficients

6. restart from step 3 until the density matrix no longer changes

For the case of an atom-centered basis set it is easy to see that the size of the basis $\{\phi_\mu\}$ grows linearly with the number of atoms $N_A$. Therefore, we have to compute $N_A^4$ four-center integrals $(\nu\lambda|\tau\mu)$. Calculating the fock matrix $F_{\mu,\nu}$ therefore requires $N_A^4$ operations, if no further tricks are applied. The formal scaling of the Hartree-Fock method is therefore $N_A^4$.

### 2.4.1 Conditioning

For an atom-centered basis we generally have $S_{\mu,\nu} \neq \delta_{\mu,\nu}$, i.e. basis functions are not orthogonal to each other, if they are centered on different atoms, as depicted in Figure 2.4. If the size of the basis or the extend of the basis functions grows, different linear combinations of basis functions can give the same expansion. Eventually, we end up with linear dependencies in the basis functions:

$$\phi_\nu(\mathbf{r}) = \sum_\mu C_{\nu\mu}\phi_\mu(\mathbf{r})$$

If a new basis function can be expressed as a linear combination of the already present ones, it obviously adds nothing new to the basis set. In a Gram-Schmidt sense this basis function would be associated with an eigenvalue that is close to zero. As a consequence the overlap matrix becomes "ill-conditioned"[2] and the inversion is no longer numerically stable. To solve this issue, one can apply a "Singular Value Decomposition", which diagonalizes the matrix and filters out all eigenvalues below a given threshold. The inversion is then carried out for the resulting submatrix.

### 2.4.2 Performance of Hartree-Fock

One advantage of the Hartree-Fock approach are that it gives a "chemical" picture of electron orbitals and bonds. It also gives a total energy and allows us to compute ground state properties. However, HF typically underestimates the total energy by a few percent.

---

[2]The condition number of a matrix is the ratio between the largest and the smallest eigenvalue of a matrix. If this number becomes large, the matrix it is ill-conditioned.
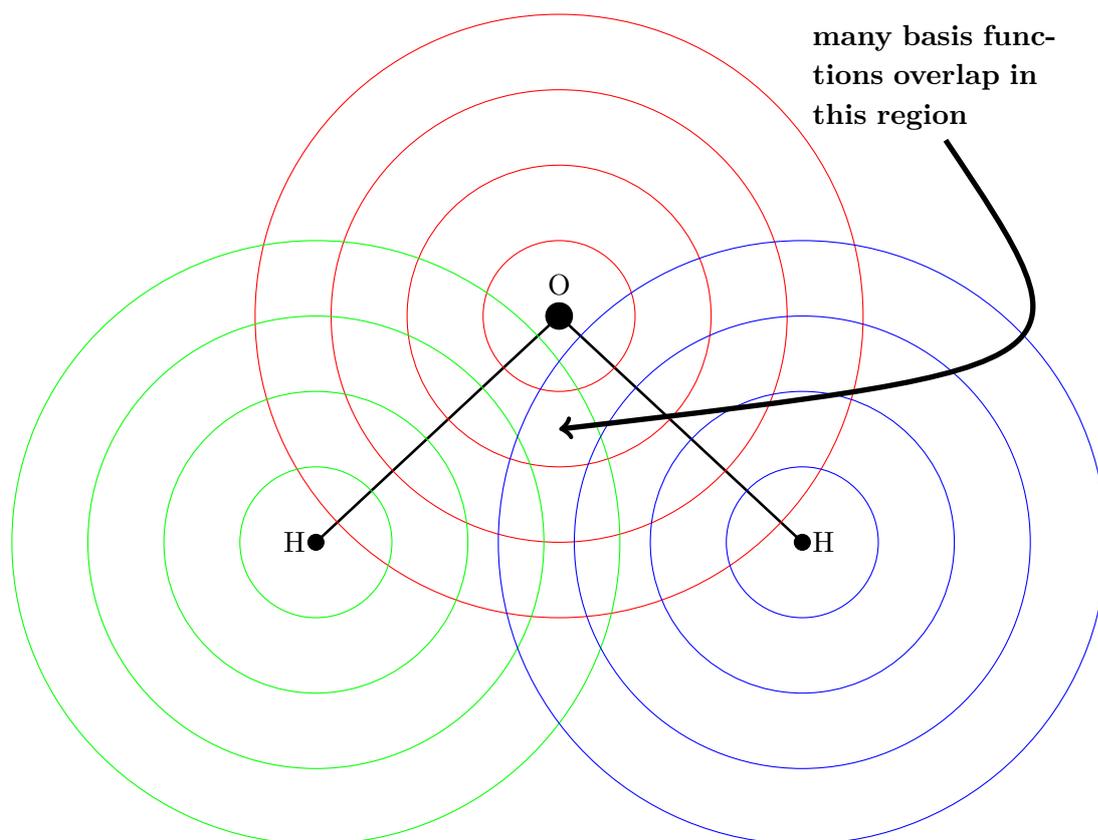
Figure 2.4: Basis set superposition between the atoms at the schematic example of a water molecule. The different circles symbolize the radial extend of different basis functions centered on each atom.

These errors become significant when we have to deal with energy differences.

In quantum chemistry, HF often underbinds by about $4eV$ per bond. This error is too large for thermochemistry, where an error of about $0.05eV$ in the transition state energy of the reaction already results in a factor of 5 error in the reaction rate. In solid state physics, Hartree-Fock is not often applied and usually overestimates lattice constants, while cohesive energies are underestimated, as in quantum chemistry.

## 2.5 Form of the exact wave function and configuration interaction

So far we have obtained the following wave function approximations from the variational principle by minimizing the energy:

**Hartree-product** $\Phi^{HP} = \phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\dots\phi_k(\mathbf{x}_N)$

**HF Slater Determinant** $\Phi^{HF} = \Phi^{SD}\left(\{\phi_i(\mathbf{x})\}\right)$

In HF we fixed the form of the wave function a priori to be a single slater determinant. This is a constraint on the shape of the wavefunction and therefore does not necessarily yield the true ground state of a system. How can we construct a better wave funtion? Let us assume that we have a complete basis $\{f_i\}$. Any function of a single variable can then be expanded exactly as

$$\Phi(\mathbf{x}_1) = \sum_i a_i f_i(\mathbf{x}_1) \tag{2.38}$$

Similarly, a function of two variables can be expanded in stages.

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i a_i(\mathbf{x}_2) f_i(\mathbf{x}_1) \tag{2.39}$$

Now we can expand the coefficient functions $a_i(\mathbf{x}_2)$ in Equation 2.39 by inserting 2.38.

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_{i,j} b_{ij} f_j(\mathbf{x}_2) f_i(\mathbf{x}_1) \tag{2.40}$$

For the special case of $\Phi$ being an fermionic wave function, we can derive further constraints on the expansion from the antisymmetry principle $\Phi(\mathbf{x}_1, \mathbf{x}_2) = -\Phi(\mathbf{x}_2, \mathbf{x}_1)$:

$$\Rightarrow b_{ij} = -b_{ji} \qquad b_{ii} = 0$$

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_{j>i} b_{ij} \left[ f_i(\mathbf{x}_1) f_j(\mathbf{x}_2) - f_i(\mathbf{x}_2) f_j(\mathbf{x}_1) \right]$$

$$= \sum_i \sum_{j>i} b_{ij} \sqrt{2} \Phi^{SD}(\mathbf{x}_1, \mathbf{x}_2) \tag{2.41}$$

This shows us, that the exact wave function is not a single Slater determinant, but an infinite sum over different determinants. Let us restrict, for simplicity, again to the two-electron case and consider the determinants which contribute to the true ground state. As basis functions we choose the Hartree-Fock orbitals and order them by their eigenvalues.

In the following we will denote the Hartree-Fock groundstate as $\Phi_0^{SD}$ and all other Slater determinants will be labeled as:

$$\Phi_a^r$$

indexes of orbitals where the excited electrons go to

indexes of orbitals where the excited electrons come from

HF
ground
state

singly excited
(one electron is pro-
moted to a higher orbital)

doubly excited
(two electrons are pro-
moted to higher orbitals)

With these definitions we can rewrite Equation 2.41 as:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = C_0\Phi_0^{SD} + \sum_{ra} C_a^r \Phi_a^r + \sum_{r<s, a<b} C_{ab}^{rs} \Phi_{ab}^{rs} \tag{2.42}$$

While $a$ and $b$ are always 1 in our two-electron example, this scheme can be general-
ized to an arbitrary number of electrons. Therefore, we can have arbitrarily complex
determinants:



HF
ground
state

singles

doubles

triples etc.
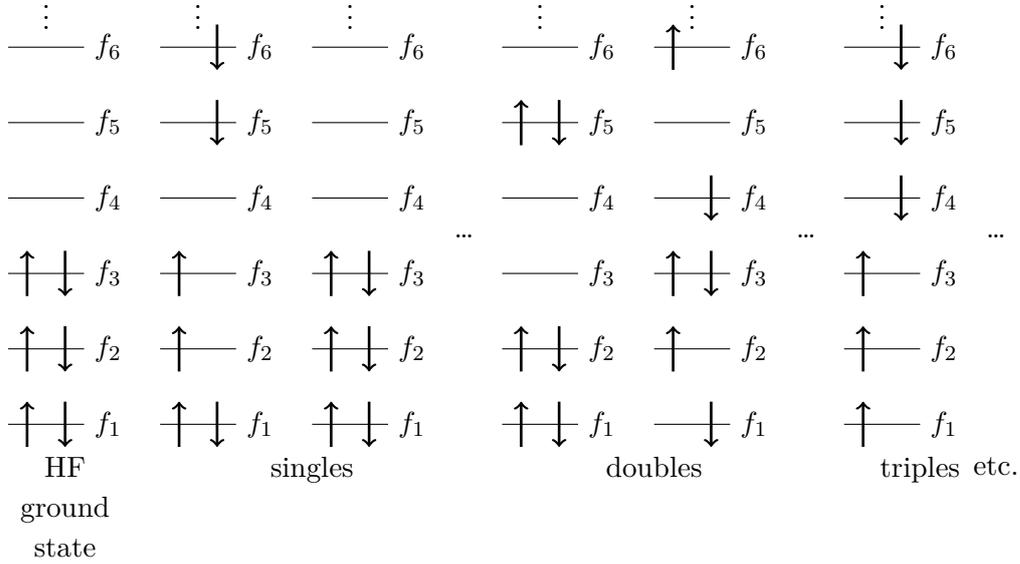
And the general form of the wave function given in Equation 2.42 then becomes:

$$\Phi^{CI}(\{\mathbf{x}_i\}) = C_0\Phi_0^{SD} + \sum_{ra} C_a^r \Phi_a^r + \sum_{r<s, a<b} C_{ab}^{rs} \Phi_{ab}^{rs} + \sum_{r<s<t, a<b<c} C_{ab}^{rs} \Phi_{abc}^{rst} + \ldots \tag{2.43}$$

The coefficients in Equation 2.43 can be obtained from the Schrödinger equation. For a finite basis set with $K$ orbitals and $N$ is the number of electrons in the system, the number of possible configuration is $\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!}$.

Let us again consider a simple example, the hydrogen dimer in a minimal basis as shown in Figure 2.5. A minimal basis means in this case that we only consider the hydrogen $1s$ orbitals $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$ located at the respective atoms.

