Computational Electronic Structure Theory

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Contents

1 Introduction 1

2 The Schrödinger Equation 2
2.1 Born-Oppenheimer Approximation 3
2.2 Antisymmetry or Pauli Exclusion Principle 5

3 Wave function based approaches 6
3.1 Hartree theory 6
3.2 Hartree and Hartree Fock 9
3.2.1 Closed shell Hartree Fock 15
3.2.2 Hartree Fock in real-space 16
3.2.3 Hartree Fock in a basis 18
3.2.4 Performance of Hartree-Fock 25
3.2.5 Koopmann's Theorem and the meaning of Hartree-Fock eigenvalues 30
3.3 Form of the exact wave function and configuration interaction 31
3.4 A brief excursion into pertubation theory 34

4 Density functional theory 37
4.1 Kohn-Sham's equations 37
4.2 Hohenberg-Kohn Theorem 38
4.3 The local density approximation 41
4.4 Generalized Gradient Approximation 43
4.5 Self-interaction and exact-exchange 44
4.6 Hybrid functionals 47
4.7 DFT and excitation energies 48

5 Green's function theory 54
5.1 Second Quantization 54
5.2 Green's function theory 56
5.2.1 The Single-Particle Green's Function 56
5.2.2 Spectral Representation of the Green's Function 57
5.2.3 Expectation value of single particle operators 58
5.3 The self-energy 61
5.4 Hedin's equations 62

1 Introduction

Computational electronic Structure Theory

Computational:

The ever growing field of Computational electronic structure theory combines theoretical physics and chemistry, math and computer science. It forms an intersticial between theoretical and experimental physics and chemistry, gaining more and more recognition as a discipline of its own. It conqueres the challenges that arise from the availability of faster and novel computer hardware (e.g. massively paralell systems, GPU, ...).

Electronic structure:

The electrons are the 'glue' that keeps matter together. They determine shape and color of all things that surround us. On the atomic level they determine the molecular and crystal structure. On the level of transport properties conductivity, heat, capacity, phase diagrams and reactivity are due to electronic interactions.

We distinguish between ground state properties, e.g. atomic structure, forces, reaction barriers and exited states which give rise to spectroscopic properties and the response of the system to external pertubations.

Theory:

It is extremly non-trivial to find a theory from firts principle, a theory that does not need additional parameters, to describe the electronic problem. The field is under constant and active development. challenging current research topics include the incorporation of finite temperatures, bond breaking and making, high T_c superconductivity. Of special interest are strong correlations because strong electron-electron interactions are not described by an effective medium.

The overall goal is to have a theory that accurately and reliably predicts material properties from first principles (and therefore has to be parameter free!).

2 The Schrödinger Equation

For a system of electrons and nuclei the non-relativistic time-independent Schödinger equation is:

$$H\Psi = E\Psi \tag{2.1}$$

where the Hamiltonian is:

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{M}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N}\sum_{a=1}^{M}\frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|}}_{H_{elec}} \tag{2.2}$$

$$-\sum_{a=1}^{M}\frac{1}{2M_a}\nabla_a^2 + \sum_{a=1}^{M}\sum_{b>a}^{M}\frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} \tag{2.3}$$

r_i : position of the electrons

R_a : position of the nuclei

Z_a : charge of the nuclei

and we have used atomic units:

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

The energy is given in Hartree.

$$[Ha] = 27.211\,\mathrm{eV}$$

It can be solved for some simple systems:

- hydrogen atom (Laguerre polynomials)
- harmonic oscillator (Hermite polynoials)
- particel in a box

In general we have to deal with many electrons ($N_{elec} \sim 10^{23}$ (!) in solids). To demonstrate the sheer complexity of a naive attempt of an exact solution of equation 2.2 let us consider a Silicon atom. Simply wanting to store the wavefunction on a grid with only 10 points in each dimensions produces a grid with 10^{3N}=10^{42} points. Assuming 128-bit double precision complex numbers, each sample point requires 16 bytes of storage, which gives approx 10^{43} bytes of data. A regular blu-ray disc holds about 50 GB and we would therefore need $\sim 10^{32}$ disks – an astronomical amount. In fact, if each disk case was a centimeter thick the stack of disks would cover the distance from the earth to the moon $\sim 10^{21}$ times!

We have to find approximations!

Different frameworks lead to different approaches that lead themselves to different approximations that work for different systems amd circumstances.
In general:

1. wavefunction (Ψ) based:
   - Quantum chemistry (finite systems): Hartree Fock pertubation theory (e. g. MP2), coupled cluster
   - Quantum Monte Carlo (finite, periodic): variational MC, diffusion MC

2. Density based ($n(\mathbf{r})$)
    - Density-funtional theory (finite, periodic)
        - many exchange-correlation funtionals
        - exact limit not easily attainable
        - fast approximations
3. Green's function based ($G\left(\mathbf{r}, \mathbf{r'}, \omega\right)$)
    - many-body pertubation theory (finite, periodic): GW, T-Matrix, BSE, FLEX, ...
    - DFT+Dynamic Mean Field Theory (DMFT) (periodic, strongly correlated)
4. Density matrix ($n(\mathbf{r}, \mathbf{r'}) = G\left(\mathbf{r}, \mathbf{r'}, t = 0\right)$) , not covered in this lecture
    - density matrix functional theory
    - few xc approximations, little explored

2.1 Born-Oppenheimer Approximation

Since the nuclei are much havier than electrons they move much slower. Therefore the potential feld by the electrons, caused by the nuclei, can be approximated by the field of fixed nuclei. The kinetic energy of the nuclei is thereby neclected and the repulsion between nuclei becomes a constant. The remaining Hamiltonian is H_{elec} (2.2), which describes the motion of N electrons in the field of M point charges.
The electronic Hamiltonia can be solved by:

$$H_{elec}\Psi_{elec} = E_{elec}\Psi_{elec} \tag{2.4}$$

with the electronic wave function:

$$\Psi_{elec} = \Psi_{elec}\left(\{\mathbf{r}_i\}, \{\mathbf{R}_a\}\right) \tag{2.5}$$

which depends on:

$$\begin{aligned} \{\mathbf{r}_i\} &\quad \text{explicitlly} \\ \{\mathbf{R}_a\} &\quad \text{parametrically} \end{aligned}$$

Additionally the total energy depends as well parametrically on positions of the nuclei.

$$E_{elec} = E_{elec}\left(\{\mathbf{R}_a\}\right) \tag{2.6}$$

The total energy for fixed nuclei is:

$$E_{tot} = E_{elec} + \sum_{a=1}^{M}\sum_{b>a}^{M}\frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} \tag{2.7}$$

This is **the electronic problrem** we are interested in!
Now we can reverse the argument and solve the problem for nuclei moving in an effective potential of the electrons. Since the electrons move much faster we can replace the electronic coordinates by average

values, which are averaged over electronic wavefunctions.

$$\begin{aligned}
H_{nucl} &= -\sum_{a=1}^{M} \frac{1}{2M_a}\nabla_a^2 + \sum_{a=1}^{M}\sum_{b>a}^{M} \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} \\
&\quad + \left\langle -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{M} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N}\sum_{a=1}^{M} \frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|} \right\rangle \\
&= -\sum_{a=1}^{M} \frac{1}{2M_a}\nabla_a^2 + \sum_{a=1}^{M}\sum_{b>a}^{M} \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} + E_{elec}\left(\{\mathbf{R}_a\}\right) \\
H_{nucl} &= -\sum_{a=1}^{M} \frac{1}{2M_a}\nabla_a^2 + E_{tot}\left(\{\mathbf{R}_a\}\right) \qquad (2.8)
\end{aligned}$$

The total energy of the **electrones provides a potential energy surface** for the motion of the nuclei. Forces can be calculated by the derivative of the total energy with respect to the coordinates of the nuclei.

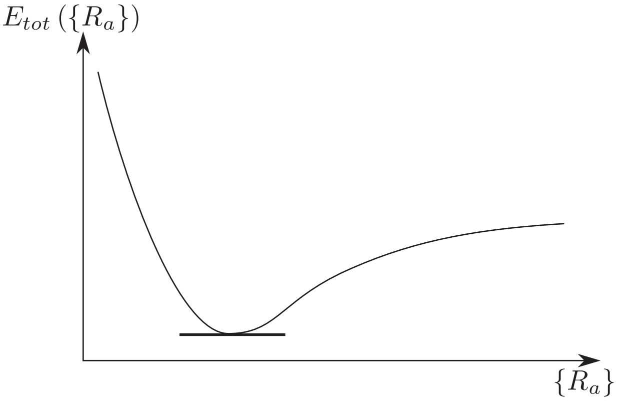


Figure 2.1: Potential energy surface

$$F \sim \frac{\mathrm{d}E_{tot}}{\mathrm{d}R_i} \qquad (2.9)$$

$$H_{nucl}\Psi_{nucl} = E\Psi_{nucl} = E\Psi_{nucl}\left(\{\mathbf{R}_a\}\right) \qquad (2.10)$$

$\Psi_{nucl}\left(\{\mathbf{R}_a\}\right)$ describes the vibrations, rotations and translations of a system.

$$\Psi\left(\{\mathbf{r}_i\}, \{\mathbf{R}_a\}\right) = \Psi_{elec}\left(\{\mathbf{r}_i\}, \{\mathbf{R}_a\}\right)\Psi_{nucl}\left(\{\mathbf{R}_a\}\right) \qquad (2.11)$$

is the full wave function of the system.
The adiabatic approximation fails for system where non-adiabatic effects, e.g. electron-phonon coupling, are import. The describtion of superconductivity is not possible in this context. The Born-Oppenheimer approximation also fails in cases where more than one energy landscape is present (molecule approaching surface).

The central goal of this lecture is to solve the electronic problem

$$H_{elec}\Psi_{elec} = E_{elec}\Psi_{elec}$$

which is given in (2.2).

2.2 Antisymmetry or Pauli Exclusion Principle

Electrons are Fermions and therefore carry a spin. The Schrödinger equation is not explicitly spin depent. We therefore have to introduce spin functions in spin variable σ.

$$\begin{array}{rcl} \uparrow & : & \alpha\left(\sigma\right) \\ \downarrow & : & \beta\left(\sigma\right) \end{array}$$

These have to be complete and orthorgonal (for convenience).

$$\begin{aligned} \int \mathrm{d}\sigma\alpha^{*}\left(\sigma\right)\alpha\left(\sigma\right) = \int \mathrm{d}\sigma\beta^{*}\left(\sigma\right)\beta\left(\sigma\right) = 1 \\ \int \mathrm{d}\sigma\alpha^{*}\left(\sigma\right)\beta\left(\sigma\right) = \int \mathrm{d}\sigma\beta^{*}\left(\sigma\right)\alpha\left(\sigma\right) = 0 \end{aligned} \tag{2.12}$$

The electrons are described by a collective coordinate:

$$\mathbf{x}\left\{\mathbf{r},\sigma\right\}, \tag{2.13}$$

the wave function is:

$$\Psi = \left(\left\{\mathbf{x}_i\right\}\right). \tag{2.14}$$

Antisymmetry:

> A many-electron wave function must be antisymmetric with respect to the interchange of the coordinate $\mathbf{x}$ of any two electrons.

$$\Psi\left(\mathbf{x}_1,\ldots,\mathbf{x}_i,\ldots,\mathbf{x}_j,\ldots,\mathbf{x}_N\right) = \Psi\left(\mathbf{x}_1,\ldots,\mathbf{x}_j,\ldots,\mathbf{x}_i,\ldots,\mathbf{x}_N\right) \tag{2.15}$$

(Generalization of the Pauli exclusion principle)
The many electron wavefuntion must satisfy:

1. The Schrodinger equation
2. Be antisymmetric.

3 Wave function based approaches

Let us imagine we only had one electron or we could postulate an effective electron-electron interaction that describes the effect of all other electrons in an average way.

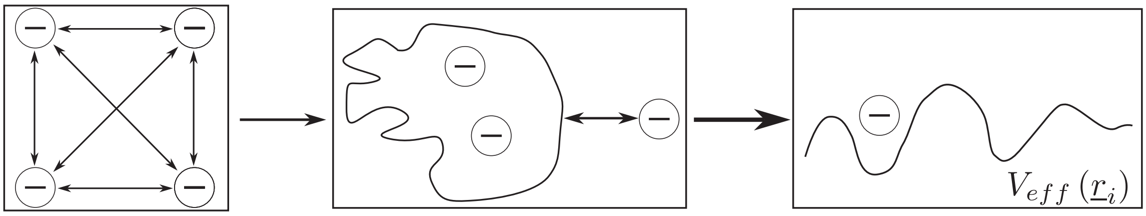


Figure 3.1: Effective electron-electron interaction

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{a=1}^{M}\frac{Z_a}{|\mathbf{r}_i-\mathbf{R}_a|}}_{\sum_i h^0(i)\text{(one electron)}}$$

$$+ \qquad \underbrace{\sum_{i=1}^{N}\sum_{j>i}^{M}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}}_{\text{couples all electrons}\Rightarrow\text{makes life difficult}}$$

3.1 Hartree theory

In quantum mechanics we have the wave-particle duality; namely the notion that the electron's position in space is given by a probability distribuntion.

$$n(\mathbf{r}) = |\psi(\mathbf{r})|^2 \tag{3.1}$$

we call $\psi(\mathbf{r})$ the spatial orbital or wave function for the electron

$$|\psi(\mathbf{r})|^2 \, dr^3 \tag{3.2}$$

is then the probability of finding the electron in the small volume element $d\mathbf{r}$. Combinded with its spin we can define spin orbitals:

$$\varphi(\mathbf{r}) = \begin{cases} \psi(\mathbf{r})\alpha(\sigma) \\ \quad\text{or} \\ \psi(\mathbf{r})\beta(\sigma) \end{cases} \tag{3.3}$$

To make progress we next consider a system of N **non-interacting** electrons having a Hamiltonian:

$$H^{NI} = \sum_{i=1}^{N} h(i) \tag{3.4}$$

$h(i)$ will general include the kinetic and potential energy of electron i, but may also contain an effective electron-electron interaction.

Each operator $h(i)$ will have a set of eigenfunctions that we take to be a set of spin orbitals.

$$h(i)\varphi_j\left(\mathbf{x}_i\right) = \epsilon_j \varphi_j\left(\mathbf{x}_i\right) \tag{3.5}$$

which are orthorgonal for convenience:

$$\int d\mathbf{x}\varphi_i\left(\mathbf{x}\right)\varphi_j\left(\mathbf{x}\right) = \delta_{ij} \tag{3.6}$$

What is the corresponding eigenfunction of H then?
Answer:

a product of the spin orbitals

$$\Psi^{HP}\left(\mathbf{x}_1, \ldots, \mathbf{x}_N\right) = \varphi_i\left(\mathbf{x}_1\right)\varphi_j\left(\mathbf{x}_2\right)\ldots\varphi_k\left(\mathbf{x}_N\right) \tag{3.7}$$

The eigenvalue of

$$H^{NI}\Psi^{NI} = E\Psi^{NI} \tag{3.8}$$

is simply the sum of eigenvalues, because $h(i)$ only acts on the orbital with corresponding coordinate $\mathbf{x}_i$:

$$E = \epsilon_i + \epsilon_j + \ldots + \epsilon_k \tag{3.9}$$

The eigenfunction Ψ^{HP} is alos called a Hartree product and is an example for an uncorrected wavefunction, because the probability of finding electron 1 in $d\mathbf{x}_1$, electron 2 in $d\mathbf{x}_2$, etc., is simply the product of probabilities:

$$\left|\varphi_i\left(\mathbf{x}_1\right)\right|^2 \left|d\mathbf{x}_1\varphi_j\left(\mathbf{x}_2\right)\right|^2 d\mathbf{x}_2 \ldots \left|\varphi_k\left(\mathbf{x}_N\right)\right|^2 d\mathbf{x}_N \tag{3.10}$$

or, if we view this differently we have factorized the wave function; a concept that is recurring throughout physics.
So if we forget for now that Ψ^{HP} does not obey the antisymmetry principle we could make the ansatz:

$$H\Psi^{HP} = E\Psi^{HP}$$

and ask, which single particle orbitals minimize the energy under the constraint that the orbitals are normalized.

$$\Longrightarrow \text{ Lagrangian: } \mathrm{L}\left[\Psi\right] = E\left[\Psi\right] - \sum_i \epsilon_i \int \mathrm{d}\mathbf{x}\varphi_i^*\left(\mathbf{x}\right)\varphi_i\left(\mathbf{x}\right)$$

The energy is given by

$$E\left[\Psi\right] = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \langle\Psi|H|\Psi\rangle$$

because Ψ^{HP} is normalized.
We already know that:

$$\langle\Psi^{HP}|h(i)|\Psi^{HP}\rangle = \langle\varphi_i|h(i)|\varphi_i\rangle$$

For the Coulomb potential we get:

$$\begin{aligned}\left\langle\Psi^{HP}\middle|\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\middle|\Psi^{HP}\right\rangle &= \int \mathrm{d}\mathbf{x}_i \ldots \mathrm{d}\mathbf{x}_N \varphi_n^*\left(\mathbf{x}_1\right)\ldots\varphi_k^*\left(\mathbf{x}_N\right)\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\varphi_n\left(\mathbf{x}_1\right)\ldots\varphi_k\left(\mathbf{x}_N\right)\\ &= \int \mathrm{d}\mathbf{x}_i \mathrm{d}\mathbf{x}_j \frac{\varphi_l^*\left(\mathbf{x}_i\right)\varphi_m^*\left(\mathbf{x}_j\right)\varphi_n\left(\mathbf{x}_i\right)\varphi_l\left(\mathbf{x}_j\right)}{|\mathbf{r}_i - \mathbf{r}_j|}\end{aligned}$$

$\Longrightarrow$ All other combinations of φ_k integrate out

$\Longrightarrow$ l and m are the occupied orbitals

$$\left\langle \Psi^{HP} \left| \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \Psi^{HP} \right\rangle = \sum_{i}^{N} \sum_{j>i}^{N} \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \frac{\varphi_i^*(\mathbf{x})\,\varphi_j^*(\mathbf{x}')\,\varphi_i(\mathbf{x})\,\varphi_j(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3.11}$$

Now our Lagrangian reads:

$$\begin{aligned} \mathrm{L}[\Phi] = & \sum_{i}^{N} \int \mathrm{d}\mathbf{x}_i \varphi_i(\mathbf{x}_i)\,h(\mathbf{x}_i)\,\varphi_i(\mathbf{x}_i) = \sum_{i}^{N} \sum_{j>i}^{N} \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \frac{\varphi_i^*(\mathbf{x})\,\varphi_j^*(\mathbf{x}')\,\varphi_i(\mathbf{x})\,\varphi_j(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} \\ & - \sum_{i}^{N} \epsilon_i \int \mathrm{d}\mathbf{x} \varphi_i^*(\mathbf{x})\,\varphi_i(\mathbf{x}) \end{aligned}$$

doing the varition with respect to φ_i^* and demanding:

$$\frac{\delta \mathrm{L}}{\delta \varphi_i^*} = 0 \qquad \forall i$$

gives:

$$\begin{aligned} 0 = h(\mathbf{x}_i)\,\varphi_i(\mathbf{x}_i) + & \underbrace{\sum_{j>i}^{N} \int \mathrm{d}\mathbf{x}' \frac{\varphi_i^*(\mathbf{x})\,\varphi_j(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} \varphi_i(\mathbf{x})}_{=} - \sum_{i}^{N} \epsilon_i \varphi_i(\mathbf{x}) \\ & \int \mathrm{d}\mathbf{x}' \sum_{j}^{N} \frac{\varphi_i^*(\mathbf{x})\,\varphi_i(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} \varphi_i(\mathbf{x}) - \underset{=}{\int \mathrm{d}\mathbf{x}' \frac{\varphi_i^*(\mathbf{x})\,\varphi_i(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} \varphi_i(\mathbf{x})} \\ & \underbrace{\int \mathrm{d}\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \varphi_i(\mathbf{x})}_{=} - \int \mathrm{d}\mathbf{r}' \frac{|\varphi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \varphi_i(\mathbf{x}) \\ & V_H(\mathbf{r})\,\varphi_i(\mathbf{x})\,. \end{aligned}$$

$$[h(\mathbf{r}) + V_H(\mathbf{r})]\,\psi_i(\mathbf{r}) - \int \mathrm{d}\mathbf{r}' \frac{|\psi_i(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} \psi_i(\mathbf{r}) = \epsilon \psi_i(\mathbf{r}) \tag{3.12}$$

are the Hartree equations.
A few points to note:

- V_H, the Hartree potential depends on the electron density: $V_H = V_H(n(\mathbf{r}), \mathbf{r})$ and the density depends on the orbitals. Therefore the Hartree equations have to be solved self-consostently.
- The sum in V_H runs over all electrons and therefore contains the interaction of an electron with itself. This is removed exactly by the 2nd, orbital dependent term.
- $h(\mathbf{r})$ and $V_H(\mathbf{r})$ are the same for all i electrons but the self-interaction correction introduces an orbital specific dependence.
- The Hartree potential is the classic electrostatic potential of a charge distribution, it is positive and therefore repulsive, e.g. for the hydrogen 1s function:

  $$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-r}$$

  we get

  $$V_H(r) = \frac{1}{r}\left(1 - (1+r)\mathrm{e}^{-2r}\right),$$

  which looks like:

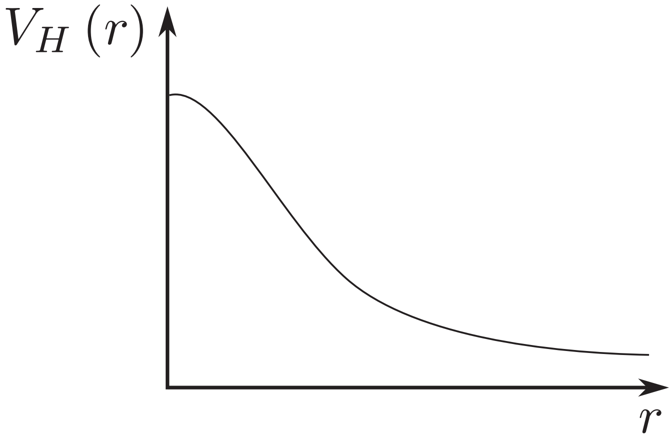


Figure 3.2: Hartree potential

It is repulsive and delocalizes the electrons.

- The Hartree potential largely counteracts the external potential:

$$-\sum_{i}^{N}\sum_{a=1}^{M}\frac{Z_a}{|\mathbf{r}_i-\mathbf{R}_a|}=-\sum_{i}\underbrace{\int \mathrm{d}\mathbf{R}\frac{n_n(\mathbf{R})}{|\mathbf{r}_i-\mathbf{R}|}}_{V_{ext}(\mathbf{r}_i)}$$

$$\Longrightarrow V_{ext}(\mathbf{r})+V_H(\mathbf{r}_i)=\int \mathrm{d}\mathbf{r}'\frac{n(\mathbf{r}')-n_n(')}{|\mathbf{r}-\mathbf{r}'|}=\int \mathrm{d}\mathbf{r}'\frac{\delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

3.2 Hartree and Hartree Fock

Ψ^{HP} is an eigenfunction of the many-electron Schrodinger equation, but it does **not** satisfy the antisymmetry requirement.
As is easily seen:

$$\Psi^{HP}(\mathbf{x}_1,\ldots,\mathbf{x}_i,\ldots,\mathbf{x}_j,\ldots,\mathbf{x}_N)=\Psi^{HP}(\mathbf{x}_1,\ldots,\mathbf{x}_j,\ldots,\mathbf{x}_i,\ldots,\mathbf{x}_N) \tag{3.13}$$

Considering the two-electron case - the hydrogen molecule:

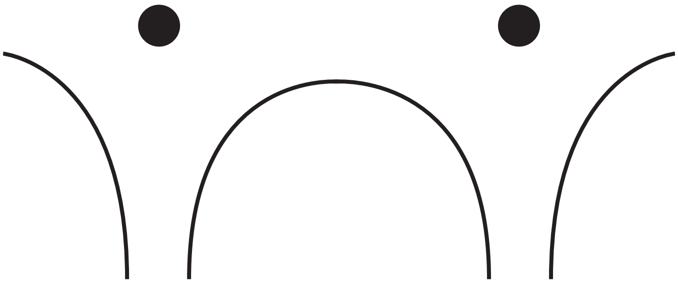


Figure 3.3: Two electron case

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

The two wavefunctions clearly distinguish the electrons.
Indistinguishable and antisymmetric:

$$\Psi\left(\mathbf{x}_1,\mathbf{x}_2\right)=\frac{1}{\sqrt{2}}[\varphi_i\underset{a}{(\mathbf{x}_1)}\varphi_j\underset{d}{(\mathbf{x}_2)}\underset{-}{-}\varphi_i\underset{c}{(\mathbf{x}_2)}\varphi_j\underset{b}{(\mathbf{x}_1)}] \tag{3.14}$$

This is mathematically equivalent to a determinat:

$$A=\begin{pmatrix} a & b \\ c & d \end{pmatrix} \qquad \mathrm{det}A=\begin{vmatrix} a & b \\ c & d \end{vmatrix}=ad-cb$$

$$\Psi\left(\mathbf{x}_1,\mathbf{x}_2\right)=\frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_i\left(\mathbf{x}_1\right) & \varphi_j\left(\mathbf{x}_1\right) \\ \varphi_i\left(\mathbf{x}_2\right) & \varphi_j\left(\mathbf{x}_2\right) \end{vmatrix}\uparrow \text{electrons}$$

$$\xrightarrow[\text{orbitals}]{}$$

or in general

$$\Psi^{SD}\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right)=\frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_i\left(\mathbf{x}_1\right) & \varphi_j\left(\mathbf{x}_1\right) & \ldots & \varphi_k\left(\mathbf{x}_1\right) \\ \varphi_i\left(\mathbf{x}_2\right) & \varphi_j\left(\mathbf{x}_2\right) & \ldots & \varphi_k\left(\mathbf{x}_2\right) \\ \vdots & \vdots & & \vdots \\ \varphi_i\left(\mathbf{x}_N\right) & \varphi_j\left(\mathbf{x}_N\right) & \ldots & \varphi_k\left(\mathbf{x}_N\right) \end{vmatrix} \tag{3.15}$$

and is commonly called a Slater determinant.
Next we will approximate the many-electron wave function by a single slater determinat and use the variational principle to determine the spin orbitals that minimize the grounnd state energy.
This gives the Hartree-Fock method/approach.
First we need the energy for a Slater determinant (SD):

$$E=\frac{\langle\Psi^{SD}|H|\Psi^{SD}\rangle}{\langle\Psi^{SD}|\Psi^{SD}\rangle}=\langle\Psi^{SD}|H|\Psi^{SD}\rangle \qquad \Longrightarrow \Psi^{SD} \text{ is normalized}$$

As we have seen H_{elec} has two distinct parts:

$$H_{elec}=\sum_i h(i)-\sum_i^N\sum_{j>i}^N\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} \tag{3.16}$$

We therefore need to evaluate two different contributions:

$$\langle\Psi^{SD}|h(i)|\Psi^{SD}\rangle$$
$$\langle\Psi^{SD}|\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}|\Psi^{SD}\rangle$$