We will denote spin down states with a bar, i.e. $\Psi_1(\mathbf{r}, \uparrow) = \Psi_1(\mathbf{r})$ and $\Psi_1(\mathbf{r}, \downarrow) = \bar{\Psi}_1(\mathbf{r})$,

$$\text{antibonding } \Psi_2(\mathbf{r}) = \frac{1}{\sqrt{2(1 - S_{12})}}[\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})]$$



$$\text{bonding } \Psi_1(\mathbf{r}) = \frac{1}{\sqrt{2(1 + S_{12})}}[\phi_1(\mathbf{r}) + \phi_2(\mathbf{r})]$$
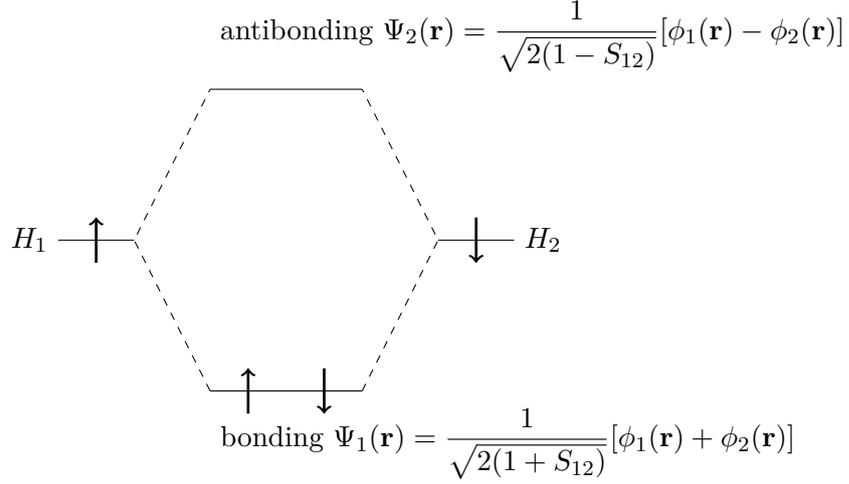
Figure 2.5: $H_2$ with a minimal basis, i.e. the $1s$ hydrogen orbitals $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$ located at their respective atoms. $S_{12}$ denotes the overlap between the two basis functions.

the HF ground state of the molecule is the Slater determinant of the "binding state":

$$\Phi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\Psi_1(\mathbf{r}_1)\bar{\Psi}_1(\mathbf{r}_2) - \Psi_1(\mathbf{r}_2)\bar{\Psi}_1(\mathbf{r}_1)\right] \tag{2.44}$$

$$|\Phi_0\rangle = |\Psi_1\bar{\Psi}_1\rangle = |1\bar{1}\rangle \tag{2.45}$$

Our determinants are then:



And we can write the full wavefunction as:

$$\left|\Phi^{CI}\right\rangle = \underbrace{C_0\left|\Phi_0\right\rangle}_{\text{ground state}} + \underbrace{C_1^2\left|2\bar{1}\right\rangle + C_{\bar{1}}^{\bar{2}}\left|1\bar{2}\right\rangle + C_1^2\left|12\right\rangle + C_1^{\bar{2}}\left|\bar{2}\bar{1}\right\rangle}_{\text{singles}} + \underbrace{C_{1\bar{1}}^{2\bar{2}}\left|2\bar{2}\right\rangle}_{\text{double}} \tag{2.46}$$

Given this genereal shape of the wave function, the variational method tells us that the corresponding ground state can be is the lowest eigenvalue of $\langle \Phi^{CI} | \mathcal{H} | \Phi^{CI} \rangle = E$. Writing the coefficients as a vector $C$, we can write the energy of the wave function as:

$$E = C \begin{pmatrix} \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle & \langle \Phi_0 | \mathcal{H} | 1\bar{2} \rangle & \langle \Phi_0 | \mathcal{H} | 2\bar{1} \rangle & \langle \Phi_0 | \mathcal{H} | 21 \rangle & \langle \Phi_0 | \mathcal{H} | \bar{2}\bar{1} \rangle & \langle \Phi_0 | \mathcal{H} | 2\bar{2} \rangle \\ \langle 1\bar{2} | \mathcal{H} | \Phi_0 \rangle & \langle 1\bar{2} | \mathcal{H} | 1\bar{2} \rangle & \langle 1\bar{2} | \mathcal{H} | 2\bar{1} \rangle & \langle 1\bar{2} | \mathcal{H} | 21 \rangle & \langle 1\bar{2} | \mathcal{H} | \bar{2}\bar{1} \rangle & \langle 1\bar{2} | \mathcal{H} | 2\bar{2} \rangle \\ \langle 2\bar{1} | \mathcal{H} | \Phi_0 \rangle & \langle 2\bar{1} | \mathcal{H} | 1\bar{2} \rangle & \langle 2\bar{1} | \mathcal{H} | 2\bar{1} \rangle & \langle 2\bar{1} | \mathcal{H} | 21 \rangle & \langle 2\bar{1} | \mathcal{H} | \bar{2}\bar{1} \rangle & \langle 2\bar{1} | \mathcal{H} | 2\bar{2} \rangle \\ \langle 21 | \mathcal{H} | \Phi_0 \rangle & \langle 21 | \mathcal{H} | 1\bar{2} \rangle & \langle 21 | \mathcal{H} | 2\bar{1} \rangle & \langle 21 | \mathcal{H} | 21 \rangle & \langle 21 | \mathcal{H} | \bar{2}\bar{1} \rangle & \langle 21 | \mathcal{H} | 2\bar{2} \rangle \\ \langle \bar{2}\bar{1} | \mathcal{H} | \Phi_0 \rangle & \langle \bar{2}\bar{1} | \mathcal{H} | 1\bar{2} \rangle & \langle \bar{2}\bar{1} | \mathcal{H} | 2\bar{1} \rangle & \langle \bar{2}\bar{1} | \mathcal{H} | 21 \rangle & \langle \bar{2}\bar{1} | \mathcal{H} | \bar{2}\bar{1} \rangle & \langle \bar{2}\bar{1} | \mathcal{H} | 2\bar{2} \rangle \\ \langle 2\bar{2} | \mathcal{H} | \Phi_0 \rangle & \langle 2\bar{2} | \mathcal{H} | 1\bar{2} \rangle & \langle 2\bar{2} | \mathcal{H} | 2\bar{1} \rangle & \langle 2\bar{2} | \mathcal{H} | 21 \rangle & \langle 2\bar{2} | \mathcal{H} | \bar{2}\bar{1} \rangle & \langle 2\bar{2} | \mathcal{H} | 2\bar{2} \rangle \end{pmatrix} C$$

$$(2.47)$$

What is most noticeable about Equation 2.47 is the block structure of the matrix. We have a blocks which contains only expectation values between configuration with the same number of excitations (marked red, green and blue in the matrix) on the diagonal and offdiagonal blocks, which contains Hamiltonian matrix elements between configurations with different numbers of excitations (highlighted with mixed colors in the matrix). In general, the matrix has the shape of Equation 2.48, where $S$ denotes the blocks for singles, $D$ for doubles and $T$ for triples.

$$\langle \Phi^{CI} | \mathcal{H} | \Phi^{CI} \rangle = C \begin{pmatrix} \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle & \langle \Phi_0 | \mathcal{H} | S \rangle & \langle \Phi_0 | \mathcal{H} | D \rangle & \langle \Phi_0 | \mathcal{H} | T \rangle & \cdots \\ \langle S | \mathcal{H} | \Phi_0 \rangle & \langle S | \mathcal{H} | S \rangle & \langle S | \mathcal{H} | D \rangle & \langle S | \mathcal{H} | T \rangle & \cdots \\ \langle D | \mathcal{H} | \Phi_0 \rangle & \langle D | \mathcal{H} | S \rangle & \langle D | \mathcal{H} | D \rangle & \langle D | \mathcal{H} | T \rangle & \cdots \\ \langle T | \mathcal{H} | \Phi_0 \rangle & \langle T | \mathcal{H} | S \rangle & \langle T | \mathcal{H} | D \rangle & \langle T | \mathcal{H} | T \rangle & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} C \quad (2.48)$$

In this matrix, different configurations interact via the Hamiltonian, therefore the name of the method "Configuration interaction" (CI). To solve this problem, all we need to know are the matrix elements.[3]

$$\mathcal{O}_1 = \sum_i h(\mathbf{r}_i) \qquad\qquad \mathcal{O}_2 = \sum_i \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$Case 1:$
$|K\rangle = |\ldots mn \ldots\rangle$
$|L\rangle = |\ldots mn \ldots\rangle$
$\qquad \langle K | \mathcal{O}_1 | L \rangle = \sum_i \langle i | h | i \rangle \qquad \langle K | \mathcal{O}_2 | L \rangle = \sum_{i,j} \langle ij | ij \rangle - \langle ij | ji \rangle$

$Case 2:$
$|K\rangle = |\ldots mn \ldots\rangle$
$|L\rangle = |\ldots pn \ldots\rangle$
$\qquad \langle K | \mathcal{O}_1 | L \rangle = \langle m | h | p \rangle \qquad \langle K | \mathcal{O}_2 | L \rangle = \sum_i \langle mi | pi \rangle - \langle mi | ip \rangle$

$Case 3:$
$|K\rangle = |\ldots mn \ldots\rangle$
$|L\rangle = |\ldots pq \ldots\rangle$
$\qquad \langle K | \mathcal{O}_1 | L \rangle = 0 \qquad \langle K | \mathcal{O}_2 | L \rangle = \langle mn | pq \rangle - \langle mn | qp \rangle$

---

[3]For a general derivation see [3, Chapter 4].

For all configurations which differ by three or more occupied orbitals, the matrix elements are zero. The matrix elements are quite simply and involve at most the Coulomb integral of four states. Since only determinants with at most two different states couple, the general matrix from Equation 2.48 simplifies to:

$$
\begin{pmatrix}
\langle\Phi_0|\mathcal{H}|\Phi_0\rangle & \langle\Phi_0|\mathcal{H}|S\rangle & \langle\Phi_0|\mathcal{H}|D\rangle & 0 & 0 & \dots \\
\langle S|\mathcal{H}|\Phi_0\rangle & \langle S|\mathcal{H}|S\rangle & \langle S|\mathcal{H}|D\rangle & \langle S|\mathcal{H}|T\rangle & 0 & \dots \\
\langle D|\mathcal{H}|\Phi_0\rangle & \langle D|\mathcal{H}|S\rangle & \langle D|\mathcal{H}|D\rangle & \langle D|\mathcal{H}|T\rangle & \langle D|\mathcal{H}|Q\rangle & \dots \\
0 & \langle T|\mathcal{H}|S\rangle & \langle T|\mathcal{H}|D\rangle & \langle T|\mathcal{H}|T\rangle & \langle T|\mathcal{H}|Q\rangle & \dots \\
0 & 0 & \langle Q|\mathcal{H}|D\rangle & \langle Q|\mathcal{H}|T\rangle & \langle Q|\mathcal{H}|Q\rangle & \dots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
$$

This simplifies the matrix considerably, leaving only the diagonal blocks and two off-diagonal blocks above and below the main diagonal, but still the matrix is enormously large. For a complete basis the configuration interaction approach would be exact. However, in practice our basis sets are never complete. Due to the $\binom{2K}{N}$ scaling of the available configurations, CI is applicable only to small systems. In general, one has always to make a trade-off between the basis set size and the number of used determinants, as depicted in Figure 2.6. The energy different between the exact CI-solution (i.e. the exact non-relativistic wave function) and the Hartree-Fock ground state is known as the "correlation energy".
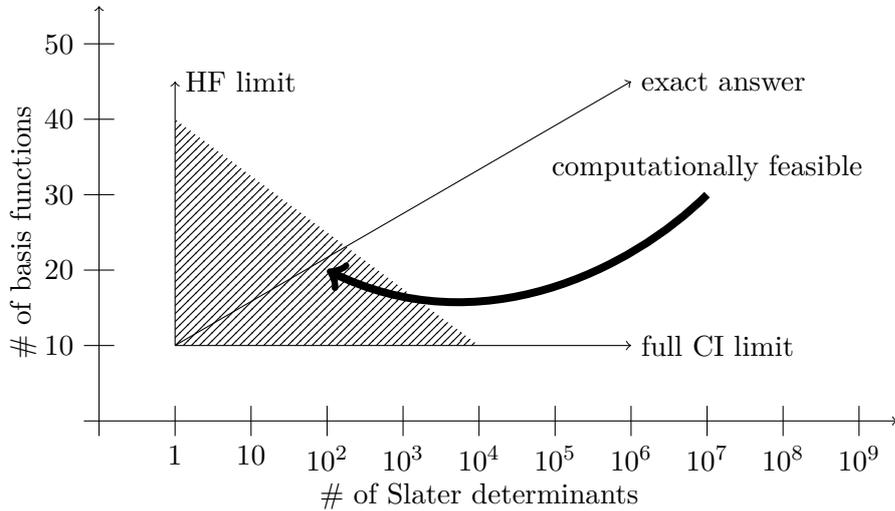


Figure 2.6: The trade-off between the number of used Slater determinants and the size of employed basis set.

Now let us return to our minimal $H_2$ example:

$$\left|\Phi^{2e}\right\rangle = C_0 \left|\Phi_0\right\rangle + C_{\bar{1}}^2 \left|2\bar{1}\right\rangle + C_{\bar{1}}^{\bar{2}} \left|2\bar{2}\right\rangle + C_1^2 \left|12\right\rangle + C_1^{\bar{2}} \left|\bar{2}\bar{1}\right\rangle + C_{1\bar{1}}^{2\bar{2}} \left|2\bar{2}\right\rangle \tag{2.49}$$

We can further simplify Equation 2.49 by spin-adaption. Since we already that the exact ground state has to be a singlet, i.e. one electron with spin up and one with spin down, only spin singlet states need to be included. $\left|\Phi_0\right\rangle$ and $\left|\bar{2}\bar{1}\right\rangle$ are singlets, and the four single excitations can be rewritten as linear combinations, giving rise to one singlet state $\left|^1\Phi_1^2\right\rangle = \frac{1}{\sqrt{2}}(\left|1\bar{2}\right\rangle + \left|2\bar{1}\right\rangle)$ and three triplet states. Our wave function then reduces to:

$$\left|\Phi^{2e}\right\rangle = C_0 \left|\Phi_0\right\rangle + C_1^2 \left|^1\Phi_1^2\right\rangle + C_{1\bar{1}}^{2\bar{2}} \left|2\bar{2}\right\rangle \tag{2.50}$$

A further simplification can be achieved by taking spatial symmetry into account. Both $\left|\Phi_0\right\rangle$ and $\left|\Phi_{1\bar{1}}^{2\bar{2}}\right\rangle$ are "gerade". $\left|^1\Phi_1^2\right\rangle$ on the other hand is "ungerade" because it contains one orbital with gerade and one with ungerade symmetry. Therefore, this ungerade state will not couple to the gerade states. Equation 2.50 therefore reduces further to:

$$\left|\Phi^{2e}\right\rangle = C_0 \left|\Phi_0\right\rangle + C_{1\bar{1}}^{2\bar{2}} \left|\bar{2}\bar{1}\right\rangle \tag{2.51}$$

The CI-matrix $\mathbf{H}$ obtained from Equation 2.51 there is a simple $2 \times 2$ matrix:

$$\mathbf{H} = \left( \begin{array}{cc} \langle\Phi_0|\mathcal{H}|\Phi_0\rangle & \langle\Phi_0|\mathcal{H}|2\bar{2}\rangle \\ \langle 2\bar{2}|\mathcal{H}|\Phi_0\rangle & \langle 2\bar{2}|\mathcal{H}|2\bar{2}\rangle \end{array} \right)$$

$$= \left( \begin{array}{cc} E_0 & K_{12} \\ K_{12} & E_2 \end{array} \right)$$

where $E_0 = E_1$ denotes the energy of the Hartree-Fock ground state. Our matrix equation to solve then is:

$$\left( \begin{array}{cc} E_0 & K_{12} \\ K_{12} & E_2 \end{array} \right) \left( \begin{array}{c} C_0 \\ C_{1\bar{1}}^{2\bar{2}} \end{array} \right) = E \left( \begin{array}{c} C_0 \\ C_{1\bar{1}}^{2\bar{2}} \end{array} \right)$$

The eigenvalues of a $2 \times 2$ matrix are:

$$\left( \begin{array}{cc} a & b \\ c & d \end{array} \right) \qquad \rightarrow E_{1/2} = \frac{a+d}{2} \pm \sqrt{\frac{(a+d)^2}{4} - (ad - bc)}$$

$$\Rightarrow E_{1/2} = \frac{E_0 + E_2}{2} \pm \sqrt{\frac{(E_0 + E_2)^2}{4} - (E_0 E_2 - K_{12}^2)}$$

$$= \frac{E_0 + E_2}{2} \pm \sqrt{\frac{(E_0^2 + 2E_0 E_2 + E_2^2)}{4} - (E_0 E_2 - K_{12}^2)}$$

$$= E_0 + \frac{E_2 - E_0}{2} \pm \sqrt{\frac{(E_2 - E_0)^2}{4} + K_{12}^2}$$

If we now define $\Delta = \frac{1}{2}(E_2 - E_0)$, we then have for the CI ground state:

$$E_0^{CI} = E_0 + \Delta - \sqrt{\Delta^2 + K_{12}^2}$$
$$= E_0^{HF} + E^{corr}$$

where $E^{corr}$ is the previously defined correlation-energy, i.e. "everything that goes beyond Hartree-Fock".

Now let us consider the dissociation limit of the hydrogen molecule, i.e. the $R \to \infty$ limit with $R$ being the interatomic distance. Since we essentially have two independent hydrogen atoms at the dissociation limit, the single particle Hamiltonian yields the energy of a hydrogen atom for both orbitals $h_{11} = h_{22} = E(H)$. All molecular two-electron integrals tend to $\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$ where $\phi_1$ is a hydrogenic orbital.

$$E^{HF}(R \to \infty) = 2h_{11} + J_{11}$$
$$\Delta = \frac{1}{2}(E_2 - E_0) = \frac{1}{2}(2h_{22} + J_{22} - 2h_{11} - J_{11}) = 0$$
$$E^{CI}(R \to \infty) = 2h_{11} + J_{11} - K_{12} = 2h_{11} + J_{11} - J_{11} = 2h_{11}$$

While the CI yields the correct energy in the dissociation energy, Hartree-Fock leads to a qualitatively wrong result, Figure 2.7 shows the resulting dissociation curves. Of course our minimal basis model is too simplistic for a real system, but full CI will always be correct and dissociate correctly. Can we understand why HF fails and CI is correct? Let us consider our Hartree-Fock wave function: At the dissociation limit, we have the bonding and antibonding wave functions are $\Psi_{1/2} = \frac{1}{\sqrt{2}}(\phi_1(\mathbf{r}) \pm \phi_2(\mathbf{r}))$. Our ground
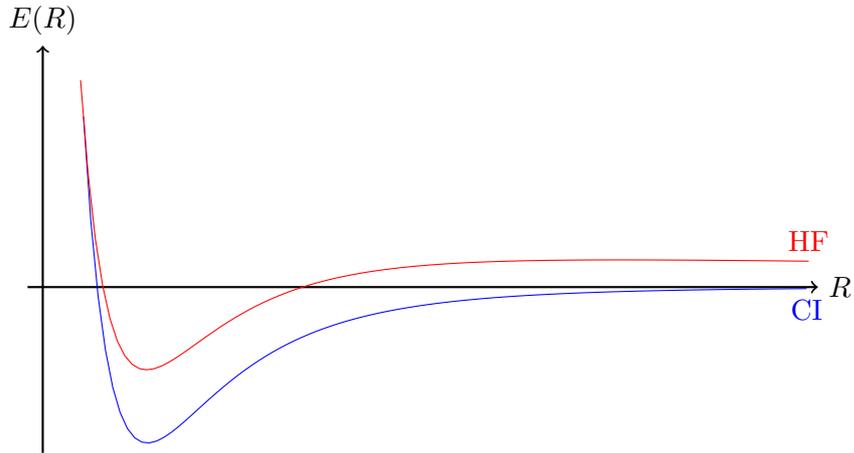


Figure 2.7: Dissociation curve of the hydrogen atom for Hartree-Fock and configuration interaction as a function of the inter-nuclear distanc $R$.

state determinant is thus:

$$|\Phi_0\rangle = |1\bar{1}\rangle$$

$$= \frac{1}{\sqrt{2}}\left[\Psi_1(\mathbf{r}_1)\bar{\Psi}_1(\mathbf{r}_2) - \Psi_1(\mathbf{r}_2)\bar{\Psi}_1(\mathbf{r}_1)\right]$$

$$= \frac{1}{\sqrt{2}}\Psi_1(\mathbf{r}_1)\Psi_1(\mathbf{r}_2)\left[\alpha(\mathbf{r}_1)\beta(\mathbf{r}_2) - \alpha(\mathbf{r}_2)\beta(\mathbf{r}_1)\right]$$

$$= \frac{1}{2\sqrt{2}}\left(\phi_1(\mathbf{r}_1) + \phi_2(\mathbf{r}_1)\right)\left(\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_2)\right)\left[\alpha(\mathbf{r}_1)\beta(\mathbf{r}_2) - \alpha(\mathbf{r}_2)\beta(\mathbf{r}_1)\right]$$

$$= \frac{1}{2\sqrt{2}}\left(\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\right)\left[\ldots\right]$$

As it can be seen the first and last term in the paranthesis are configurations which correspond to a double occupancy of one of the hydrogen atoms. When the atoms are very far away from each other, the double occupancy costs Coulomb energy and is therefore unfavorable. Now consider the exited state $\left|\Phi_{1\bar{1}}^{2\bar{2}}\right\rangle$:

$$\left|\Phi_{1\bar{1}}^{2\bar{2}}\right\rangle = \frac{1}{\sqrt{2}}\Psi_2(\mathbf{r}_1)\Psi_2(\mathbf{r}_2)\left[\alpha(\mathbf{r}_1)\beta(\mathbf{r}_2) - \alpha(\mathbf{r}_2)\beta(\mathbf{r}_1)\right]$$

$$= \frac{1}{2\sqrt{2}}\left(\phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\right)\left[\ldots\right]$$

The structure is similar to the ground state determinant, but the single occupancy terms have the opposite sign. At dissociation both determinants have the same energy and become degenerate. Therefore, the exact wave-function should be a linear combination of them. It turns out that in full CI at dissociation we obtain $C_0 = 1$ and $C_{1\bar{1}}^{2\bar{2}} = -1$.

$$\left|\Phi^{CI}\right\rangle = |\Phi_0\rangle - \left|\Phi_{1\bar{1}}^{2\bar{2}}\right\rangle$$

$$= \frac{1}{\sqrt{2}}\left(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\right)\left[\alpha(\mathbf{r}_1)\beta(\mathbf{r}_2) - \alpha(\mathbf{r}_2)\beta(\mathbf{r}_1)\right]$$

This is what we expected and would have drawn intuitively. The wave function is a singlet and antisymmetric and the electrons are indistinguishable. Also in atomic orbitals, the exact wave function is a sum of determinants: $\left|\Phi^{CI}\right\rangle = \frac{1}{\sqrt{2}}(|\phi_1\phi_2\rangle + |\phi_2\phi_1\rangle)$. For $H_2$ dissociation, and nearly all degenerate cases in general, the exact wave function is a sum of Slater determinants. The Hartree-Fock mean filed is then not enough. This situation is often referred to as "multi reference", because more than one HF determinant could be taken as reference energy in $E = E^{HF} = E^{corr}$. The correlation that brings the correct result in this case is often called "static correlation".

# 3 Density Functional Theory

In the previous chapter we have considered theories that work with the many-body wave function to solve the electronic Schrödinger equation. However, the many-body wave function $\Psi = \Psi(\{\mathbf{x}_i\})$ is quite an unwieldy object with its $3N$-many coordinates. Would it not be nicer to work with objects that just depend on one variable, like the density $n = n(\mathbf{r})$?

This is not unreasonable, because knowing the the wave function implies we also know the density:

$$n(\mathbf{r}) = N \int \dots \int |\Psi(\{\mathbf{x}_i\})|^2 \ \mathrm{d}\sigma \ \mathrm{d}\mathbf{x}_2 \dots \ \mathrm{d}\mathbf{x}_N \qquad (3.1)$$

$$\int n(\mathbf{r}) \ \mathrm{d}\mathbf{r} = N$$

Which electronic coordinates we integrate out, does not matter for a properly antisymmetrized wave function.