For simplicity this will be illustrated for the two-electron example:

$$\begin{aligned}
&\int \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\frac{1}{\sqrt{2}}[\varphi_i\left(\mathbf{x}_1\right)\varphi_j\left(\mathbf{x}_2\right)-\varphi_i\left(\mathbf{x}_2\right)\varphi_j\left(\mathbf{x}_1\right)]h(1)[\varphi_i\left(\mathbf{x}_1\right)\varphi_j\left(\mathbf{x}_2\right)-\varphi_i\left(\mathbf{x}_2\right)\varphi_j\left(\mathbf{x}_1\right)]\\
=&\int \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\frac{1}{\sqrt{2}}[\varphi_i\left(\mathbf{x}_1\right)\varphi_j\left(\mathbf{x}_2\right)h(1)\varphi_i\left(\mathbf{x}_1\right)\varphi_j\left(\mathbf{x}_2\right)-\varphi_i\left(\mathbf{x}_1\right)\varphi_j\left(\mathbf{x}_2\right)h(1)\varphi_i\left(\mathbf{x}_2\right)\varphi_j\left(\mathbf{x}_1\right)\\
&+\varphi_i\left(\mathbf{x}_2\right)\varphi_j\left(\mathbf{x}_1\right)h(1)\varphi_i\left(\mathbf{x}_2\right)\varphi_j\left(\mathbf{x}_1\right)-\varphi_i\left(\mathbf{x}_2\right)\varphi_j\left(\mathbf{x}_1\right)h(1)\varphi_i\left(\mathbf{x}_1\right)\varphi_j\left(\mathbf{x}_2\right)]
\end{aligned}$$

After integrating over $\mathbf{x}_2$:

$$\int \mathrm{d}\mathbf{x}_1\frac{1}{\sqrt{2}}[\varphi_i\left(\mathbf{x}_1\right)h(1)\varphi_i\left(\mathbf{x}_1\right)-\varphi_j\left(\mathbf{x}_1\right)h(1)\varphi_j\left(\mathbf{x}_1\right)]$$

$h(2)$ yields an identical result.

$$\Longrightarrow \langle \Psi^{SD} | \sum_i h(i) | \Psi^{SD} \rangle = \sum_i \langle \varphi_i \left(\mathbf{x}_1 \right) | h(i) | \varphi_i \left(\mathbf{x}_1 \right) \rangle$$

This is the same result we obtained in the derivation of the Hartree approximation. The general proof can be found in *Szabo and Ostlund* (and might be given as an appendix).
For the Coulomb operator we again consider two electrons first:

$$\Psi^{SD}_{2-e} = \frac{1}{\sqrt{2}} \left[\varphi_i \left(\mathbf{x}_1 \right) \varphi_j \left(\mathbf{x}_2 \right) - \varphi_i \left(\mathbf{x}_2 \right) \varphi_j \left(\mathbf{x}_1 \right) \right]$$

$$\begin{aligned} & \int \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \frac{1}{2} \left[\varphi^*_i \left(\mathbf{x}_1 \right) \varphi^*_j \left(\mathbf{x}_2 \right) - \varphi^*_i \left(\mathbf{x}_2 \right) \varphi^*_j \left(\mathbf{x}_1 \right) \right] \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & \qquad * \left[\varphi_i \left(\mathbf{x}_1 \right) \varphi_j \left(\mathbf{x}_2 \right) - \varphi_i \left(\mathbf{x}_2 \right) \varphi_j \left(\mathbf{x}_1 \right) \right] \\ = & \int \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \frac{1}{2} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \end{aligned}$$

$$\begin{array}{llcccccc} *[& a) & \varphi_i \left(\mathbf{x}_1 \right) & \varphi_j \left(\mathbf{x}_2 \right) & \varphi_i \left(\mathbf{x}_1 \right) & \varphi_j \left(\mathbf{x}_2 \right) & 12 & 12 \\ & b) & +\varphi_i \left(\mathbf{x}_2 \right) & \varphi_j \left(\mathbf{x}_1 \right) & \varphi_i \left(\mathbf{x}_2 \right) & \varphi_j \left(\mathbf{x}_1 \right) & 21 & 21 \\ & c) & -\varphi_i \left(\mathbf{x}_1 \right) & \varphi_j \left(\mathbf{x}_2 \right) & \varphi_i \left(\mathbf{x}_2 \right) & \varphi_j \left(\mathbf{x}_1 \right) & 12 & 21 \\ & d) & -\varphi_i \left(\mathbf{x}_2 \right) & \varphi_j \left(\mathbf{x}_1 \right) & \varphi_i \left(\mathbf{x}_1 \right) & \varphi_j \left(\mathbf{x}_2 \right)] & 21 & 12 \\ & & \downarrow & \downarrow & \downarrow & \downarrow & & \\ & & i & j & i & j & & \end{array}$$

- down the columns ($\downarrow$) always the same orbitals
- across ($\rightarrow$) filled by different combinations

However,this is not the most convenient way of writing it. So let's reorder each term so that we have a different integration order.

	$\mathbf{x}_1$	$\mathbf{x}_2$	$\mathbf{x}_1$	$\mathbf{x}_2$
a)	i	j	i	j
b)	j	i	j	i
c)	i	j	j	i
d)	j	i	i	j

We obtain the same pattern, but now in the orbital indicies.
If we define:

$$\langle ij|kl \rangle = \int \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \varphi_i \left(\mathbf{x} \right) \varphi_j \left(\mathbf{x}' \right) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_k \left(\mathbf{x} \right) \varphi_l \left(\mathbf{x}' \right) \tag{3.17}$$

then the matrix element for the Coulomb operater becomes:

$$\left\langle \Psi^{SD} \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \Psi^{SD} \right\rangle = \frac{1}{2} \left[\langle ij|ij \rangle + \langle ji|ji \rangle \right] + \frac{1}{2} \left[\langle ij|ji \rangle + \langle ji|ij \rangle \right]$$

or in general with:

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

$$\left\langle \Psi^{SD} \left| V^{ee} \right| \Psi^{SD} \right\rangle = \frac{1}{2} \sum_m^N \sum_{n \neq m}^N \underbrace{\langle mn|mn \rangle}_{(1)} - \underbrace{\langle mn|nm \rangle}_{(2)}$$

(1) As we will see, this will again give rise to the Hartree potential

(2) This term is new and gives exchange because indices are exchanged

$\Longrightarrow$ The energy of a single Slater determinant:

$$E_{HF} = \left\langle \Psi^{SD} \left| H_{elec} \right| \Psi^{SD} \right\rangle = \sum_{n}^{N} \langle n|h|n\rangle + \frac{1}{2} \sum_{nm}^{N} \langle mn|mn\rangle - \langle mn|nm\rangle$$

with

$$\langle n|h|n\rangle = \int \mathrm{d}\mathbf{x} \varphi_n^* \left(\mathbf{x}\right) h(\mathbf{x}) \varphi_n \left(\mathbf{x}\right)$$

Now we make one important observation:

> Altough we have a many electron wave-function and a many electron hamiltonian we can write the energy of a Slater determinat in terms of 1 and 2 electron integrals only.

$\Longrightarrow$ This of course follows from the fact that the Coulomb potential is a two-electron operator!

$\Longrightarrow$ As we will see later: This is one of the key foundations of quantum chemistry

To find the minimum of the Hartree-Fock energy we again define a Lagrangian:

$$\begin{aligned} \mathrm{L}\left[\Psi^{SD}\right] &= \mathrm{E}\left[\Psi^{SD}\right] - \sum_{m}^{N} \epsilon_m \int \mathrm{d}\mathbf{x} \varphi_m^* \left(\mathbf{x}\right) \varphi_m \left(\mathbf{x}\right) \\ &= \sum_{m}^{N} \int \mathrm{d}\mathbf{x} \varphi_m^* \left(\mathbf{x}\right) h(\mathbf{x}) \varphi_m \left(\mathbf{x}\right) - \sum_{m}^{N} \epsilon_m \int \mathrm{d}\mathbf{x} \varphi_m^* \left(\mathbf{x}\right) \varphi_m \left(\mathbf{x}\right) \\ &+ \sum_{m}^{N} \sum_{n \neq m}^{N} \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \left[\frac{\varphi_m^* \left(\mathbf{x}\right) \varphi_n^* \left(\mathbf{x}'\right) \varphi_m \left(\mathbf{x}\right) \varphi_n \left(\mathbf{x}'\right)}{|\mathbf{r} - \mathbf{r}'|} - \frac{\varphi_m^* \left(\mathbf{x}\right) \varphi_n^* \left(\mathbf{x}'\right) \varphi_n \left(\mathbf{x}\right) \varphi_m \left(\mathbf{x}'\right)}{|\mathbf{r} - \mathbf{r}'|} \right] \end{aligned} \tag{3.18}$$

- φ_m^* shows up twice in (3.18) $\Longrightarrow$ cancels factor of 2

and in analogy:

$$\frac{\delta \mathrm{L}}{\delta \varphi_i^*} = 0 \qquad \forall i$$

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

$$V_H \left(\mathbf{x}\right) \int \mathrm{d}\mathbf{x}' \frac{\varphi_m^* \left(\mathbf{x}'\right) \varphi_m \left(\mathbf{x}\right) \varphi_m \left(\mathbf{x}'\right)}{|\mathbf{r} - \mathbf{r}'|}$$

$$\Longrightarrow \underbrace{\left[h(\mathbf{x}) + V_H \left(\mathbf{x}\right)\right] \varphi_m \left(\mathbf{x}\right) - \sum_{n}^{N} \int \mathrm{d}\mathbf{x}' \frac{\varphi_n^* \left(\mathbf{x}'\right) \varphi_n \left(\mathbf{x}\right)}{|\mathbf{r} - \mathbf{r}'|}}_{\text{Fock Operator } \hat{f}} \varphi_m \left(\mathbf{x}'\right) = \epsilon_m \varphi_m \left(\mathbf{x}\right) \tag{3.19}$$

To rewrite equation (3.19) in a more convenient form we apply from the left $\sum_m \int \mathrm{d}\mathbf{x}\varphi_m^* (\mathbf{x})$:

$$\begin{aligned}\sum_m \epsilon_m &= \sum_m \int \mathrm{d}\mathbf{x}\varphi_m^* (\mathbf{x}) \left[h(\mathbf{x}) + V_H (\mathbf{x})\right] \varphi_m (\mathbf{x}) - \sum_{nm}^N \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \frac{\varphi_m^* (\mathbf{x}') \varphi_n^* (\mathbf{x}') \varphi_n (\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} \varphi_m (\mathbf{x}') \\ &= \sum_n^N \langle n|h|n\rangle + \sum_{nm}^N \langle mn|mn\rangle - \langle mn|nm\rangle \\ &= E^{HF} = \frac{1}{2} \sum_{nm}^N \langle mn|mn\rangle - \langle mn|nm\rangle\end{aligned}$$

$$E^{HF} = \sum_m \epsilon_m - \underbrace{\frac{1}{2} \sum_{nm}^N \langle mn|mn\rangle - \langle mn|nm\rangle}_{(*)} \tag{3.20}$$

(∗) cancels double counting of Coulomb repulsion and exchange in the sum of eigenvalues (which counts interaction $i \leftrightarrow j$ once for i and a 2nd time for j)

we define the density matrix:

$$n (\mathbf{x}, \mathbf{x}') = \sum_n^N \varphi_n^* (\mathbf{x}) \varphi_n (\mathbf{x}') \tag{3.21}$$

(note: the diagonal of the the density matrix is the density)
We also define the non-local potential:

$$\Sigma^{HF} (\mathbf{x}, \mathbf{x}') = -\frac{n (\mathbf{x}, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3.22}$$

$$\Longrightarrow \left[h(\mathbf{x}) + V_H (\mathbf{x})\right] \varphi_m (\mathbf{x}) + \int \mathrm{d}\mathbf{x}' \Sigma^{HF} (\mathbf{x}, \mathbf{x}') \varphi_m (\mathbf{x}') = \epsilon_m \varphi_m (\mathbf{x}) \tag{3.23}$$

Often this equation is also written like this:

$$\underset{\substack{\downarrow \\ \text{independent of } \{\varphi_i(\mathbf{x})\}}}{h(\mathbf{x})\varphi_m (\mathbf{x})} \qquad + \qquad \underset{\substack{\downarrow \\ \text{dependent of } \{\varphi_i(\mathbf{x})\}}}{\int \mathrm{d}\mathbf{x}' V^{HF} (\mathbf{x}, \mathbf{x}') \varphi_m (\mathbf{x}')} \qquad = \epsilon_m \varphi_m (\mathbf{x})$$

$$\hat{f} = \hat{h} + \hat{V}^{HF} \quad \text{is the Fock operator} \tag{3.24}$$

- The Fock-operator is an effective one electron operator
- It replaces the many-body Schrodinger equation by a set of one electron equations, where each electron moves in an effective field, also called mean-field
- The mean-field is an important concept because it allows us to seperate the many-electron problem into one-electron problems:

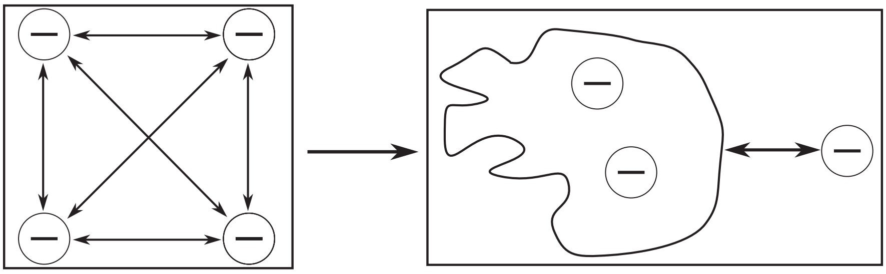


Figure 3.4: Effective Potential

- The wave-function of electron m does no longer explicitly depend on that of all other electrons only implicitly through V_{HF}
- In fact, it is actually possible to speak of one-electron wavefunctions or orbitals, which is not really possible for the full many-body wave-function $\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N\right)$.
- The Fock operator has two parts

$$\hat{f} = \underset{\{\varphi_i(\mathbf{x})\}\text{-independent}}{\underset{\downarrow}{\hat{h}}} + \underset{\{\varphi_i(\mathbf{x})\}\text{-dependent}}{\underset{\downarrow}{\hat{V}^{HF}}}$$

$\Longrightarrow$It has to be solved self-consistently.