## 3.1 Kohn-Sham equations

Let us assume for now, that we can build an exact theory based on the density and worry about the proofs later. Let us also assume that we have an auxiliary system of non-interacting electrons that has the same ground state density as the real interacting system. The auxiliary system is another manifestation of a mean-field. The non-interacting electrons move in an effective potential $V = V_{\mathrm{aux}}(\mathbf{x}) = V_{\mathrm{eff}}(\mathbf{x})$, which we
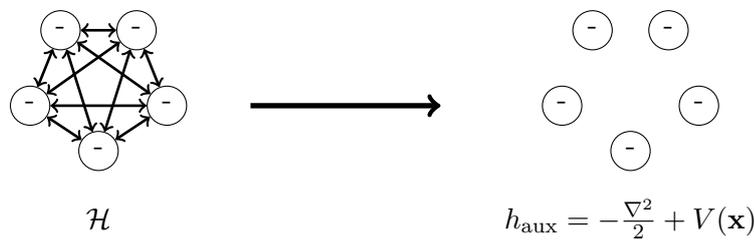


Figure 3.1: The mapping from the interacting system to a non-interacting auxiliary system.

assume to be representable as a multiplicative potential ("v-representable"). $V_{\text{eff}}$ does not have to be a physically meaningful potential, nor does the total wave function have to be physical. As we will see later, we can still obtain the exact ground-state total energy using $V_{\text{eff}}$.

The advantage of the auxiliary system is that we know how to deal with it:

$$\mathcal{H} \to \sum_{i=1}^{N} h_{\text{aux}}(\mathbf{x}_i) = H_{\text{aux}}(\{\mathbf{x}_i\}) \tag{3.2}$$

The full many-body Hamiltonian becomes a sum of single particle ones. This we know how to deal with from Hartree-Fock:

$$h_{\text{aux}}(\mathbf{x}_i)\varphi_i(\mathbf{x}_i) = \epsilon_i \varphi_i(\mathbf{x}_i)$$

Therefore, the many-body wave function is a single Slater determinant, but it will be different from the Hartree-Fock solution because the orbitals $\phi_i$ are different.

Our electronic density is then:

$$n(\mathbf{r}) = \sum_{i=1}^{N} \int |\varphi_i(\mathbf{r}, \sigma)|^2 \ d\sigma \tag{3.3}$$

which can be easily verified for the two-electron case:

$$
\begin{aligned}
n(\mathbf{r}) &= 2 \iint \frac{1}{2} |\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2) - \varphi_i(\mathbf{x}_2)\varphi_j(\mathbf{x}_1)|^2 \ d\sigma_1 \ d\mathbf{x}_2 \\
&= \frac{1}{2} \iint |\Psi_i(\mathbf{r}_1)\alpha(\sigma_1)\Psi_j(\mathbf{r}_2)\beta(\sigma_2) - \Psi_i(\mathbf{r}_2)\alpha(\sigma_2)\Psi_j(\mathbf{r}_1)\beta(\sigma_1)|^2 \ d\sigma_1 \ d\mathbf{x}_2 \\
&= \iint d\sigma_1 \ d\mathbf{x}_2 \Big[ \Psi_i^*(\mathbf{r}_1)\Psi_i(\mathbf{r}_1)\Psi_j^*(\mathbf{r}_2)\Psi_j(\mathbf{r}_2)\alpha^*(\sigma_1)\alpha(\sigma_1)\beta^*(\sigma_2)\beta(\sigma_2) \\
&\qquad\qquad + \Psi_j^*(\mathbf{r}_1)\Psi_j(\mathbf{r}_1)\Psi_i^*(\mathbf{r}_2)\Psi_i(\mathbf{r}_2)\beta^*(\sigma_1)\beta(\sigma_1)\alpha^*(\sigma_2)\alpha(\sigma_2) \\
&\qquad\qquad - \Psi_i^*(\mathbf{r}_1)\Psi_j(\mathbf{r}_1)\Psi_j^*(\mathbf{r}_2)\Psi_i(\mathbf{r}_2)\alpha^*(\sigma_1)\beta(\sigma_1)\beta^*(\sigma_2)\alpha(\sigma_2) \\
&\qquad\qquad - \Psi_j^*(\mathbf{r}_1)\Psi_i(\mathbf{r}_1)\Psi_i^*(\mathbf{r}_2)\Psi_j(\mathbf{r}_2)\beta^*(\sigma_1)\alpha(\sigma_1)\alpha^*(\sigma_2)\beta(\sigma_2) \Big] \\
&= \int \Big[ |\Psi_i(\mathbf{r}_1)\alpha(\sigma_1)|^2 + |\Psi_j(\mathbf{r}_1)\beta(\sigma_1)|^2 \Big] \ d\sigma_1 \\
&= \sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2
\end{aligned}
$$

In terms of the density and the orbitals, we can then write down the Coulomb energy $E_H[n]$ and the kinetic energy $T_s[n]$:

$$E_H[n] = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \ d\mathbf{r} \ d\mathbf{r}' \tag{3.4}$$

$$T_s[n] = -\frac{1}{2} \sum_{i=1}^{N} \int \langle \varphi_i | \nabla^2 | \varphi_i \rangle \, \mathrm{d}\sigma \tag{3.5}$$

$$\Rightarrow E_{\mathrm{aux}}[n] = T_s[n] + \underbrace{\int V_{\mathrm{eff}}(\mathbf{r}) n(\mathbf{r})}_{E_{\mathrm{ext}}} + E_H + E_{xc} \tag{3.6}$$

In Equation 3.6, $E_{xc}$ is the only term that contains interactions beyond Hartree and therefore we call it "exchange-correlation".

We now apply the same procedure as in the derivation of the Hartree and HF equations:

$$\mathcal{L}[n] = E_{\mathrm{aux}}[n] - \sum_{i=1}^{N} \sum_{j=1}^{N} \lambda_{ij} \left[ \int \varphi_i^*(\mathbf{x}) \varphi_j(\mathbf{x}) \, \mathrm{d}\mathbf{x} - \delta_{ij} \right]$$

$$\frac{\delta \mathcal{L}}{\delta \varphi_i^*} = 0 \quad \forall i$$

$$\Rightarrow \sum_{j=1}^{N} \lambda_{ij} \varphi_j = \frac{\delta T_s}{\delta \varphi_i^*} + \left[ \frac{\delta E_{\mathrm{aux}}}{\delta n} + \frac{\delta E_H}{\delta n} + \frac{\delta E_{xc}}{\delta n} \right] \frac{\delta n}{\delta \varphi_i^*}$$

$$\sum_{j=1}^{N} \lambda_{ij} \varphi_j = \frac{1}{2} \nabla^2 \varphi_i(\mathbf{x}) + \left[ V_{\mathrm{aux}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \varphi_i(\mathbf{x})$$

As before, we can bring these equations into canonical form by applying a unitary transformation. Furthermore, we can simplify the expression by noting that the equation is spin-independent.

$$\Rightarrow \left[ -\frac{1}{2} \nabla^2 + V_{\mathrm{eff}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \lambda_i \varphi_i(\mathbf{r}) \tag{3.7}$$

$$V_{\mathrm{eff}}(\mathbf{r}) = V_{\mathrm{aux}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \tag{3.8}$$

$V_{\mathrm{eff}}$ is the *exact* effective potential that the electrons move in. The auxiliary system of non-interacting particles was first proposed by Kohn and Sham in 1965. That is why we call the framework Kohn-Sham (KS) density functional theory. The full complexity of the real system and all the many-body interactions have been wrapped into $V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$.

## 3.2 Hohenberg-Kohn Theorems

Let us now proof that the density is sufficient for an exact ground state theory. We have just discussed one way to recast

$$\mathcal{H}\Psi = E\Psi$$

$$\mathcal{H} = -\underbrace{\sum_{i=1}^{N} \frac{\nabla_i^2}{2}}_{T} + \underbrace{\sum_{i=1}^{N} V_{\mathrm{eff}}(\mathbf{r}_i)}_{V^{ne}} + \underbrace{\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V^{ee}}$$

in terms of the density. It is in principle self-evident that the external potential, i.e. the positions of the nuclei, determines the properties of the system, but is this also true for the density?

### 3.2.1 Hohenberg-Kohn Theorem I

*The ground state density $n(\mathbf{r})$ uniquely determines the potential up to an arbitrary constant.*

For the proof of this theorem let us assume non-degenerate ground states. Suppose we have two external potentials $V_{\text{eff}}^1(\mathbf{r})$ and $V_{\text{eff}}^2(\mathbf{r})$ that differ by more than a constant, but lead to the same density $n(\mathbf{r})$.

$$
\begin{array}{ccl}
V_{\text{ext}}^1(\mathbf{r}) & \neq & V_{\text{ext}}^2(\mathbf{r}) + \text{const} \\
\downarrow & & \downarrow \\
\mathcal{H}^1 & & \mathcal{H}^2 \qquad \text{two different Hamiltonians} \\
\downarrow & & \downarrow \\
\Phi^1 & & \Phi^2 \qquad \text{two different wave functions}
\end{array}
$$

Then by the variational principle we wave

$$\langle\Phi_2|\mathcal{H}_1|\Phi_2\rangle > \langle\Phi_1|\mathcal{H}_1|\Phi_1\rangle = E_1 \tag{3.9}$$

but also

$$\langle\Phi_2|\mathcal{H}_1|\Phi_2\rangle = \langle\Phi_1|\mathcal{H}_2|\Phi_1\rangle + \overbrace{\langle\Phi_1|\mathcal{H}_1 - \mathcal{H}_2|\Phi_1\rangle}^{T \text{ and } V^{ee} \text{are the same}}$$

$$= E_2 + \int \left[V_{\text{eff}}^1(\mathbf{r}) - V_{\text{eff}}^2(\mathbf{r})]n(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{3.10}$$

$$\Rightarrow E_1 < E_2 + \int \left[V_{\text{eff}}^1(\mathbf{r}) - V_{\text{eff}}^2(\mathbf{r})]n(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{3.11}$$

The same relations of course hold true if we swap the indexes in Equation 3.9 and 3.10. Thereby we obtain

$$E_2 < E_1 + \int \left[V_{\text{eff}}^2(\mathbf{r}) - V_{\text{eff}}^1(\mathbf{r})]n(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{3.12}$$

Adding Equation 3.11 and 3.12, we obtain

$$E_1 + E_2 < E_1 + E_2 \tag{3.13}$$

which is obviously a contradiction. Our initial assumption therefore must be wrong and there cannot be two different potentials yielding the same ground state density.

As a corollary we also know that the many-body wave functions for ground and excited states are fully determined by the ground state density, because the Hamiltonian is fully determined by the external potential. Therefore, all properties of the system are fully determined by the ground state density.

### 3.2.2 Hohenberg-Kohn Theorem II

*A universal functional for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any given $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum of this functional and the density that minimizes the functional is the exact ground state density.*

For simplicity, we will restrict our proof to v-representable densities, i.e. those ones that can be represented by a potential.[1] First we need to define the functional from the Hamiltonian:

$$E_{HK}[n] = T[n] + V_{ee}[n] + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad = \underbrace{F[n]}_{universal} + \underbrace{\int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r}}_{specific}$$

Since $T[n]$ and $V_{ee}[n]$ are determined only the density, this part of the functional is universal and only the $V_{\text{ext}}$ contribution is system-specific due to its dependence on the nuclear coordinates. Suppose now that $n_1(\mathbf{r})$ is the ground state density of $V_{\text{ext}}^1(\mathbf{r})$.

$$E_1 = E_{HK}[n_1] = \langle \Phi_1 | \mathcal{H} | \Phi_1 \rangle$$

Let us now consider a different density $n_2(\mathbf{r})$ that corresponds to a different $\Phi_2$.

$$E_1 = E_{HK}[n_1] = \langle \Phi_1 | \mathcal{H} | \Phi_1 \rangle < \langle \Phi_2 | \mathcal{H} | \Phi_2 \rangle = E_{HK}[n_2] = E_2$$

The Hohenberg-Kohn functional evaluated at the ground state density therefore gives the lowest energy. If the functional of the density is known, than the total energy of the system can be obtained by variational minimization with respect to the density. The Hohenberg-Kohn functional therefore only provides access to the ground state, unlike Configuration Interaction which also gives the excited states.