V^{HF} is called the self-consistent-field (scf) in which the electrons move.

1. Start with an initial guess for $\{\varphi_i\}$
2. Calculate $n(\mathbf{x})$, $n(\mathbf{x}, \mathbf{x}')$ and $V^{HF}(\mathbf{x})$
3. Solve the HF equations (3.19) for a new set of $\{\varphi_i\}$
4. Check for convergence (is $n(\mathbf{x})$, $n(\mathbf{x}, \mathbf{x}')$ or the total energy the same, within a given tolerance, as in the previous iteration.
   - If not: repeat calculaion (go to 1.)
   - If yes: finished

- $V_H(\mathbf{x})\,\varphi_m(\mathbf{x}) = \int \mathrm{d}\mathbf{x}' \sum_n \frac{\varphi_n^*(\mathbf{x}')\,\varphi_n(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}\varphi_m(\mathbf{x})$
- $\int \mathrm{d}\mathbf{x}'\Sigma(\mathbf{x}, \mathbf{x}')\,\varphi_m(\mathbf{x}) = \int \mathrm{d}\mathbf{x}' \sum_n \frac{\varphi_n^*(\mathbf{x}')\,\varphi_m(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}\varphi_n(\mathbf{x})$
  φ_n, φ_m have been exchanged $\Longrightarrow$ arises from antisymmetry, Σ is called the exchange operator

Hartree Theory V_H: Coulomb
Hartree-Fock Theory: Coulomb and echange
Befor we proceed to an expression of the Hartree-Fock equation that one would solve in the computer let's have a different look at the Coulomb and exchange terms.

3.2.1 Closed shell Hartree Fock

Let's consider a system with an even number of electrons and this scenario:

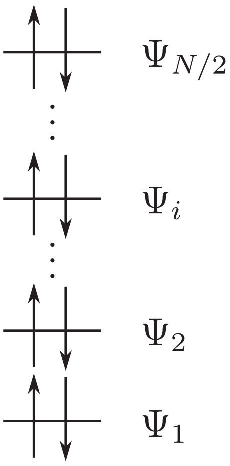


Figure 3.5: Closed Shell

The spatial orbitals are restricted to be the same for spin ↑ and ↓.
$\Longrightarrow$ we can pair up orbitals:

$$\begin{aligned}\varphi_1(\mathbf{x}) &= \psi_1(\mathbf{r})\,\alpha(\omega) = \psi_1(\mathbf{x})\\ \varphi_2(\mathbf{x}) &= \psi_1(\mathbf{r})\,\beta(\omega) = \bar{\psi}_1(\mathbf{x})\end{aligned}$$

$\Longrightarrow$ The Slater Determinat of $\varphi_1,\ \varphi_2,\ \ldots,\ \varphi_N$ becomes a Slater determinant of the functions $\psi_1,\ \bar{\psi}_1,\ \psi_2,\ \bar{\psi}_2,\ \ldots,\ \psi_{N/2}$, and the energy:

$$\begin{aligned}E &= \sum_n^N \langle n|h|n\rangle + \frac{1}{2}\sum_n^N \sum_{n\neq m}^N \langle mn|mn\rangle - \langle mn|nm\rangle\\ &= \sum_n^N \langle n|h|n\rangle + \frac{1}{2}\sum_n^N \sum_m^N \langle mn|mn\rangle - \langle mn|nm\rangle\\ &= \sum_n^{N/2} \langle n|h|n\rangle + \sum_n^{N/2} \langle \bar{n}|h|\bar{n}\rangle + \frac{1}{2}\sum_n^N \sum_m^N \langle mn|mn\rangle - \langle mn|nm\rangle\\ &\qquad\quad\downarrow\\ &\qquad\int \mathrm{d}\mathbf{r}\mathrm{d}\sigma \psi_n^*(\mathbf{r})\,\alpha^*(\sigma)\,h(\mathbf{r})\,\psi_n(\mathbf{r})\,\alpha(\sigma) = \int \mathrm{d}\mathbf{r}\mathrm{d}\sigma \psi_n^*(\mathbf{r})\,\beta^*(\sigma)\,h(\mathbf{r})\,\psi_n(\mathbf{r})\,\beta(\sigma)\\ &\quad = \int \mathrm{d}\mathbf{r} \psi_n^*(\mathbf{r})\,h(\mathbf{r})\,\psi_n(\mathbf{r}) = (n|h|n) = h_{nn}\end{aligned}$$

$$= 2\sum_n^{N/2}(n|h|n) + \frac{1}{2}\sum_n^{N}\sum_m^{N}\langle mn|mn\rangle - \langle mn|nm\rangle$$

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

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

$$\begin{aligned} = 2\sum_n^{N/2}(n|h|n) + \frac{1}{2}\sum_n^{N/2}\sum_m^{N/2}&\langle mn|mn\rangle - \langle mn|nm\rangle \\ &+ \langle m\bar{n}|m\bar{n}\rangle - \langle m\bar{n}|\bar{n}m\rangle \\ &+ \langle \bar{m}n|\bar{m}n\rangle - \langle \bar{m}n|n\bar{m}\rangle \\ &+ \langle \bar{m}\bar{n}|\bar{m}\bar{n}\rangle - \langle \bar{m}\bar{n}|\bar{n}\bar{m}\rangle \\ &\quad\ \sigma\sigma'\sigma\sigma' \qquad \sigma\sigma'\sigma\sigma' \end{aligned}$$

$$\int \mathrm{d}\sigma\mathrm{d}\sigma' \ldots$$

For these integrals to be non-zero the 1st and 3rd position and the 2nd and 4th position have to both have a bar or non.
$\Longrightarrow$with $(mn|kl) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\psi_m^*(\mathbf{r})\psi_n^*(\mathbf{r}')\psi_k(\mathbf{r})\psi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

$$E = 2\sum_n^{N/2}(n|h|n) + \sum_{nm}^{N/2} 2\underbrace{(mn|mn)}_{J_{mn}} - \underbrace{(mn|nm)}_{K_{mn}} \tag{3.25}$$

$$J_{mn} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\psi_m^*(\mathbf{r})\,\psi_n^*(\mathbf{r}')\,\psi_m(\mathbf{r})\,\psi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{|\psi_m(\mathbf{r})|^2\,|\psi_n(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \tag{3.26}$$

The Coulomb integral J_{mn} is the classical Coulomb repulsion between two charge distributions $|\psi_m(\mathbf{r}')|^2$ and $|\psi_n(\mathbf{r}')|^2$

$$K_{mn} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\psi_m^*(\mathbf{r})\,\psi_n^*(\mathbf{r}')\,\psi_n(\mathbf{r})\,\psi_m(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3.27}$$

The exchange integral K_{mn} has no classical analog.

3.2.2 Hartree Fock in real-space

The Hartree Fock Self Consistent Field Equation in real-space follows either from the expression for E^{HF} by minimizing the Lagrangian or by integrating out the spin in the spin-dependent HF-equations:

$$f(\mathbf{r})\,\psi_m(\mathbf{r}) = [h(\mathbf{r}) + V_H(\mathbf{r})]\,\psi_m(\mathbf{r}) + \underbrace{\int \mathrm{d}\mathbf{r}' \sum_n^{N/2} \frac{\psi_n(\mathbf{r})\,\psi_n^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_m(\mathbf{r}')}_{\int \mathrm{d}\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}')\,\psi_m(\mathbf{r}')} = \epsilon_m\psi_m(\mathbf{r}) \tag{3.28}$$

The kinetic energy can be written as high order finite difference expansion on a grid (see fig. (3.6)).

$$\nabla_x^2\psi = \sum_{n=-M}^{M} C_n\psi(x_i + nh, y_j, z_k) + \mathcal{O}(h^{2N+2}) \tag{3.29}$$

For further information see G.D. Smith - Numerical solutions of Partial Differential Equations, Finite Difference Methods, Oxford University Pree, new York, 1978.

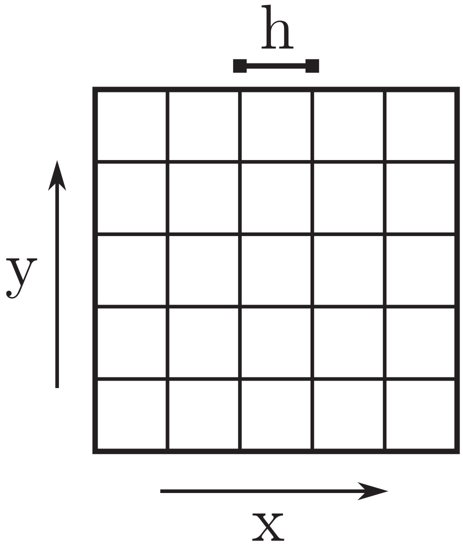


Figure 3.6: Integration grid

With this expansion for the kinetic energy the Hartree fock equations could be solved on a grid with suitable quadratures for the integrals.
However, the pproblem are the core states!
Take e.g.a 1s state (fig. (3.7)): It is tightly bound to the nucleus and many grid points are required to resolve the wavefunctions near the nucleus.

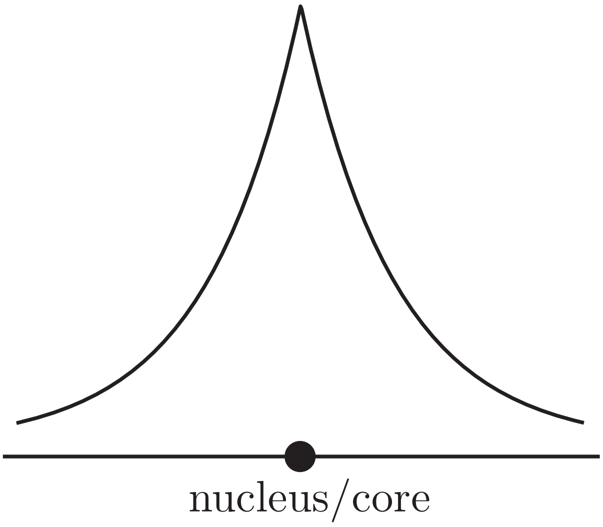


Figure 3.7: 1s state radial function.

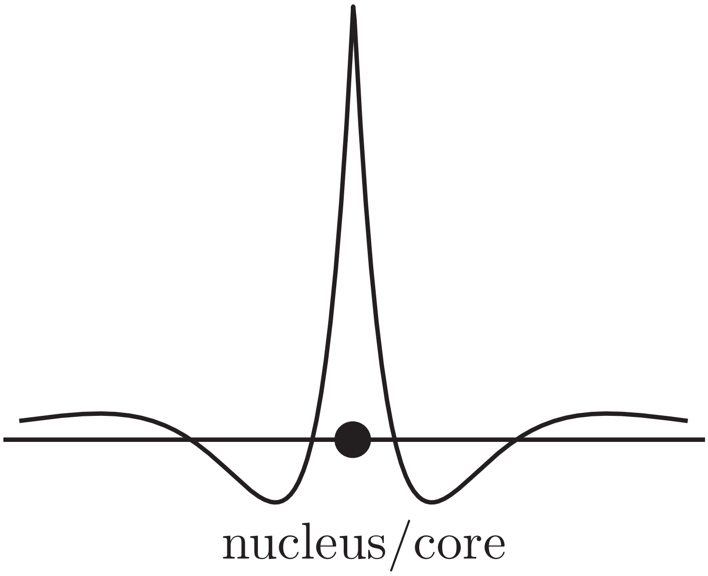


Figure 3.8: 3s state radial function.

Even a 3s state (fig. (3.8)) has rapid oscillations in the core region to satisfy orthogonality.

3.2.3 Hartree Fock in a basis

Solution to this problem:

- Introduce a basis
- build the rapid ocillations in the core region into the basis e.g. basis functions could be orbitals of free atoms

Without specifying the type of basis functions yet we introduce a set of K-many basis functions.

$$\left\{\phi_\mu\left(\mathbf{r}\right), \mu = 1 \ldots K\right\} \tag{3.30}$$

The molecular orbitals can then be expanded in this basis:

$$\psi_i\left(\mathbf{r}\right) = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu\left(\mathbf{r}\right) \tag{3.31}$$

- If $\{\phi_\mu\}$ was complete this would be an exact expansion
- In general $\{\phi_\mu\}$ is **not** complete

Inserting the expansion into the Hartree Fock equation (3.19).

$$\hat{f}\psi_i = \epsilon_i\psi_i$$

with

$$f = F\left(\mathbf{r},\mathbf{r}'\right) = h\left(\mathbf{r}\right)\delta\left(\mathbf{r}-\mathbf{r}'\right) + V^{HF}\left(\mathbf{r},\mathbf{r}'\right)$$

we obtain

$$\int \mathrm{d}\mathbf{r}' F\left(\mathbf{r},\mathbf{r}'\right)\sum_{\mu}^{K} C_{\mu i}\phi_\mu\left(\mathbf{r}'\right) = \epsilon_i \sum_{\mu}^{K} C_{\mu i}\phi_\mu\left(\mathbf{r}\right) \tag{3.32}$$

Acting with $\int \mathrm{d}\mathbf{r}\phi_\nu^*(\mathbf{r})$ from the left yields:

$$\sum_\mu^K C_{\mu i} \underbrace{\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_\nu^* F(\mathbf{r},\mathbf{r}')\phi_\mu(\mathbf{r}')}_{F_{\nu\mu}} = \epsilon_i \sum_\mu^K C_{\mu i} \underbrace{\int \mathrm{d}\mathbf{r}\phi_\nu^*(\mathbf{r})\phi_\mu(\mathbf{r})}_{S_{\nu\mu}} \tag{3.33}$$

Overlap matrix $S_{\nu\mu}$: Basis functions are in general not orthonormal

$$\Longrightarrow \sum_\mu^K F_{\nu\mu}C_{\mu i} = \epsilon \sum_\mu^K S_{\nu\mu}C_{\mu i} \tag{3.34}$$

- We have transformed the Hartree Fock equations for single particle states to a Hartree Fock equation for the expansion coefficients

This can be written in matrix form.

$$\mathbf{FC} = \mathbf{SC}\epsilon \tag{3.35}$$

Where $\mathbf{C}$ is a $K \times K$ square matrix of the expansion coefficents and ϵ a diagonal matrix of singe particle energies.

$$\epsilon = \begin{pmatrix} \epsilon_1 & & & 0 \\ & \epsilon_2 & & \\ & & \ddots & \\ 0 & & & \epsilon_K \end{pmatrix} \tag{3.36}$$

Note that equation (3.35) produces only as many eigenvalues as there are basis functions, i.e. K-many.
$\Longrightarrow$ K-many basis functions can only expand K-many single particle states.
Equation (3.35) is the **Roothan equation**, which is central to quatum chemistry.
We have moved form:

$$H_{elec}\Psi_{elec} = E_{elec}\Psi_{elec}$$

to the Roothan equation:

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

in two steps:

- Single determinat approximation (conceptual or physical approximation)
- Introduction of a basis (expansion of wavefunctions) (practical or computational approximation)

To solve Roothaan's equations all that is left to do is to derive equations for $\mathbf{F}$ in the basis and for a given basis term this into equations that can be implemented.

$$\begin{aligned} F(\mathbf{r},\mathbf{r}') =& h(\mathbf{r}) + v_H(\mathbf{r}) + \Sigma(\mathbf{r},\mathbf{r}') \\ & \downarrow \\ & (\nu|h|\mu) \end{aligned} \tag{3.37}$$

The density:

$$\begin{aligned} n(\mathbf{r}) &= 2\sum_i^{N/2} |\psi_i(\mathbf{r})|^2 = \sum_i^{N/2} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \\ &= 2\sum_i^{N/2}\sum_\nu C_{\nu i}^*\phi_\nu^*(\mathbf{r})\sum_\mu C_{\mu i}^*\phi_\mu^*(\mathbf{r}) \\ &= \sum_{\mu\nu} \underbrace{\sum_i 2C_{\nu i}C_{\mu i}}_{P_{\mu\nu}\text{ - density matrix}} \phi_\nu^*(\mathbf{r})\phi_\mu(\mathbf{r}) \\ &= \sum_{\mu\nu} P_{\mu\nu}\phi_\nu^*(\mathbf{r})\phi_\mu(\mathbf{r}) \end{aligned}$$

The Hatree potential:

$$
\begin{aligned}
V_{\mu\nu}^{H} &= \int \mathrm{d}\mathbf{r}\phi_{\nu}^{*}\left(\mathbf{r}\right) v_{H}\left(\mathbf{r}\right)\phi_{\mu}\left(\mathbf{r}\right) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_{\nu}^{*}\left(\mathbf{r}\right)\frac{n\left(\mathbf{r}\right)'}{\left|\mathbf{r}-\mathbf{r}'\right|}\phi_{\mu}\left(\mathbf{r}\right) \\
&= \sum_{nm} P_{nm}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\frac{\phi_{\nu}^{*}\left(\mathbf{r}\right)\phi_{n}^{*}\left(\mathbf{r}'\right)\phi_{m}\left(\mathbf{r}'\right)\phi_{\mu}\left(\mathbf{r}\right)}{\left|\mathbf{r}-\mathbf{r}'\right|} \\
&= \sum_{nm} P_{nm}(\nu n|\mu m)
\end{aligned}
$$

The exchange operator:

$$
\begin{aligned}
\Sigma_{\mu\nu} &= \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_{\nu}^{*}\left(\mathbf{r}\right)\Sigma\left(\mathbf{r},\mathbf{r}'\right)\phi_{\mu}\left(\mathbf{r}'\right) \\
&= \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_{\nu}^{*}\left(\mathbf{r}\right)\sum_{i}^{N/2}\frac{\psi_{i}\left(\mathbf{r}\right)\psi_{i}^{*}\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}\phi_{m}u\left(\mathbf{r}'\right) \\
&= \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_{\nu}^{*}\left(\mathbf{r}\right)\sum_{nm}\underbrace{\sum_{i}^{N/2}C_{ni}^{*}C_{mi}}_{\frac{1}{2}P_{nm}}\frac{\phi_{m}\left(\mathbf{r}\right)\psi_{n}^{*}\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}\phi_{m}u\left(\mathbf{r}'\right) \\
&= -\frac{1}{2}P_{nm}(\nu n|m\mu)
\end{aligned}
$$

$$
\Longrightarrow F_{\nu\mu} = \underbrace{h_{\nu\mu}}_{\text{independent on P}} + \underbrace{\sum_{nm}\left[(\nu n|\mu m) - \frac{1}{2}(\nu n|m\mu)\right]}_{\text{dependent on P}} \tag{3.38}
$$

The Roothaan equations are non-linear.

$$
\begin{aligned}
\mathbf{F} &= \mathbf{F}\left(\mathbf{P}\right) = \mathbf{F}\left(\mathbf{C}\right) \\
\mathbf{F}\left(\mathbf{C}\right)\mathbf{C} &= \mathbf{S}\mathbf{C}\epsilon
\end{aligned}
$$

Iterative or self-consistent solution of the Roothaan equation:

1. Choose a basis
2. Calculate the integrals $\Sigma_{\mu\nu}$, $h_{\mu\nu}$, $(\nu n|\mu m)$
3. Initialize P_{nm}
4. Compute $F_{\mu\nu}$
5. Solve the Roothaan equations $\Longrightarrow$ New coefficients $C_{\nu i}$ $\Longrightarrow$ new P_{nm}
   Repeat steps 4 and 5 until P_{nm} does not change anymore.

Scaling:
For an atom centered basis it is easy to see that our basis $\{\phi_\mu\}$ grows liniear with the number of atoms N.

$\Longrightarrow$ N^4 many integrals $(\nu n|\mu m)$ are required

$\Longrightarrow$ Computation of $F_{\mu\nu}$ requires N^4 operations if no further tricks and reductions are employed

$\Longrightarrow$ The formal scaling of Hartree Fock is N^4

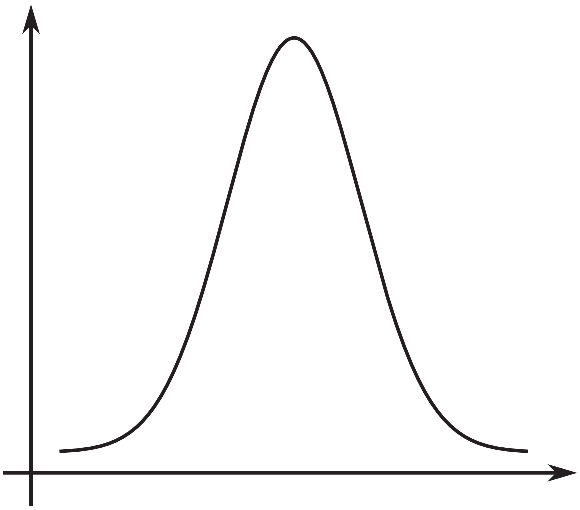


Figure 3.9: Gaussian

One solution, a fast basis:
Gauss orbital (or Gaussians)

$$\psi_{\mathbf{n}\gamma}(\mathbf{r}) = A_{n_x n_y n_z} x^{n_x} y^{n_y} z^{n_z} \mathrm{e}^{-\gamma r^2} \qquad \text{Kartesian Gaussians (fig. 3.9)} \tag{3.39}$$

with $n_x + n_y + n_z = L$ we obtain the familiar functions from spherical symmetry (tab. (3.1)).
Atom centered Gaussisans:

$$\phi_{\mathbf{an}\gamma}(\mathbf{r}) = \phi_{\mathbf{n}\gamma}(\mathbf{r} - \mathbf{R}_a) \qquad \text{with } \mathbf{R}_a \text{ the position of atom a} \tag{3.40}$$

Important properties:

- Fourier transformation of a Gaussian is also a Gaussian

$$\mathrm{e}^{-\gamma r^2} \xrightarrow{\mathrm{FT}} \sqrt{\frac{\pi}{\gamma}} \mathrm{e}^{-\frac{\pi^2}{\gamma} k^2} \tag{3.41}$$

$\Longrightarrow$ benefitial for solid state calculations

L	#	orbital type	n_x	n_y	n_z	$\phi_{\mathbf{n}\gamma}\left(x\left(\frac{2\gamma}{\pi}\right)^{3/4}\mathrm{e}^{-\gamma r^2}\right)$
0	1	s	0	0	0	1
1	2	p_x	1	0	0	$2\sqrt{\gamma}x$
	3	p_y	0	1	0	$2\sqrt{\gamma}y$
	4	p_z	0	0	1	$2\sqrt{\gamma}z$
2	5	d_{xz}	1	0	1	$4\gamma xz$
	6	d_{yz}	0	1	1	$4\gamma yz$
	7	d_{xy}	1	1	0	$4\gamma xy$
	8	$d_{3z^2-r^2}$				$\frac{2\gamma}{\sqrt{3}}\left(3z^2 - r^2\right)$
	9	$d_{x^2-y^2}$				$2\gamma\left(x^2 - y^2\right)$
	10	s				$\frac{4\gamma r^2}{\sqrt{15}}$

Table 3.1: Parameters for cartesian Gaussians up to $n_x + n_y + n_z = L = 2$. The last three rows for $L = 2$ follow from the linear combination of $x^2,\ y^2,\ z^2$-orbitals.

- The product of two Gaussians yields another at a different position:

$$e^{-\alpha(\mathbf{r}-\mathbf{R}_a)^2} e^{-\beta(\mathbf{r}-\mathbf{R}_b)^2} = e^{-\delta D^2} e^{-\xi(\mathbf{r}-\mathbf{X})^2} \tag{3.42}$$

  with the center of mass $\mathbf{X} = \frac{\alpha \mathbf{R}_a + \beta \mathbf{R}_b}{\alpha+\beta}$ and $D = \mathbf{R}_a - \mathbf{R}_b$ as well as, $\delta = \frac{\alpha\beta}{\alpha+\beta}$.
  For the cartesian functions a similar relation can be derived (fig (3.10)):

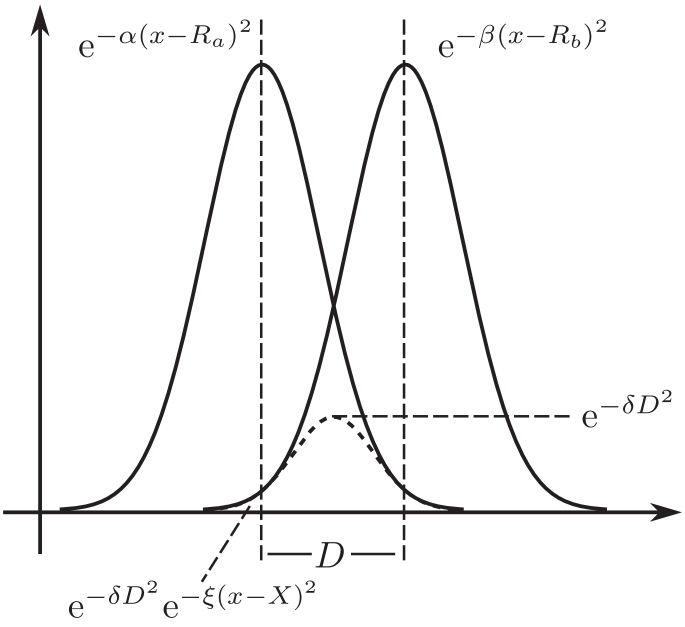


Figure 3.10: Product of two s-type Gaussians

$$(x-R_a)^i (x-R_b)^j = \sum_{n=0}^{i+j} \sum_{l} \binom{i}{n-l} \binom{i}{l} (-1)^{b-l} \frac{\alpha^{j-l}\beta^{i-n-l}}{(\alpha+\beta)^{i+j-n}} D^{i+j-n} (x-X)^n \tag{3.43}$$

$$T_{\mathbf{ijn}} = D^{\mathbf{i+j-n}} e^{-\delta D^2} \prod_{m=x,y,z} M_{i_m j_m n_m} \tag{3.44}$$

$$\Longrightarrow \phi_{\mathbf{a}\mathbf{i}\alpha}(\mathbf{r}) \phi_{\mathbf{b}\mathbf{j}\beta}(\mathbf{r}) = \sum_{\mathbf{n}}^{\mathbf{i+j}} T_{\mathbf{ijn}} \phi_{\mathbf{n}\mathbf{X}\xi}(\mathbf{r}) \tag{3.45}$$

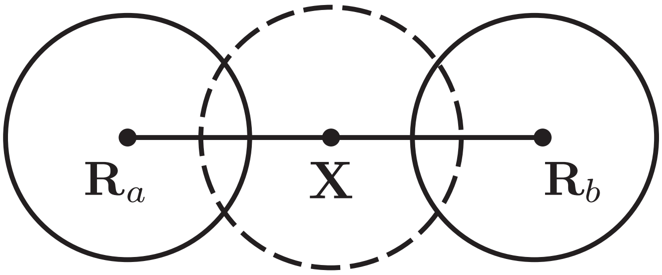


Figure 3.11: Product of Gaussian orbitals on two different atoms

- Products of Gauss orbitals on two different atoms can be expanded in Gauss orbitals centered on their center of mass
- The transformation tensor is given analytically, to compute k center integrals

$$(\nu n|\mu m) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\phi_\nu^* (\mathbf{r})\, \phi_n^* (\mathbf{r}')\, \phi_\mu (\mathbf{r})\, \phi_m (\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3.46}$$

we have to expand the two products for $\mathbf{r}$ and $\mathbf{r}'$ into Gaussians around their respective centers of mass.
$\Longrightarrow$ Then the problem is reduced to calculating the Coulomb integral of two Gaussians.