With these two theorems we established a one-to-one correspondence between $V_{\text{ext}}$ and $n$, as drawn schematically in Figure 3.2. However, our proofs have the problem that they went back to the many-body wave functions. The proofs offer neither a prescription to determine the kinetic energy from the density, nor for generating the density. This is where the Kohn-Sham equations (see section 3.1) comes in as a practical scheme. Our next step is therefore to find suitable approximations for the exchange-correlation energy $E_{xc}[n]$.

---

[1] A general proof without this constraint can be found in [5].

$$V_{\text{ext}}(\mathbf{r}) \longleftrightarrow n(\mathbf{r})$$

determines $\mathcal{H}$ and gives all many-body wave functions

determines the ground state density

$$\Phi_i \xrightarrow{\text{pick the ground state}} \Phi_0$$
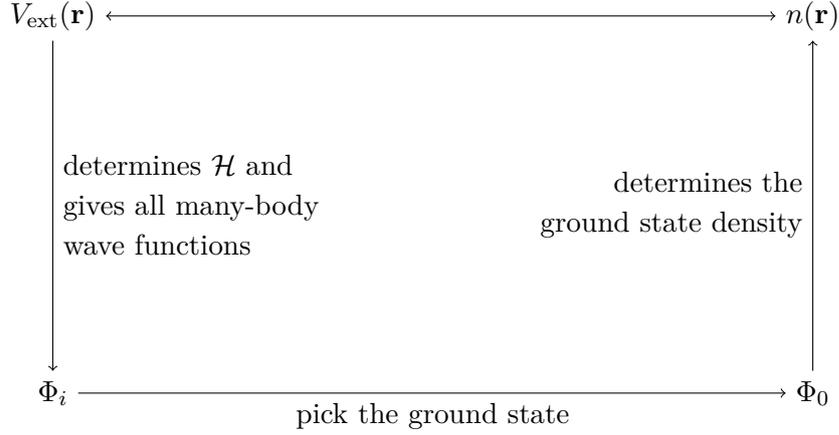
Figure 3.2: schematic representation of DFT

## 3.3 Exchange-Correlation Functionals

Going back to the definition of the Kohn-Sham functional $E_{KS}[n]$ (initially defined as $E_{aux}[n]$ in Equation 3.6), we need to approximate $E_{xc}[n]$, but what exactly does it have to incorporate? Let us compare $E_{KS}[n]$ and $E_{HK}[n]$:

$$E_{HK}[n] = F[n] - \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r}$$

$$= T[n] + V^{ee}[n] - \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r}$$

$$E_{KS}[n] = T_s[n] - \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r} + E_H[n] + E_{xc}[n]$$

$$\Rightarrow E_{xc}[n] = \underbrace{T[n] - T_s[n]}_{\text{kinetic energy}} + \underbrace{V^{ee}[n] - E_H[n]}_{\text{electron-interaction}}$$

The first term is the difference between the kinetic of the interacting and non-interacting electrons, and the second term is the difference between the full electron-electron interaction energy and the classic Coulomb energy. In general, $E_{xc}[n]$ will be small compared to the other terms, because $T_s[n]$ and $E_H[n]$ capture a lart part of $T[n]$ and $V^{ee}[n]$. Therefore, simple approximations might already be successful.

### 3.3.1 The local density approximation

For inhomogeneous systems with a slowly varying density, the system locally looks like it has a constant density. Therefore the external potential will also be constant and the system is similar to the homogeneous electron gas, as shown in Figure 3.3. Let us use

this to construct a local approximation to $E_{xc}$

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}\big(n(\mathbf{r})\big) \, \mathrm{d}\mathbf{r}$$

where $\epsilon_{xc}\big(n(\mathbf{r})\big)$ denotes the energy density (i.e. energy per electron) at point $\mathbf{r}$ in space, that depends only on the density at this point.

$\epsilon_{xc}\big(n(\mathbf{r})\big)$ for the homogeneous electron gas is known accurately from Quantum Monte Carlo calculations. The exchange contribution is even known analytically.

$$\epsilon_x\big(n(\mathbf{r})\big) = \frac{3k_F}{4\pi}$$

$$k_F = \big(3\pi^2 n(\mathbf{r})\big)^2$$

$$\epsilon_{xc}\big(n(\mathbf{r})\big) = \frac{3}{4}\left(\frac{3}{\pi}n(\mathbf{r})\right)^{1/3}$$

$$\Rightarrow E_x[n] = \int n(\mathbf{r})\epsilon_x\big(n(\mathbf{r})\big) \, \mathrm{d}\mathbf{r}$$

$$= \int n(\mathbf{r})\frac{3}{4}\left(\frac{3}{\pi}n(\mathbf{r})\right)^{1/3} \, \mathrm{d}\mathbf{r}$$

$$= \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n(\mathbf{r})^{4/3} \, \mathrm{d}\mathbf{r} \tag{3.14}$$

Equation 3.14 is a very simple expression: All we need to know is the density at any given point in space and the exchange energy is then simply the integral over the density to the power 4/3. The exchange contribution to $V_{xc}(\mathbf{r})$ can be calculated straight forwardly as the functional derivative:

$$V_x(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} = \epsilon_x\big(n(\mathbf{r})\big) + n(\mathbf{r})\frac{\delta\epsilon_x\big(n(\mathbf{r})\big)}{\delta n(\mathbf{r})}$$
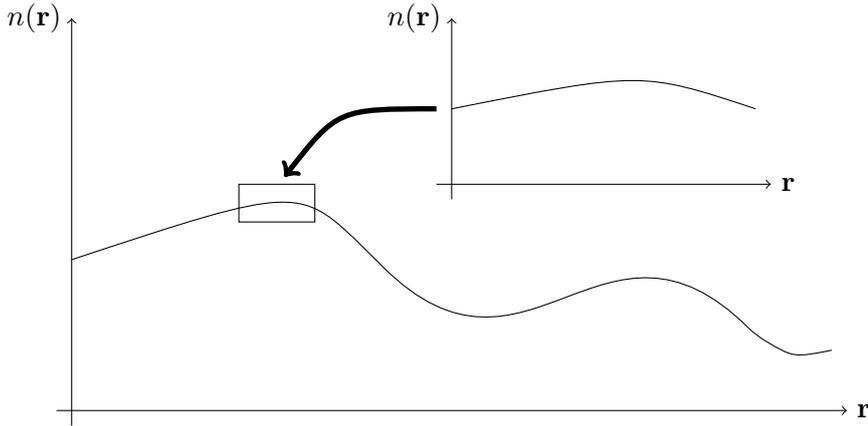


Figure 3.3: Local densities in an inhomogeneous system

$$\Rightarrow V_x(\mathbf{r}) = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{1/3}(\mathbf{r}) + n(\mathbf{r})\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{-2/3}(\mathbf{r})$$

$$= \left(\frac{3}{\pi}\right)^{1/3} n^{1/3}(\mathbf{r}) \tag{3.15}$$

Equation 3.15 is the final and very simple expression for the exchange contribution to the exchange-correlation potential in the local density approximation.

The correlation energy density for the homogeneous electron gas is not known analytically, but can be computed to very high precision using Quantum Monte Carlo[2] techniques, as shown in Figure 3.4.

An analytic expression for this behavior was first estimated by Wigner in 1938:
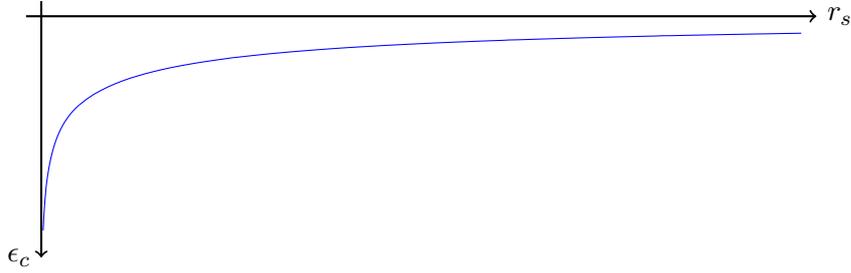


Figure 3.4: Exchange energy density in the homogeneous electron gas as a function of the density parameter $r_s$.

$$\epsilon_c[n] = -\frac{0.44}{r_s + 7.8}$$

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} = \frac{1.919}{k_F}$$

Later, better approximations became available, e.g. by Perdew and Zunger (based on work by Gell-Mann and Brückner for the $r_s \leq 1$ case):

$$\epsilon_c[n] = \begin{cases} A \ln r_s + B + C r_s \ln r_s + D r_s & r_s \leq 1 \\ \dfrac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s} & r_s > 1 \end{cases}$$

The numerical values for the parameters can be found in Ref [6]. The local density approximation can also be extended to the spin polarized case:

$$E_{xc}^{LSDA}[n^\uparrow, n^\downarrow] = \int n(\mathbf{r})\epsilon_{xc}\left(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})\right) d\mathbf{r}$$

---

[2]Like CI, QMC is a method that works directly with the many body wave function.

or, written in terms of the spin polarization $\eta(\mathbf{r})$:

$$\eta(\mathbf{r}) = \frac{n^{\uparrow}(\mathbf{r}) - n^{\downarrow}(\mathbf{r})}{n(\mathbf{r})}$$

$$E_{xc}^{LSDA}[n, \eta] = \int n(\mathbf{r})\epsilon_{xc}\bigg(n(\mathbf{r}), \eta(\mathbf{r})\bigg) \, \mathrm{d}\mathbf{r}$$

Now we need reference data for the spin polarized homogeneous electron gas and appropriate parametrizations, which can also be found in Ref [6].

**LDA summary**

The local density approximation is by construction exact or at least very accurate for the homogeneous electron gas and thus is expected to perform well for systems with slowly varying density, e.g. simple metals. Typically, it gives dissociation energies of molecules and cohesive energies of solids to within 10-20%. Bond lengths and lattice constants are typically too small by 1-2%. The evaluation of the exchange-correlation term is very efficient, because $E_{xc}$ and $v_{xc}$ are simple, analytic expressions of the density and therefore scale linearly with the system size. The orthonormalization of the Kohn-Sham orbitals in the solution of the KS-equations then formally requires $/mathcalO(N^3)$ operations. LDA therefore has a formal scaling one order better than Hartree-Fock and also a lower prefactor because $E_{xc}^{LDA}$ is cheaper to evaluate than $E_x^{HF}$. However, LDA has problems with self-interaction and systems with rapidly varying densities, e.g atoms and is therefore not suited for thermochemisty.

### 3.3.2 Generalized Gradient Approximations

LDA is based on the assumption of a homogeneous, but the radial density of e.g. an Argon (see Figure 3.5) atom is far from this assumption and has a clearly visible shell
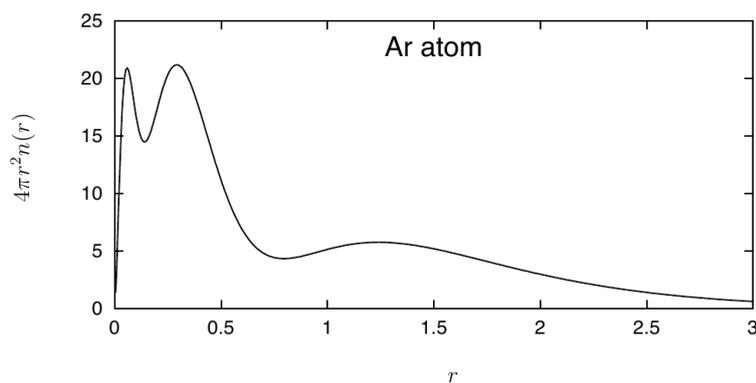


Figure 3.5: Radial density of an isolated Argon atom (taken from Ref [7])

structure. The idea to overcome the shortcomings of LDA is to include the gradients of the electron density in $E_{xc}$:

$$E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int n(\mathbf{r})\epsilon_{xc}\left(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}), \left|\nabla n^\uparrow(\mathbf{r})\right|, \left|\nabla n^\downarrow(\mathbf{r})\right|\right) \, d\mathbf{r}$$

$$= \int \epsilon_x^{HEG}[n] \underbrace{F_{xc}\left(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}), \left|\nabla n^\uparrow(\mathbf{r})\right|, \left|\nabla n^\downarrow(\mathbf{r})\right|\right)}_{F_{xc} \text{ scales exchange through correlation}} \, d\mathbf{r}$$

where GGA denotes the "Generalized Gradient Approximation". Instead of using the gradient directly, it makes sense with a scaled gradient:

$$S(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{2k_F(\mathbf{r})n(\mathbf{r})}$$

which measures the gradient on the scale of the density itself. A major advantage of this rescaling is that the gradient remains well-behaved even close to the nucleus, as shown in Figure 3.6.
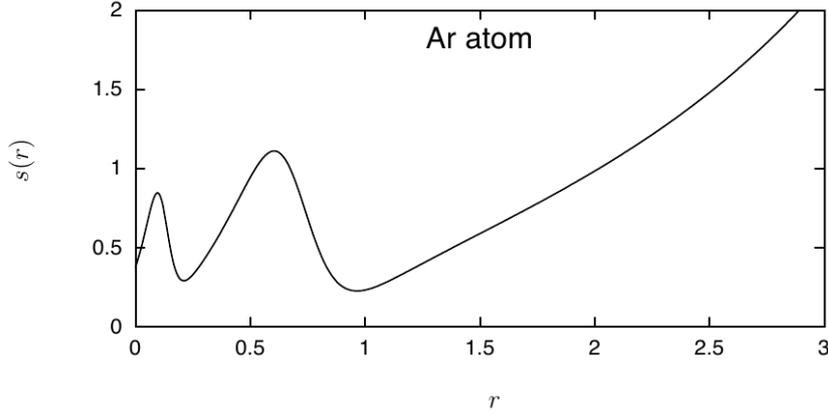


Figure 3.6: Rescaled density gradient of an isolated Argon atom (taken from Ref [7])

$$E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int \epsilon_x^{HEG}[n]F_{xc}\left(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}), S^\uparrow(\mathbf{r}), S^\downarrow(\mathbf{r})\right) \, d\mathbf{r}$$

There exists no unique form or parametrization for $F_{xc}$ and therefore many different parametrizations have been proposed. Most of them fall into two categories:

- satisfy a certain number of exact constraints

- fitted to a benchmark data set

In general, GGAs work best in the regime for which they were designed for.

### 3.3.3 Coupling Constant integration, exchange correlation-hole or "Why is LDA so successful also in inhomogeneous systems?"

Let us look at a coupling constant integration, where we rescale the electronic interaction:

$$\mathcal{H}_\lambda = T + \lambda V^{ee} \int n(\mathbf{r}) V_\lambda(\mathbf{r}) \, d\mathbf{r}$$

where we adjust the external potential $V_\lambda(\mathbf{r})$ such that the density is fixed to $n(\mathbf{r})$ for all coupling strengths $\lambda$. For $\lambda = 1$ we recover the full Hamiltonian of the interacting system and thus the full many-body wave function. For $\lambda = 0$ on the other hand, we obtain the Hamiltonian of the non-interacting Kohn-Sham system.

| | $\mathcal{H}_\lambda$ | $\Phi_\lambda$ | $V_\lambda(\mathbf{r})$ |
|---|---|---|---|
| $\lambda = 1$ | $\mathcal{H}_e$ | $\Psi$ | $V(\mathbf{r})$ |
| $\lambda = 0$ | $\mathcal{H}_{KS}$ | $\Phi_{KS}^{SD}$ | $V_{eff}^{KS}(\mathbf{r})$ |

$$
\begin{aligned}
E_{xc} &= T - T_s + V^{ee} - E_H \\
&= T + V_{\lambda=1}^{ee} - \left[ T_s + V_{\lambda=0}^{ee} \right] - E_H \\
&= \langle \Phi_\lambda | T + \lambda V^{ee} | \Phi_\lambda \rangle \Big|_{\lambda=1} - \langle \Phi_\lambda | T + \lambda V^{ee} | \Phi_\lambda \rangle \Big|_{\lambda=0} - E_H \\
&= \int_0^1 \frac{d}{d\lambda} \langle \Phi_\lambda | T + \lambda V^{ee} | \Phi_\lambda \rangle \, d\lambda - E_H
\end{aligned}
\tag{3.16}
$$

Since $E_\lambda = \langle \Phi_\lambda | T + \lambda V^{ee} | \Phi_\lambda \rangle$, we now can use the Hellmann-Feynman theorem. The derivative is then:

$$
\frac{dE_\lambda}{d\lambda} = \underbrace{\frac{d}{d\lambda'} \langle \Phi_\lambda | T + \lambda V^{ee} | \Phi_\lambda \rangle \Big|_{\lambda'=\lambda}}_{=0 \text{ due to variational principle}} + \left\langle \Phi_\lambda \left| \frac{dH_\lambda}{d\lambda} \right| \Phi_\lambda \right\rangle
$$

$$
\Rightarrow \frac{dE_\lambda}{d\lambda} = \left\langle \Phi_\lambda \left| \frac{dH_\lambda}{d\lambda} \right| \Phi_\lambda \right\rangle
\tag{3.17}
$$

Inserting Equation 3.17 into 3.16 then yields

$$
E_{xc} = \int_0^1 \langle \Phi_\lambda | V^{ee} | \Phi_\lambda \rangle - E_H
\tag{3.18}
$$

This equation implies that we can obtain the exchange-correlation energy by a coupling-constant integration over the electronic interaction. This coupling constant integration incorporates the difference between $T$ and $T_s$ in $E_{xc}$.

To compute the integrals of $T$ and $V^{ee}$ over the wave function we introduce the 1- and 2-electron density matrices.

$$\varrho_1(\mathbf{r}\sigma, \mathbf{r}'\sigma) := N \int \ldots \int \Phi^*(\mathbf{r}'\sigma, \mathbf{x_2} \ldots \mathbf{x}_N) \Phi^*(\mathbf{r}\sigma, \mathbf{x_2} \ldots \mathbf{x}_N) \, \mathrm{d}\mathbf{x_2} \ldots \, \mathrm{d}\mathbf{x}_N$$

$$\varrho_2(\mathbf{r}, \mathbf{r}') := N(N-1) \sum_{\sigma, \sigma_2} \int \ldots \int \left| \Phi(\mathbf{r}\sigma, \mathbf{r}'\sigma_2, \ldots \mathbf{x}_N) \right| \, \mathrm{d}\mathbf{x_3} \ldots \, \mathrm{d}\mathbf{x}_N$$

The density is then simply $n(\mathbf{r}) = \sum_{sigma} \varrho_1(\mathbf{r}\sigma, \mathbf{r}\sigma)$ and we have

$$\langle \Phi | T | \Phi \rangle = -\frac{1}{2} \sum_{\sigma} \int \nabla^2 \varrho_1(\mathbf{r}\sigma, \mathbf{r}'\sigma) \Big|_{\mathbf{r}'=\mathbf{r}} \, \mathrm{d}\mathbf{r} \tag{3.19}$$

$$\langle \Phi | V^{ee} | \Phi \rangle = \frac{1}{2} \iint \frac{\varrho_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' \, \mathrm{d}\mathbf{r} \tag{3.20}$$

In other words, if we knew the 1- and 2-electron density, we could calculate the ground-state exactly. This is the reason, why some effort is devoted to density-matrix functional theory.

$\varrho_2(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\mathbf{r}' \, \mathrm{d}\mathbf{r}$ is the joint probability of finding an electron in volume $\mathrm{d}\mathbf{r}$ at $\mathbf{r}$ and a second electron in $\mathrm{d}\mathbf{r}'$ at $\mathbf{r}'$. By standard probability theory, this is the product of the probability of finding an electron in $\mathrm{d}\mathbf{r}$ and the conditional probability $n_2(\mathbf{r}, \mathbf{r}')$ of finding an electron in $\mathrm{d}\mathbf{r}$ given there was one in $\mathrm{d}\mathbf{r}'$:

$$\varrho_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) n_2(\mathbf{r}, \mathbf{r}')$$

Since $\int \varrho_2(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\mathbf{x}' = (N-1)n(\mathbf{r})$ holds, we obtain:

$$\int \varrho_2(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\mathbf{r}' = N - 1$$

which is indicative of a hole, i.e. one electron less. For $\Phi^\lambda$ we now define the exchange-correlation hole $n_2(\mathbf{r}|\mathbf{r}')$:

$$n_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) + n_{xc}^\lambda(\mathbf{r}, \mathbf{r}') \tag{3.21}$$

$$\underbrace{\int n_2(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\mathbf{r}'}_{=N-1} = \underbrace{\int n(\mathbf{r}) \, \mathrm{d}\mathbf{r}'}_{=N} + \underbrace{\int n_{xc}^\lambda(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\mathbf{r}'}_{=-1} \tag{3.22}$$

This tells us that if an electron is definitely at position $\mathbf{r}$, it is missing from the rest of the system. The exchange-correlation energy can now be written as [8]:

$$E_{xc}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}) \bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \tag{3.23}$$

$$\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 n_{xc}^\lambda(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\lambda$$
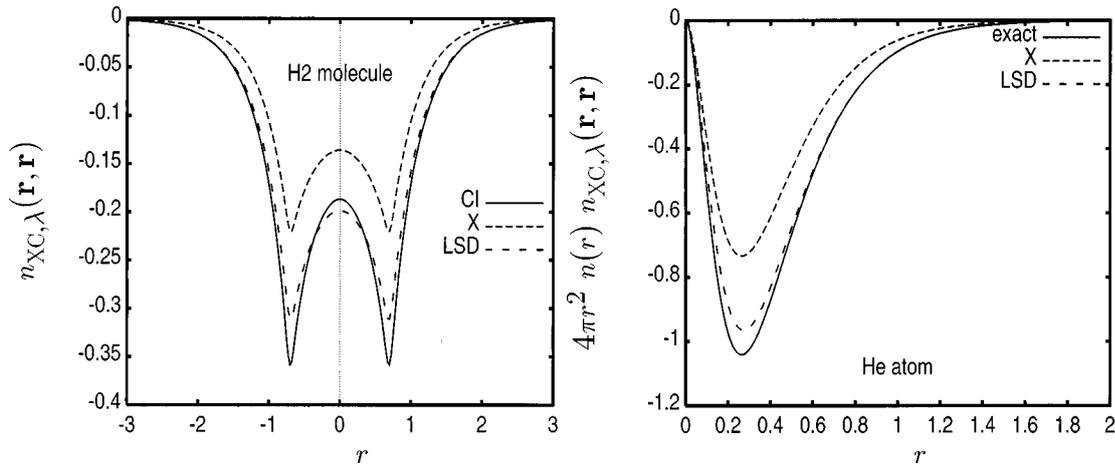
Figure 3.7: spherical average of the XC-hole in $H_2$ and $He$ for LSDA [9]

The exchange-correlation energy is just the electrostatic interaction between each electron and the coupling constant averaged exchange-correlation-hole that surrounds it. The hole is created by three different effects:

**Pauli Principle:** electrons with equal spin are kept apart in space

**Self-interaction:** an electron cannot interact with itself

**Coulomb repulsion:** keeps two electrons apart in space

We now can make the variable transformation $\mathbf{R} = \mathbf{r}' - \mathbf{r}$ in Equation 3.23:

$$E_{xc}[n] = \frac{1}{2} \int n(\mathbf{r}) \int R^2 \frac{1}{R} \underbrace{\int \bar{n}_x c(\mathbf{r}, \mathbf{R})\, \mathrm{d}\Omega}_{\text{spherical average}} \, \mathrm{d}R\, \mathrm{d}\mathbf{r}$$

This means that the exchange-correlation energy only depends on the spherical average of the XC-hole. This is of course much easier to approximate than the full hole. In LSDA the XC-hole is spherically symmetric:

$$n_{xc}^{LSDA}(\mathbf{r}, \mathbf{r}') = n_{xc}^{HEG}\left(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r}'), \left|\mathbf{r} - \mathbf{r}'\right|\right)$$

In practice, this spherical symmetry deviates considerably from the shape of the actual hole, but the spherical average is well reproduced as shown in Figure 3.7.