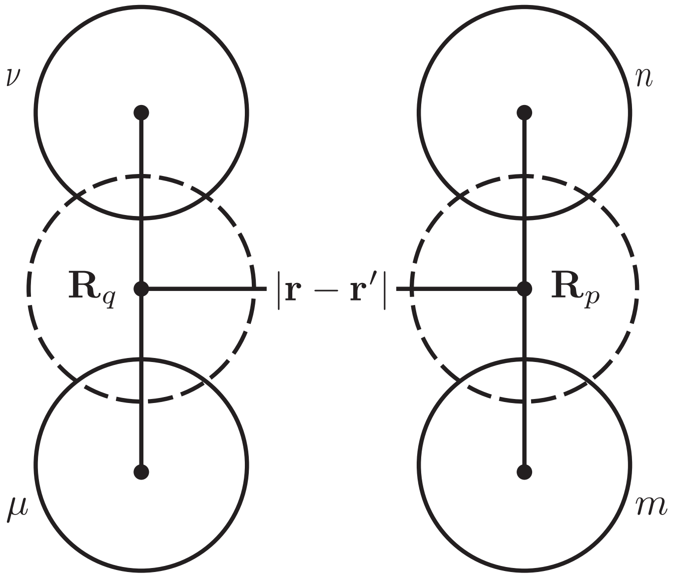


Figure 3.12: k-center integrals

Let us consider two s-type Gaussians at the centers $\mathbf{R}_q$ and $\mathbf{R}_p$. We then have to solve the following integral (the derivation is quite tedious and can be done by inserting the Fourier transformations of the Gaussians and $\frac{1}{r}$):

$$\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\mathrm{e}^{-p|\mathbf{r}-\mathbf{R}_p|^2}\mathrm{e}^{-q\left|\mathbf{r}'-\mathbf{R}_q\right|^2}}{|\mathbf{r}-\mathbf{r}'|} = \frac{2\pi^{\frac{5}{2}}}{pq(p+q)^{1/2}} F_0\left(\frac{pq}{p+q}\left|\mathbf{R}_p-\mathbf{R}_q\right|^2\right) \tag{3.47}$$

with

$$F_0(t) = t^{1/2} \int_0^{t^{1/2}} \mathrm{d}y \mathrm{e}^{-y^2} = \frac{1}{2} \left(\frac{\pi}{t}\right)^{1/2} \operatorname{erf}\left(t^{1/2}\right) \tag{3.48}$$

erf is the error function, avaiable in any/most programming languages.
The Coulomb integral of two Gaussians is known analytically.

Now all that is left to do is to determine the Cpolomb integral of two arbitrary cartesian Gaussians. We do this by observing that the derivative if an s-type Gaussian produces higher order Gaussians.

$$\text{for one dimension} \quad \underset{\substack{\uparrow \\ \text{note: normalization is different}}}{\phi_n (r-R)} = (r-R)^n \, \mathrm{e}^{-\alpha(r-R)^2}$$

$$\begin{aligned}
\frac{\mathrm{d}\phi_0 (r-R)}{\mathrm{d}R} &= 2\alpha (r-R) \, \mathrm{e}^{-\alpha(r-R)^2} = 2\alpha\phi_0 (r-R) \\
\frac{\mathrm{d}^2\phi_0 (r-R)}{\mathrm{d}R^2} &= -2\alpha \mathrm{e}^{-\alpha(r-R)^2} + 2\alpha (r-R) \frac{\mathrm{d}\phi_0 (r-R)}{\mathrm{d}R} \\
&= 2\alpha \left[-\phi_0 (r-R) + 2\alpha (r-R)^2 \mathrm{e}^{-\alpha(r-R)^2}\right] \\
&= 2\alpha \left[2\alpha\phi_2 (r-R) - \phi_0 (r-R)\right]
\end{aligned}$$

So we make the ansatz:

$$\frac{\mathrm{d}^i\phi_0 (r-R)}{\mathrm{d}R^i} = \sum_{j\leq i} D_{ij} (r-R)^i \, \mathrm{e}^{-\alpha(r-R)^2} \tag{3.49}$$

Which gives us the recursion relation:

$$\begin{aligned}
D_{ij} &= -2\alpha D_{i-1,\, j-1} + (j+1) D_{i-1,\, j+1} \\
\text{with} \qquad D_{00} &= 1 \qquad \text{and} \qquad D_{ij} = 0 \quad \forall \quad i,j < 0 \wedge j > i
\end{aligned} \tag{3.50}$$

$\Longrightarrow$ Since derivations in x, y,z, are seperable:

$$\nabla_{\mathbf{R}}^{\mathbf{n}} \phi_{\mathbf{a}0\alpha} (\mathbf{r}) = \frac{\mathrm{d}^{n_x}}{\mathrm{d}R_x^{n_x}} \frac{\mathrm{d}^{n_y}}{\mathrm{d}R_y^{n_y}} \frac{\mathrm{d}^{n_z}}{\mathrm{d}R_z^{n_z}} \phi_{\mathbf{a}0\alpha} (\mathbf{r}) = \sum_{\mathbf{m}}^{m_i \leq n_i} D_{\mathbf{nm}} \phi_{\mathbf{am}\alpha} (\mathbf{r}) \tag{3.51}$$

The diagonal elements of $D_{\mathbf{nm}}$ are non-zero and therefore $D_{\mathbf{nm}}$ is invertable and we can write:

$$\phi_{\mathbf{am}\alpha} (\mathbf{r}) = \sum_{\mathbf{n}} D_{\mathbf{nm}}^{-1} \nabla_{\mathbf{R}}^{\mathbf{n}} \phi_{\mathbf{a}0\alpha} (\mathbf{r}) \tag{3.52}$$

$\Longrightarrow$ In other words, the other cartesian Gauss functions follow from the s-functions through a recursion relation involving the derivatives. Since the Coulomb integral of two s-functions is known analytically (see eq. (3.47)), as well as their derivatives $\nabla_{\mathbf{R}_a}^{\mathbf{n}}$ and $\nabla_{\mathbf{R}_b}^{\mathbf{n}}$ (see eq.(3.51)), the Coulomb integral of 2 arbitray Gaussians can be computed fast via a recursion relation.
Recipe for computing $(\nu n|\mu m)$ (also see fig. (3.12)):

1. Expand products $\phi_\nu\phi_\mu$ and $\phi_n\phi_m$ in Gauss orbitals around their centers of mass
2. Evaluate recursion relations for the Coulomb integrals on the centers $\mathbf{R}_p$ and $\mathbf{R}_q$

Advantages:

- No 6-dimensional real-space integral $\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$ has to be performed $\Longrightarrow$ fast
- Efficient algorithms and screening prosedures have been developed for carrying out the expansions and recursions $\Longrightarrow$ fast, even on the fly evaluation of 4-center integrals is possible $\Longrightarrow$ on the fly saves memory!

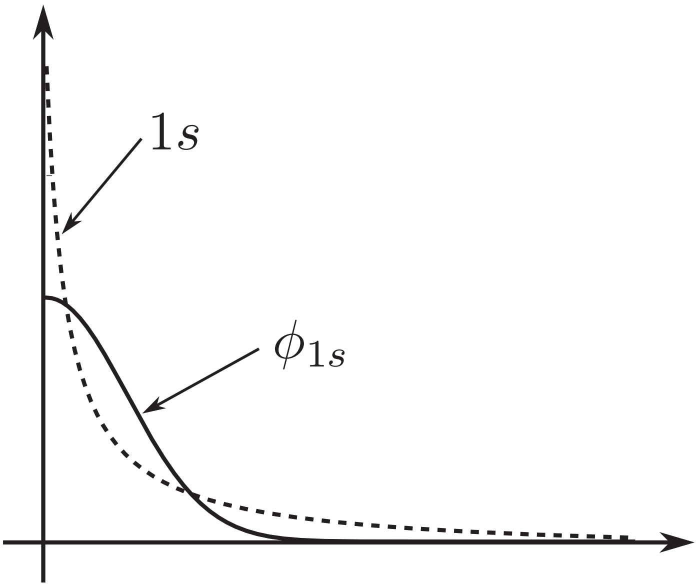


Figure 3.13: Comparison between Gaussian 1s function and actual 1s function

Remark:

- The procedure outlined here is for illustrative purposes, but by no means the most efficient.

Disentvantages:

- Gaussians miss the cusp for 1s functions (certainly not ideal for core states)
- Difficult to design basis sets (exponents, number of functions) that allow for a systematic accuracy analysis

3.2.4 Performance of Hartree-Fock

Table 3.2: Hartree-Fock total energies for selected atoms and simple molecules.

E_{tot} [Ha]	H	He	Be	Mg	H_2	LiH
HF[*]	−0.5	−2.8610	−14.5697	−199.6900	−1.1371	−7.9872
CI[†]	−0.5	−2.9362	−14.6674	−200.0530	−1.1660	−8.0400
deviation (CI-HF)	0.0	−0.0427	−0.0977	−0.3630	−0.0289	−0.0528
in %	0	1.5	0.7	0.2	2.5	0.7

[*] FHI-aims calculations with cc-pV5Z Gaussian basis set
[†] from Chakravorty *et. al.* Phys. Rev. A **47**, 3649 (1993)
L. Wolniewicz J. Chem. Phys. **99**, 1851 (1993)
X. Li and J. Paldus, J. Chem. Phys. **118**, 2470 (2003)

- Hartree-Fock underestimates the total energy compared to escentially exact Configuration Interaction calculations
- The underestimation is only a small persentage of the correlation enrgy
- However, this can be decisive for energy differences

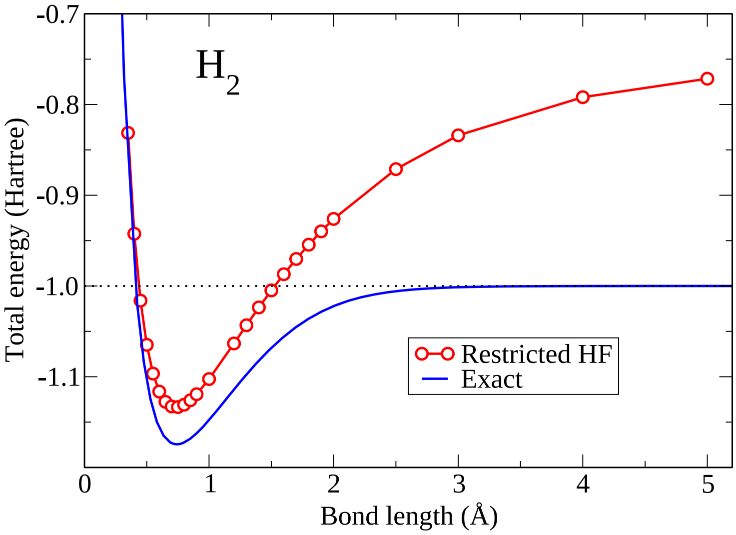
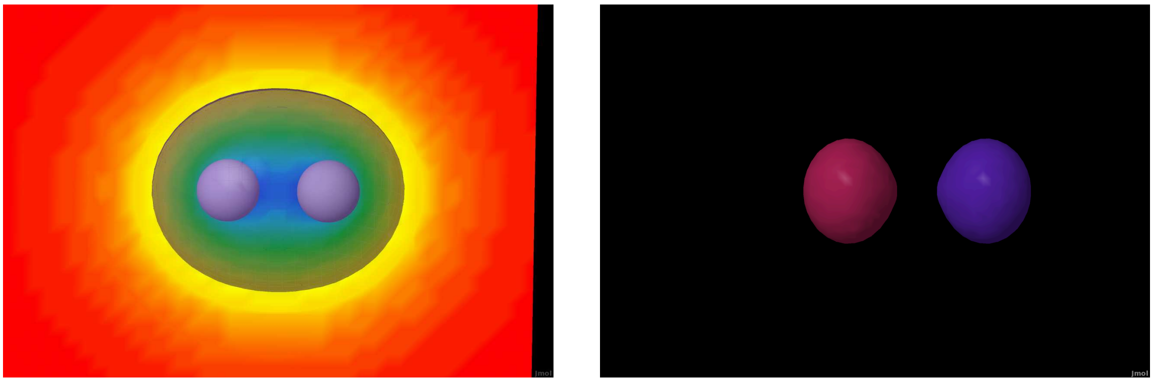


Figure 3.14: Total energy of H_2 in restricted closed-shell Hartree-Fock as a function of the interatomic distance.