## 3.4 Self-interaction

Our DFT energy expression is

$$E_{tot} = T_s[n] + E_{ext}[n] + E_H[n] + E_{xc}[n]$$

Let us recall that in $E_H$ we summed over all occupied single particle states of the system for convenience:

$$E_H = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' = \frac{1}{2} \sum_{i,j} \int \frac{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'$$

$$= \frac{1}{2} \sum_{i,j} \int \frac{|\psi_i(\mathbf{r})|^2 \, |\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'$$

So when $i = j$ an electron interacts with itself and we have "self-interaction". In Hartree-Fock, this term is exactly cancelled by the exchange energy:

$$E_x = -\frac{1}{2} \sum_{i,j} \int \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'$$

For $i = j$ these terms exactly cancel the self-interaction in the Hartree energy. However, for LDAs and GGAs, these terms do not cancel:

$$E_{xc}^{LDA/GGA} = \int n(\mathbf{r})\epsilon_{xc}\left( n(\mathbf{r}), \mathbf{r}, |\nabla n(\mathbf{r})|, \dots \right) \mathrm{d}\mathbf{r}$$

$$= \sum_i \int |\psi_i(\mathbf{r})|^2 \, \epsilon_{xc}\left( n(\mathbf{r}), \mathbf{r}, |\nabla n(\mathbf{r})|, \dots \right) \mathrm{d}\mathbf{r}$$

Perdew and Zunger defined a 1-electron self-interaction error on this basis:[6]

$$\delta_i = \frac{1}{2} \int \frac{|\psi_i(\mathbf{r})|^2 \, |\psi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' + E_{xc}\left[ |\psi_i(\mathbf{r})|^2 \right]$$

In general, $\delta_i$ is not zero. As we have seen earlier in the Hartree-Fock chapter, the self-interaction error has a tendency to delocalize, it is therefore largest for localized states.

## 3.5 Hybrid functionals

As we have seen, Hartree-Fock contains too much exact exchange, while LDA/GGA suffer from the self-interaction error. A pragmatic solution to this problem is the "hybrid functional", as it was first adopted in Quantum Chemistry:

$$E_{xc}^{hyb} = E_{xc}^{DFT} + \alpha \left( E_x^{HF} - E_x^{DFT} \right)$$

In this simplest form a portion of the DFT exchange is replaced by the exact exchange, while correlation remains on the DFT level. A popular choice is the PBE functional with

$\alpha = 0.25$, the result is known as PBE0. There also exist more complex parametrizations like the popular B3LYP functional.

Another option is the range-seperation of the exact exchange:

$$\frac{1}{r} = \underbrace{\frac{1}{r}\text{erf}(r)}_{\text{short range}} + \underbrace{\frac{1}{r}\text{erfc}(r)}_{\text{long range}}$$

Now one can either replace the long- or the short-range with DFT exchange.

In the hybrid functionl formalism, the single particle equations are usually derived like in Hartree-Fock with $\frac{\delta E}{\delta \phi^*}$ and not like in DFT by $\frac{\delta E}{\delta n}$:

$$V_{xc}^{hyb}(\mathbf{r}, \mathbf{r}') = [V_{xc}(\mathbf{r}) - \alpha V_x(\mathbf{r})]\,\delta(\mathbf{r} - \mathbf{r}') + \alpha \Sigma_x^{HF}(\mathbf{r}, \mathbf{r}')$$

So we end up with a non-local potential.

## 3.6 Excitations in DFT and HF
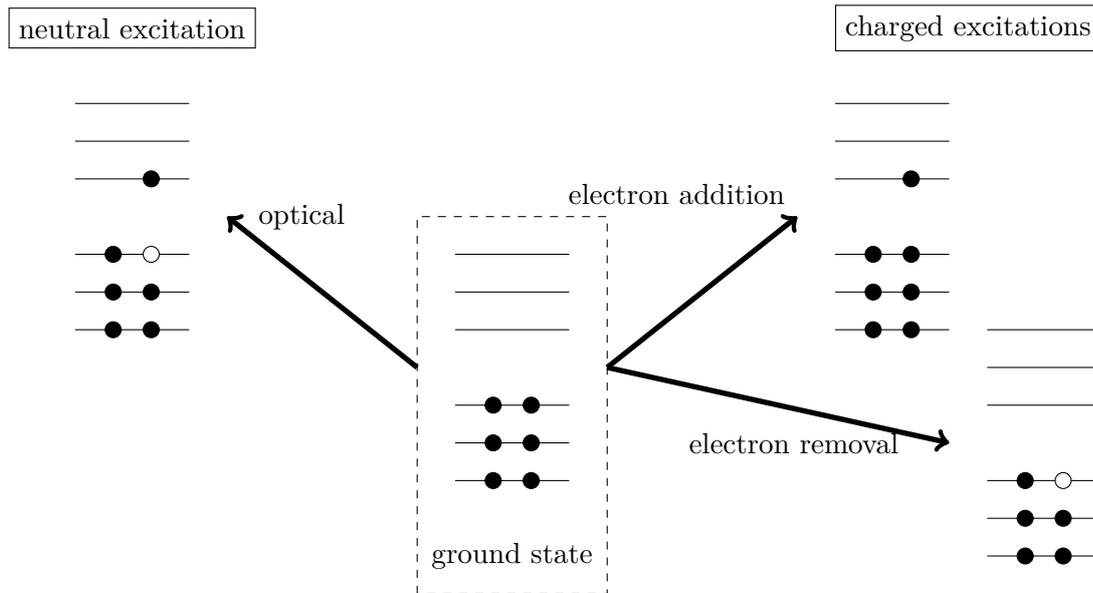


Figure 3.8: Excitation processes

The excitation energy is generally defined as $\epsilon_s = E_{final}^{tot} - E_{initial}^{tot}$. In the case of neutral excitations (see Figure 3.8) the excitation energies are $\epsilon_s = E(N, s) - E(N)$. In the case of wave function based approaches the $E(N, s)$ are the higher eigenvalues of the Schrödinger equation. Charged excitations that remove electrons yield the ionization energies $\epsilon_s = E(N-1, s) - E(N)$ and those that add electrons yield the electron affinity

$\epsilon_s = E(N) - E(N+1, s)$. These energies cannot be derived from the spectrum of the Hamiltonian.

### 3.6.1 Koopmans' theorem and the meaning of Hartree-Fock eigenvalues

Let us reconsider the HF eigenvalue equation (Equation 2.30):

$$\epsilon_n \varphi_n(\mathbf{x}) = h(\mathbf{r})\varphi_n(\mathbf{x}) - \int V_H(\mathbf{r}) + \Sigma^{HF} \varphi_n(\mathbf{x}') \, \mathrm{d}\mathbf{x}'$$

$$\Rightarrow \epsilon_m \delta_{mn} = \iint \varphi_m^*(\mathbf{x}) \left[ h(\mathbf{x}) + \sum_i^N \frac{\phi_i^*(\mathbf{x}')\phi_i(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \right] \varphi_n(\mathbf{x}) \, \mathrm{d}\mathbf{x}' \, \mathrm{d}\mathbf{x}$$

$$+ \iint \varphi_m^*(\mathbf{x}) \left[ \sum_i^N \frac{\phi_i^*(\mathbf{x}')\phi_i(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} \right] \varphi_n(\mathbf{x}') \, \mathrm{d}\mathbf{x}' \, \mathrm{d}\mathbf{x}$$

$$\Rightarrow \epsilon_m = h_{mm} + \sum_i^N \langle mi|mi \rangle - \langle mi|im \rangle \tag{3.24}$$

Now let us consider an occupied state "a":

$$\epsilon_a = h_{aa} + \sum_i^N \langle ai|ai \rangle - \langle ai|ia \rangle$$

Equation 3.24 shows that the eigenvalue belonging to this state is its kinetic and external energy plus Coulomb and exchange from all remaining electrons, because the $i = a$ term vanishes. This suggests that $\epsilon_a$ is the removal energy of electron $a$ or the ionization energy (or "ionization potential" $IP$) if "a" is the highest occupied state.

$$IP = E(N-1) - E(N)$$
$$\text{in HF:} \quad E(N-1) = \langle \Phi_{N-1}^{SD} | \mathcal{H} | \Phi_{N-1}^{SD} \rangle$$
$$E(N) = \langle \Phi_N^{SD} | \mathcal{H} | \Phi_N^{SD} \rangle$$

In general, the two slater determinants are not composed of the same orbitals! But let us assume for a moment that they are and we removed electron $c$:

$$E(N) = \sum_a^N \left[ h_{aa} + \frac{1}{2} \sum_i^N \langle ai|ai \rangle - \langle ai|ia \rangle \right]$$

$$E_c(N-1) = \sum_{a \neq c}^N \left[ h_{aa} + \frac{1}{2} \sum_{i \neq c}^N \langle ai|ai \rangle - \langle ai|ia \rangle \right]$$

$$\Rightarrow IP_c = E_c(N-1) - E(N)$$

$$= -\langle c|h|c \rangle - \sum_i^N \langle ci|ci \rangle - \langle ci|ic \rangle = -\epsilon_c$$

The eigenvalues of occupied Hartree-Fock orbitals are the negative ionization energies, provided the orbitals are not allowed to relax. For the unoccupied states we can derive an analogue expression for the electron affinity $EA$:

$$EA_r = E(N) - E_r(N+1) = -\epsilon_r$$

**Koopmans' theorem**

Given an N-electron Hartree-Fock single determinant $\Phi_N^{SD}$ with occupied and unoccupied (virtual) spin orbital energies $\epsilon_a$ and $\epsilon_r$, then the ionization potential to produce an $(N-1)$-electron single determinant $\Phi_{a,N-1}^{SD}$ with identical spin orbitals, obtained by removing an electron from spin orbital $\varphi_a$ and the electron affinity to produce an $(N+1)$-electron Slater determinant $\Phi_{r,N-1}^{SD}$ with identical spin orbitals, obtained by adding an electron to spin orbital $\varphi_r$, are just $-\epsilon_a$ and $-\epsilon_r$, respectively.

### 3.6.2 Excitation Energies in DFT

DFT is a ground state theory and as such only the ionization potential $I = E(N-1) - E(N)$, the electron affinity $A = E(N) - E(N+1)$ and the gab $E_{gap} = I - A$ can be computed exactly. All quantities involing an "s" are excited states of the system that cannot be expressed as differences of two ground states. When one tries to prepare an excited state $E(N, s)$, there are several problems:

- Finding a suitable constraint to keep the system in the state "s" may not be possible or it may not survive the self-consistent cycle.

- Excited state densities are not unique (unlike ground state densities), i.e. there is no Hohenberg-Kohn theorem for excited states.

What about the DFT eigenvalues? In Hartree-Fock we have Koopmans' Theorem, but there is no counterpart in DFT. But it can be proven that the highest Kohn-Sham eigenvalue of a finite system equals the negative of the ionization potential $I = -\epsilon_N^{KS}(N)$. A hand-waving argument is: The asymptotic long-range density of a bound system is governed by the occupied state with the highest eigenvalue. Since the density is supposed to be exact, so must the eigenvalue be. A more rigorous proof can be found in [10, 11]. For approximate functionals, this relation will in general not be true.

**Janak's Theorem**

Janak's Theorem[12] establishes a relation between the Kohn-Sham eigenvalues and the derivative of the total energy:

$$\frac{\partial E}{\partial f_i} = \epsilon_i \tag{3.25}$$

where $f_i$ is the occupation number of a given state.

Proof: Let $\varphi_i$ be the KS state that solves

$$\left[-\frac{\nabla^2}{2} + V_{KS}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$$

The corresponding density is build according to $n(\mathbf{r}) = \sum_i f_i\,|\varphi(\mathbf{r})|^2$. Then we have:

$$\frac{\partial E[n]}{\partial f_i} = \frac{\partial}{\partial f_i}\left[-\frac{1}{2}f_i\int\varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})\,\mathrm{d}\mathbf{r} + E_{ext}[n] + E_H[n] + E_{xc}[n]\right]$$

$$= -\frac{1}{2}\int\varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})\,\mathrm{d}\mathbf{r} + \int\frac{\delta}{\delta n(\mathbf{r})}\left[E_{ext}[n] + E_H[n] + E_{xc}[n]\right]\frac{\partial n(\mathbf{r})}{\partial f_i}\,\mathrm{d}\mathbf{r}$$

$$= \int\varphi_i^*(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \epsilon_i$$

If we now integrate Janak's Theorem over $\mathrm{d}f$ and use the midpoint approximation, we obtain:

$$E(N+1, i) - E(N) = \int_0^1\epsilon_i(f)\,\mathrm{d}f \approx \epsilon_i(0.5)$$

Excitation energies are therefore approximately given by the value of the eigenvalue at half occupation. This is also known as a Slater or Slater-Janak's transition state. The problem remains that for all but the highest (lowest) occupied (unoccupied) state, occupations need to be suitably constrained.