Figure (3.14) shows the restricted Hartree Fock energy for H_2 as a function of the interatomic distance. The curve shows 3 distinct regimes:

- Repulsion at short distances
- A minimum at intermediate distances (to see if it actually binds one has to look at the binding energy)
- Levelling out at dissociation



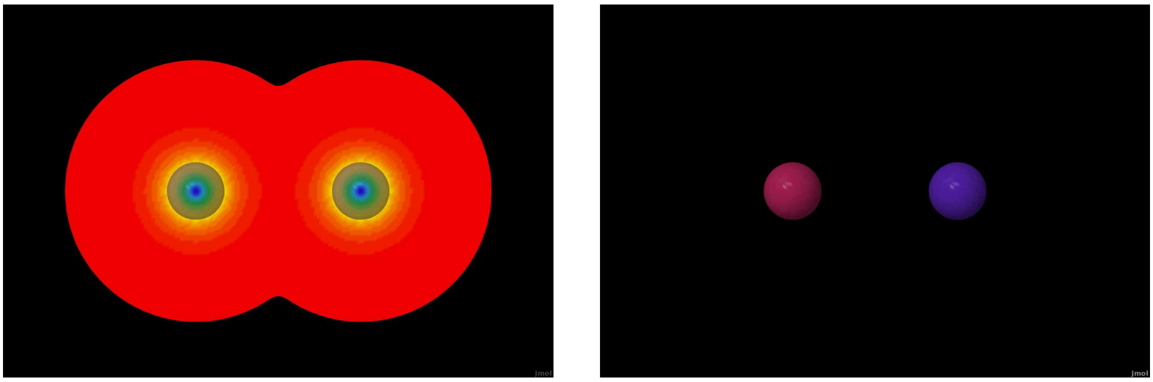
(a) Wavefunction of the bonding state of H_2 at equilibrium in restricted closed-shell Hartree-Fock. The two spheres mark the atoms, the ellipsoid is an isosurface plot of the orbital and the shading corresponds to the wavefunctions on a 2D cut through the molecule.

(b) Isosurface of the wavefunction for the anti-bonding state of H_2 at equilibrium in restricted closed-shell Hartree-Fock. The lobe on the left corresponds to negative values and the lobe on the right to positive ones.

Figure 3.15: The wavefunction for the bonding and anti-bonding state of H_2 at equilibrium in restricted closed-shell Hartree-Fock.

Figures (3.15, 3.16) show the two lowest Hartree Fock single particle orbitals at the equilibrium bond distance and close to dissociation at 6Å.

- The bonding state is occupied by 2 electrons



(a) Wavefunction of the bonding state of H_2 at a binding distance of 6 Å in restricted closed-shell Hartree-Fock. The two spheres that mark the atoms are hidden under the isosurface plot of the orbital. The shading corresponds to the wavefunctions on a 2D cut through the molecule.

(b) Isosurface of the wavefunction for the anti-bonding state of H_2 at a binding distance of 6 Å in restricted closed-shell Hartree-Fock. The sphere on the left corresponds to negative and the one on the right to positive values.

Figure 3.16: The wavefunction for the bonding and anti-bonding state of H_2 at a binding distance of 6 Å in restricted closed-shell Hartree-Fock.

- The antibonding state is empty
- The bonding state derives from a positive superposition of the 1s states of the two hydrogen atoms and the anitbonding state from a negative superposition (This is most obvious at dissociation (6Å)).

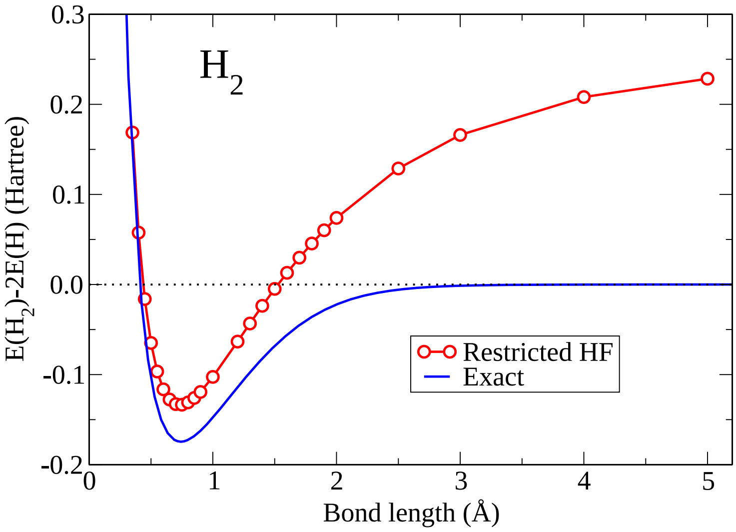


Figure 3.17: Binding energy of H_2 in restricted closed-shell Hartree-Fock as a function of the interatomic distance. The exact curve is taken from L. Wolniewicz, J. Chem. Phys. **99**, 1851 (1993)

Figure (3.17) shows the binding energy

$$E_{bind} = E\left(H_2\right) - 2E\left(H\right) \tag{3.53}$$

compared to exact calculations.

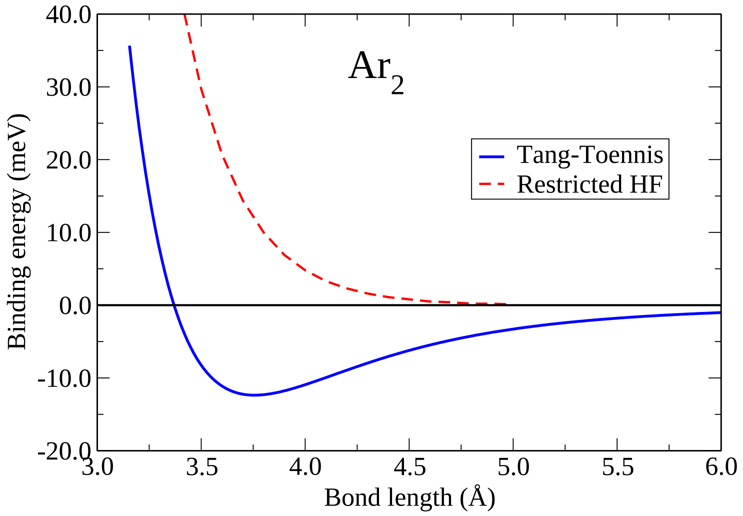


Figure 3.18: Binding energy of Ar_2 in restricted closed-shell Hartree-Fock as a function of the interatomic distance. The reference curve bt K. T. Tang and J. P. Toennies (J. Chem. Phys. **118**, 4976 (2003)) is based on theoretical modeling of experimental data.

- The equilibrium distance in Hartree Fock is good
- The binding energy is underestimated
- The dissociation limit is incorrect

Figure (3.18) shows the binding energy curve of a van der Waals bonded dimer.

- Ar atom is closed shell - no covalent bond
- Binding energy is much lower (meV)
- Hartree-Fock gives no binding in this case!
- But correct dissociation limit

Theoretical descrition of bond breaking and bond making is a great challenge!

Table 3.3: Individual energies (in Ha) for reactants and the transition state of the reaction $OH + H_2 \rightarrow H + H_2O$. The deviation is measured with respect to accurate Coupled Cluster (CCSD(T) CBS cc-pV(Q,5)Z) calculations. The experimental value is taken from Y. Zhao and D. G. Truhlar, J. Phys. Chem. A **110**, 13126 (2006).

	OH	H_2	H	H_2O	TS
HF	−75.4284825	−1.1336606	−0.5000000	−76.0680526	−76.5283317
deviation (CCSD(T)-HF)	−0.2482897	−0.0409171	0.0000000	−0.3092634	−0.3148024

reaction barrier	forward	reverse	forward	reverse
HF	0.92 eV	1.08 eV	21.2 kcal/mol	24.9 kcal/mol
Exp.	0.22 eV	0.92 eV	5.09 kcal/mol	21.2 kcal/mol

Hartree Fock in chemestry (see tab. (3.3):

- Typically underbinds by about $4eV$ per bond $\Longrightarrow$ too large for thermo chemistry (energy for dissociation)
- $1kcal/mol$ ($\sim 1/20eV$) error in transistion state energy of a chemical reaction gives a factor of 5 error in the reaction rate

Table 3.4: Lattice constants (in Å) of some solids in HF. Values are taken K. Doll and H. Stoll, Phys. Rev. B **56**, 10121 (1997)

cohesive energy (eV)	LiF	NaF	KF	LiCl	NaCl	KCl
HF	4.011	4.636	5.450	5.281	5.791	6.548
Exp.	4.010	4.609	5.311	5.106	5.595	6.248
deviation	0.02%	0.6%	2.6%	3.4%	3.5%	4.8%

Table 3.5: Cohesive energy ($E(solid) - \sum_i E(atom_i)$) of some solids in HF. Values are taken from R. Dovesi *et al.* Reviews in Computational Chemistry, Volume 21 and K. Doll and H. Stoll, Phys. Rev. B **56**, 10121 (1997)

cohesive energy (eV)	LiF	LiCl	NaF	NaCl	KF	KBr	KCl	MgO	Si	Be
HF	6.81	5.70	5.95	5.31	5.65	4.94	5.54	7.25	6.67	1.87
Exp.	8.92	7.24	8.00	6.68	7.70	6.27	6.75	10.26	9.50	3.31
deviation	23.7%	21.2%	25.6%	20.5%	26.6	21.2%	17.9%	29.3%	29.7%	43.6%

Hartree Fock in condensed matter (see tab. (3.2.4)):

- Not often applied
- Lattice constants overestimated
- cohesive energies underestimated significantly (like in chemistry)

3.2.5 Koopmann's Theorem and the meaning of Hartree-Fock eigenvalues

Eigenvalue equation:

$$
\begin{aligned}
&\int \mathrm{d}\mathbf{x}' F\left(\mathbf{x},\mathbf{x}'\right)\varphi_m\left(\mathbf{x}'\right) = \epsilon_m \varphi_m\left(\mathbf{x}'\right) \qquad | \quad \times \int \mathrm{d}\mathbf{x}\varphi_n^*\left(\mathbf{x}\right) \\
\Longrightarrow &\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\varphi_n^*\left(\mathbf{x}\right) F\left(\mathbf{x},\mathbf{x}'\right)\varphi_m\left(\mathbf{x}'\right)\epsilon_m\delta_{nm} \\
\Longrightarrow &\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\varphi_n^*\left(\mathbf{x}\right)\left[h\left(\mathbf{x}\right)\delta\left(\mathbf{x}-\mathbf{x}'\right)\sum_i^N \frac{\varphi_i^*\left(\mathbf{x}'\right)\varphi_i\left(\mathbf{x}'\right)}{\left|\mathbf{r}-\mathbf{x}'\right|} + \sum_i^N \frac{\varphi_i^*\left(\mathbf{x}'\right)\varphi_i\left(\mathbf{x}\right)}{\left|\mathbf{r}-\mathbf{x}'\right|}\right]\varphi_n\left(\mathbf{x}'\right) = \epsilon_n \\
\Longrightarrow & h_{nn} + \sum_i^N \langle ni|ni\rangle - \langle ni|in\rangle = \epsilon_n
\end{aligned}
$$

Now consider an occupied state (a):

$$
\begin{aligned}
\epsilon_a &= h_{aa} + \sum_i^N \langle ai|ai\rangle - \langle ai|ia\rangle \\
&= h_{aa} + \sum_{i\neq a}^N \langle ai|ai\rangle - \langle ai|ia\rangle \\
&\text{because} \qquad \langle aa|aa\rangle - \langle aa|aa\rangle = 0
\end{aligned}
$$

ϵ_a is the kinetic and external energy of an electron in state a plus Coulomb and exchange energy with all remaining $N-1$ electrons. This suggests that ϵ_a is the removal energy of electron a or the ionization potential (IP), a is the highest occupied state.

$$
\mathrm{IP} = E(N-1) - E(N) \tag{3.54}
$$

in Hartree-Fock:

$$
\begin{aligned}
E(N-1) &= \left\langle \Psi_{N-1}^{SD} | H_{elec} \Psi_{N-1}^{SD} \right\rangle \\
E(N) &= \left\langle \Psi_{N}^{SD} | H_{elec} \Psi_{N}^{SD} \right\rangle
\end{aligned}
$$

Ψ_N^{SD} and Ψ_{N-1}^{SD} are generally not composed of the same orbitals. If for a moment we assume that they are, we obtain:

$$
\begin{aligned}
E(N) &= \sum_a^N \langle a|h|a\rangle + \frac{1}{2}\sum_{ai}^N \langle ai|ai\rangle - \langle ai|ia\rangle \\
E_c(N-1) &= \sum_{a\neq c}^N \langle a|h|a\rangle + \frac{1}{2}\sum_{a\neq c,\ i\neq c}^N \langle ai|ai\rangle - \langle ai|ia\rangle
\end{aligned}
$$

where c is the electron that has been removed.

$$
\begin{aligned}
\mathrm{IP} &= E(N-1) - E(N) \\
&= -\langle c|h|c\rangle - \frac{1}{2}\sum_{a,\ i=c}^N \langle ac|ac\rangle - \langle ac|ca\rangle - \frac{1}{2}\sum_{i,\ a=c}^N \langle ci|ci\rangle - \langle ci|ic\rangle \\
&= -\langle c|h|c\rangle - \sum_i \langle ci|ci\rangle - \langle ci|ic\rangle \\
&= -\epsilon_c
\end{aligned}
$$

$\Longrightarrow$ The eigenvalues of occupied Hartree-Fock orbitals are the negativ ionization energies, provided the orbitals are not allowed to change (relax).

For the unoccupied states with orbital energy ϵ_r we can derive an analogous expression:

$$\mathrm{EA} = E(N) - E_r(N+1) = -\epsilon_r \tag{3.55}$$

Where EA is the electron affinity.
Koopman's theorem:

> Given an N-electron Hartree-Fock single determinant Ψ_N^{SD} with occuoied and unoccupied (virtual) spin orbital energies ϵ_a and ϵ_r, then the ioniszation potential to produce an (N-1)-electron single determinat Ψ_{N-1}^{SD} with identical spin orbitals, obtained by removing an electron from spin orbital φ_a and the electron affinity to produce an (N+1)-electron singe determinatn Ψ_{N+1}^{SD} with identical spin orbitals obtained by adding an electron to spin orbital φ_r are just $-\epsilon_a$ and $-\epsilon_r$ respectively.