### Derivative Discontinuity

Let us consider the gap of a large, but finite system (so large that it could be a solid). The gap is given by:

$$E_{gap} = I - A = E(N+1) - 2E(N) + E(N-1)$$

We also know that the highest occupied state in exact DFT is exact:

$$E_{gap} = \epsilon_{N+1}^{KS}(N+1) - \epsilon_N^{KS}(N)$$
$$= \underbrace{\epsilon_{N+1}^{KS}(N+1) - \epsilon_{N+1}^{KS}(N)}_{\Delta_{xc}} + \underbrace{\epsilon_{N+1}^{KS}(N) - \epsilon_N^{KS}(N)}_{E_{gap}^{KS}}$$

The KS-gap is therefore not the real gap of the system, but what is $\Delta_{xc}$? Because our system is very large, we have $N \gg 1 \rightarrow \Delta n(\mathbf{r}) \rightarrow 0$ for $N \rightarrow N+1$, i.e. the density change is infinitesimal. The Hartree and external potential therefore will not change. The kinetic energy will only change when the orbitals change, but we consider

cases where they do not change. Therefore, $\Delta_{xc}$ can only come from changes in the exchange-correlation potential:

$$\Delta_{xc} = \left( \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_N + 1 - \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_N \right) + \mathcal{O}\left( \frac{1}{N} \right)$$

The derivative of $E_{xc}$ with respect to the particle number changes discontinuously and $V_{xc}$ therefore changes by a constant $\Delta_{xc}$. Even exact KS calculations will not capture the gap, if only the KS-eigenvalues are considered. For the latest news about derivative discontinuities see reference [13].

# 4 Green's Function Theory

In this chapter we will briefly review methods based on Green's function, in particular the *GW* approach. For Green's function theory it is convenient to work with second quantization, therefore we will start this chapter with a brief review of what you should remember from your advanced quantum mechanics courses.

## 4.1 Second Quantization

The many-body wave function $\Phi_N = |k_1, k_2 \ldots k_N\rangle$ we used so far can also be expressed in terms of the fermionic creation and annihilation operators.
The creation operator $a_k^\dagger$ creates a particle in the state $k$ and the annihilation operator $a_k$ annihilates one (creates a hole) in state $k$.

$$a_k^\dagger |k_1, k_2 \ldots k_N\rangle = |k, k_1, k_2 \ldots k_N\rangle$$
$$a_k |k, k_1, k_2 \ldots k_N\rangle = |k_1, k_2 \ldots k_N\rangle$$

These operators have a set of anti-commutation relations.

$$\left\{ a_k, a_{k'}^\dagger \right\} = \delta_{k,k'}$$
$$\{a_k, a_{k'}\} = \left\{ a_k^\dagger, a_{k'}^\dagger \right\} = 0$$

Based on these operators, which act on states, we can also define operators which act in real-space, the so called field-operators with the same anti-commutators:

$$\psi^\dagger(\mathbf{x}) = \sum_k a_k^\dagger \varphi_k^*(\mathbf{x})$$
$$\psi(\mathbf{x}) = \sum_k a_k \varphi_k(\mathbf{x})$$
$$\left\{ \psi(\mathbf{x}), \psi^\dagger(\mathbf{x}') \right\} = \delta(\mathbf{x}, \mathbf{x}')$$
$$\left\{ \psi(\mathbf{x}), \psi(\mathbf{x}') \right\} = \left\{ \psi^\dagger(\mathbf{x}), \psi^\dagger(\mathbf{x}') \right\} = 0$$

The Hamiltonian in terms of these operators is then given as:

$$\mathcal{H} = \sum_{ij} \langle i|h|j\rangle \, a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} (ij|kl) \, a_i^\dagger a_j^\dagger a_k a_l$$

For the following discussion, it is convenient to switch to the Heisenberg notation for the field operators:

$$\psi(\mathbf{x}, t) = e^{i\mathcal{H}t}\psi(\mathbf{x})e^{-i\mathcal{H}t}$$

If we now apply the field operator to the many-body states:

$$\begin{aligned}
\langle N|\psi(\mathbf{x}, t)|N+1, s\rangle &= \left\langle N\left|e^{i\mathcal{H}t}\psi(\mathbf{x})e^{-i\mathcal{H}t}\right|N+1, s\right\rangle \\
&= \left\langle N\left|e^{iE(N)t}\psi(\mathbf{x})e^{-iE(N+1,s)t}\right|N+1, s\right\rangle \\
&= e^{-\epsilon_s t}f_s(\mathbf{x}) \\
\epsilon_s &= E(N) - E(N+1, s) \\
f_s(\mathbf{x}) &= \left\langle N\left|\sum_k a_k \varphi_k(\mathbf{x})\right|N+1, s\right\rangle \\
&= \langle N|\varphi_s(\mathbf{x})|N\rangle = \varphi_s(\mathbf{x})
\end{aligned}$$

## 4.2 The single-particle Green's Function

The single-particle Green's function is defined as:

$$\begin{aligned}
G(\mathbf{x}t, \mathbf{x}'t') &= -i\left\langle N\left|\hat{T}\left\{\psi(\mathbf{x}, t)\psi^\dagger(\mathbf{x}', t')\right\}\right|N\right\rangle \\
&= -i\left\langle N\left|\psi(\mathbf{x}, t)\psi^\dagger(\mathbf{x}', t')\right|N\right\rangle\Theta(t - t') \\
&\quad + i\left\langle N\left|\psi^\dagger(\mathbf{x}', t')\psi(\mathbf{x}, t)\right|N\right\rangle\Theta(t' - t)
\end{aligned}$$

where $\hat{T}$ denotes the time ordering operator. In a physical picture, the Green's function for $t > t'$ creates an electron to the system at $\mathbf{x}'$ and $t'$ and propagates it to $\mathbf{x}$, where it is removed at time $t$. For $t < t'$ the same thing happens for a hole. The Green's function is therefore an electron and hole propagator.

Making use of the Heisenberg notation, we can rewrite the Green's function as:

$$\begin{aligned}
G(\mathbf{x}t, \mathbf{x}'t') &= -i\left\langle N\left|e^{i\mathcal{H}t}\psi(\mathbf{x})e^{-i\mathcal{H}t}e^{i\mathcal{H}t'}\psi^\dagger(\mathbf{x}')e^{-i\mathcal{H}t'}\right|N\right\rangle\Theta(t - t') \\
&\quad + i\left\langle N\left|e^{i\mathcal{H}t'}\psi^\dagger(\mathbf{x}')e^{-i\mathcal{H}t'}e^{i\mathcal{H}t}\psi(\mathbf{x})e^{-i\mathcal{H}t}\right|N\right\rangle\Theta(t' - t) \\
&= -i\left\langle N\left|\psi(\mathbf{x})e^{-i(\mathcal{H}-E(N))(t-t')}\psi^\dagger(\mathbf{x}')\right|N\right\rangle\Theta(t - t') \\
&\quad + i\left\langle N\left|\psi^\dagger(\mathbf{x}')e^{-i(\mathcal{H}-E(N))(t'-t)}\psi(\mathbf{x})\right|N\right\rangle\Theta(t' - t)
\end{aligned}$$

Now we insert the completeness relation for the Fock-space:

$$\mathbf{1} = |vac\rangle\langle vac| + \sum_s |\Phi_s^1\rangle\langle\Phi_s^1| + \ldots + \sum_s |\Phi_s^N\rangle\langle\Phi_s^N| + \ldots$$

$$\Rightarrow G(\mathbf{x}t, \mathbf{x}'t') = -i\sum_s \langle N|\psi(\mathbf{x})|N+1, s\rangle e^{-i(E(N+1,s)-E(N))(t-t')}$$

$$\times \langle N+1, s|\psi^\dagger(\mathbf{x}')|N\rangle \Theta(t-t')$$

$$+ i\sum_s \langle N|\psi(\mathbf{x})|N-1, s\rangle e^{-i(E(N-1,s)-E(N))(t'-t)}$$

$$\times \langle N-1, s|\psi^\dagger(\mathbf{x}')|N\rangle \Theta(t'-t)$$

In a more compact notation, we can write:

$$G(\mathbf{x}t, \mathbf{x}'t') = -i\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')e^{-i\epsilon_s(t-t')}\left[\Theta(t-t')\Theta(\epsilon_s-\mu) - \Theta(t'-t)\Theta(\mu-\epsilon_s)\right]$$

where $\mu$ denotes the chemical potential or Fermi-level and

$$\epsilon_s = E(N+1, s) - E(N) \qquad f_s(\mathbf{x}) = \langle N|\psi(\mathbf{x})|N+1, s\rangle \qquad \text{for } \epsilon_s > \mu$$
$$\epsilon_s = E(N) - E(N-1, s) \qquad f_s(\mathbf{x}) = \langle N-1, s|\psi(\mathbf{x})|N\rangle \qquad \text{for } \epsilon_s < \mu$$

The energies $\epsilon_s$ correspond to the true many-body excitation energies!
For explicitly time-independent Hamiltonians, $G$ only depends on $t - t' = \tau$. Therefore we can switch to the frequency axis:

$$\Theta(\pm\tau) = \lim_{\eta\to 0} \pm\frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{e^{i\omega\tau}}{\omega \pm i\eta}\,\mathrm{d}\omega$$

$$\Rightarrow G(\mathbf{x}, \mathbf{x}', \omega) = \lim_{\eta\to 0^+}\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')\left[\frac{\Theta(\epsilon_s-\mu)}{\omega - (\epsilon_s - i\eta)} + \frac{\Theta(\mu-\epsilon_s)}{\omega - (\epsilon_s + i\eta)}\right]$$

The true many-body excitation energies are the poles of the Green's function! The total energy is also accessible through the Green's function by means of the Galitskii-Migdal formula: [14]

$$E_0 = -\frac{i}{2}\int \lim_{\mathbf{x}'\to\mathbf{x}}\lim_{t'\to t^+}\left[\frac{\partial}{\partial t} - h(\mathbf{x})\right]G(\mathbf{x}t, \mathbf{x}'t')$$

We now have a quantity that gives us both the total energy, as well as charged one-particle excitations. But how can we compute it? The solution is Hedin's GW formalism (presented without proof [15]), which is Dyson's equation starting from an initial Green's function $G_0$ (e.g from DFT/HF):

$$G = G_0 + G_0\Sigma G$$

$$\Sigma(\mathbf{r}, \mathbf{r}', t) = iG(\mathbf{r}, \mathbf{r}', t)W(\mathbf{r}, \mathbf{r}', t) \qquad\qquad\qquad \text{self-energy}$$

$$W(\mathbf{r}, \mathbf{r}', t) = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega)\frac{1}{|\mathbf{r}'' - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}'' \qquad\qquad \text{screened Coulomb interaction}$$

$$\epsilon(\mathbf{r}, \mathbf{r}'', \omega) = \delta(\mathbf{r} - \mathbf{r}') - \int \frac{1}{|\mathbf{r} - \mathbf{r}''|}P(\mathbf{r}'', \mathbf{r}', \omega)\, \mathrm{d}\mathbf{r}'' \qquad\qquad \text{dielectric funtion}$$

$$P(\mathbf{r}'', \mathbf{r}', \omega) = -iG(\mathbf{r}, \mathbf{r}', t)G(\mathbf{r}', \mathbf{r}, -t) \qquad\qquad\qquad \text{polarizability}$$

We now work with the screened rather than the bare Coulomb-interaction!. Dyson's equation can be rewritten as:

$$[h(\mathbf{r}) + V_H(\mathbf{r})]\,\varphi_s(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_s)\varphi_s(\mathbf{r}')\, \mathrm{d}\mathbf{r}' = \epsilon_s\varphi_s(\mathbf{r})$$

which is reminiscent of the HF equation.

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