Table 3.6: Lowest ionization potentials (in eV) of some small molecules in HF. Values taken from A. Szabo and N. S. Ostlund, Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory (Dover)

ionization potential (eV)	CH_4	NH_3	H_2O	FH
HF	14.86	11.65	13.80	17.69
Exp.	14.40	10.88	12.60	15.81
deviation	3.1%	7.1%	9.5%	11.9%

Hartree Fock:

- Overestimates ionization potentials (see tab. (3.2.5))
- Undersetimates electron affinities - often negative ions are not stable in Hartree-Fock

In solids (see fig. (3.19):

- Band gap severly overestimated, Hartree Fock $\sim 6eV$, experiment $\sim 0.7eV$
- Shape of bands is correct, but bandwidth considerably overestimated

3.3 Form of the exact wave function and configuration interaction

In the previous section we had introduced a single slater determinant formed by occupying the lowest spin orbitals. But we can also occupy differently.

In total there are $\binom{2k}{N} = \frac{(2k)!}{N!(2k-N)!}$ many configurations. We have seen that a single slater determinant of Hartree-Fock spin orbitals gives the Hartree-Fock approximation to:

$$H_{elec}\Psi_{elec} = E_{elec}\Psi_{elec}$$

How can we expand the full many-body wave-function Ψ_{elec}? Suppose we have a complete basis $\{\chi_i\}$. A function of a single variable can than be exactly expanded as:

$$\Phi\left(\mathbf{x}_1\right) = \sum_i a_i \chi_i\left(\mathbf{x}_1\right) \tag{3.56}$$

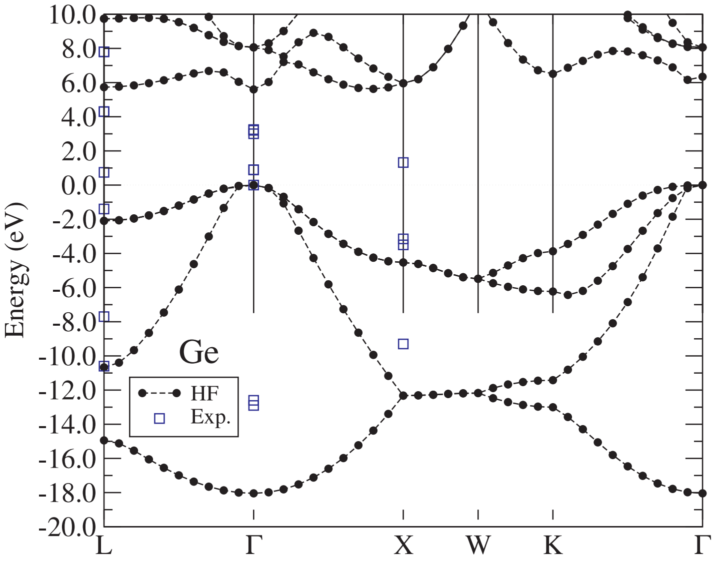


Figure 3.19: HF band structure of the Germanium crystal. Experimental values (squares) correspond to direct and inverse photoemission spectroscopy and are taken from Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer-Verlag, New York, 1982) and A. L. Wachs *et al.* Phys. Rev. B **32**, 2326 (1985)

A function of two variables can be expanded in stages:

$$\Phi\left(\mathbf{x}_1, \mathbf{x}_2\right) = \sum_i a_i\left(\mathbf{x}_2\right)\chi_i\left(\mathbf{x}_1\right) \tag{3.57}$$

Inserting eq. (3.56):

$$\Phi\left(\mathbf{x}_1, \mathbf{x}_2\right) = \sum_{ij} b_{ij}\chi_i\left(\mathbf{x}_1\right)\chi_j\left(\mathbf{x}_2\right) \tag{3.58}$$

If Φ is supposed to be a fermionic wave-function we require antisymmetry:

$$\Phi\left(\mathbf{x}_1, \mathbf{x}_2\right) = -\Phi\left(\mathbf{x}_2, \mathbf{x}_1\right)$$

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

$$\begin{aligned}\Longrightarrow \Phi\left(\mathbf{x}_1, \mathbf{x}_2\right) &= \sum_i \sum_{j>i} b_{ij}\left[\chi_i\left(\mathbf{x}_1\right)\chi_j\left(\mathbf{x}_2\right) - \chi_i\left(\mathbf{x}_2\right)\chi_j\left(\mathbf{x}_1\right)\right] \\ &= \sum_{j>i} b_{ij}\sqrt{2}\Psi^{SD}\left(\mathbf{x}_1, \mathbf{x}_2\right)\end{aligned}$$

An arbitrary antisymmetric function can be expanded in terms of all unique determinats formed in terms a complete set of one-variable funtions $\chi_i\left(\mathbf{x}\right)$.
This can be easily generalized to the N-body wafe-function:

$$\Psi_{elec} = C_0, \Psi_0 + \sum_{ra} C_a^r \Psi_a^r + \sum_{a<b,\ r<s} C_{ab}^{rs}\Psi_{ab}^{rs} + \sum_{a<b<c,\ r<s<t} C_{abc}^{rst}\Psi_{abc}^{rst} + \ldots \tag{3.59}$$

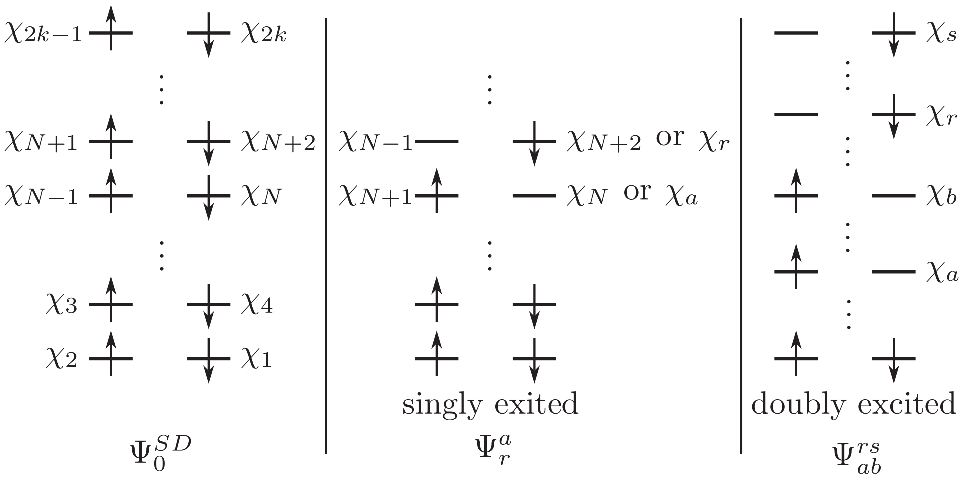


Figure 3.20: Single slater determinats with different occupation.

The coefficients are then obtained by diagonalizing.

$$\langle \Psi_{elec}|H_{elec}|\Psi_{elec}\rangle = \begin{array}{c|ccccc} & & \Psi_a^r & \Psi_{ab}^{rs} & \Psi_{abc}^{rst} & \cdots \\ & \Psi_0 & S & D & T & \cdots \\ \hline \Psi_0 & \langle\Psi_0|H|\Psi_0\rangle & \langle\Psi_0|H|S\rangle & \langle\Psi_0|H|D\rangle & \cdots & \cdots \\ S & \langle S|H|\Psi_0\rangle & \langle S|H|S\rangle & \langle S|H|D\rangle & \cdots & \cdots \\ D & \langle D|H|\Psi_0\rangle & \langle D|H|S\rangle & \langle D|H|D\rangle & \cdots & \cdots \\ T & \langle T|H|\Psi_0\rangle & \cdots & & \vdots & \\ \vdots & & & \ddots & & \end{array} \tag{3.60}$$

and the matrix elements are given by:

	$O_1 = \sum_i h(i)$	$O_2 = \sum_i \sum_{i<j} \frac{1}{\lvert\mathbf{r}_i - \mathbf{r}_j\rvert}$
case 1: $\lvert K\rangle = \lvert \dots mn \dots\rangle$	$\langle K\lvert O_1\rvert K\rangle = \sum_m \langle m\lvert h\rvert m\rangle$	$\langle K\lvert O_2\rvert K\rangle = \frac{1}{2}\sum_{mn} \langle mn\lvert mn\rangle - \langle mn\lvert nm\rangle$
case 2: $\lvert K\rangle = \lvert \dots mn \dots\rangle$ $\lvert L\rangle = \lvert \dots pn \dots\rangle$ (differ by one)	$\langle K\lvert O_1\rvert L\rangle = \langle m\lvert h\rvert p\rangle$	$\langle K\lvert O_2\rvert L\rangle = \sum_n \langle mn\lvert pn\rangle - \langle mn\lvert np\rangle$
case 3: $\lvert K\rangle = \lvert \dots mn \dots\rangle$ $\lvert L\rangle = \lvert \dots pq \dots\rangle$ (differ by two)	$\langle K\lvert O_1\rvert L\rangle = 0$	$\langle K\lvert O_2\rvert L\rangle = \langle mn\lvert pq\rangle - \langle mn\lvert qp\rangle$

and zero otherwise

- The martrix elements are quite simple and involve at most the Coulomb integrals of 4 states.
- Each slater determinant describes a configuration of electrons in the spin orbitals. Through the Hamiltonian these configurations interact with each other.

$\Longrightarrow$ Configuration Interaction (CI)

For a complete basis CI would be exact but:

- Basis is never complete

- $\binom{2k}{N}$ many configurations
  $\Longrightarrow$ Complexity grows exponentially
  $\Longrightarrow$ Only applicable to small systems
- Defines correlation energy

$$E_{corr} = E_{elec} - \underbrace{E_0}_{=E_{HF}} \tag{3.61}$$

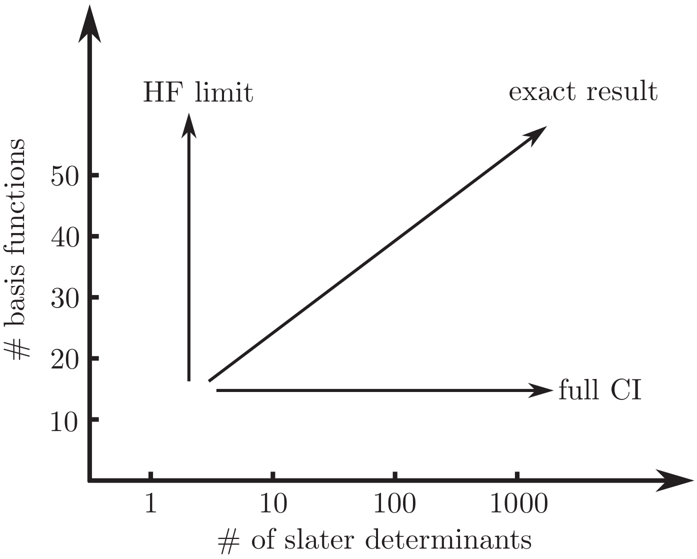


Figure 3.21: Evolution of Hartree Fock and Correlation Interaction with respect to the number of basis functions and included slater determinants. The number of slater determinats can be reduced, according to the level of sophistication in the approach/approximation.

3.4 A brief excursion into pertubation theory

Another way to go beyond Hartree-Fock is to use pertubation theory. If we treat H_{HF} as zeroth order approximation to H_{elec} we can write:

$$H_{elec} = H_{HF} + V \qquad \text{where} \quad V := H_{elec} - H_{HF} \tag{3.62}$$

or more generally:

$$H_{elec} = H_0 + V \tag{3.63}$$

where H_0 is any Hamiltonian we can solve easily:

$$H_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)} \quad \text{or} \quad H_0 |\Psi_i^{(0)}\rangle = E_i^{(0)} |\Psi_i^{(0)}\rangle \tag{3.64}$$

For Hartree-FocK $\Psi_i^{(0)}$ are the ground state slater determinants and all excited slater determinants formed from the Hartree-Fock single particle orbitals. If now $\Psi_i^{(0)}$ is close to Ψ_{elec} the effect of the pertubation V is small.

$\Longrightarrow$ Maybe there is an expansion that systematically improves the wave-function and the energy.

For this we introduce an expansion parameter λ:

$$H = H_0 + \lambda V \qquad \begin{cases} \lambda = 0 & H = H_0 \\ \lambda = 1 & H = H_{elec} \end{cases} \tag{3.65}$$

and then expand in powers of λ:

$$E_i^{elec} = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots \tag{3.66}$$

$$|\Psi^{elec}\rangle = |\Psi_i^0\rangle + \lambda|\Psi_i^1\rangle + \lambda^2|\Psi_i^2\rangle + \dots \tag{3.67}$$

We now wish to express the n-th order quantities in terms of the zeroth order quantities. For that we introduce the intermediate normalization:

$$\langle\Psi_i^0|\Psi_i^0\rangle = 1 \qquad \text{and} \qquad \langle\Psi_i^0|\Psi_i^n\rangle = 0 \;\; \forall \;\; n > 0 \tag{3.68}$$

and insert eq. (3.66) and eq. (3.67) into eq. (3.65):

$$(H_0 + \lambda V)\left(|\Psi_i^0\rangle + \lambda|\Psi_i^1\rangle + \lambda^2|\Psi_i^2\rangle + \dots\right) = \left(E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots\right)\left(|\Psi_i^0\rangle + \lambda|\Psi_i^1\rangle + \lambda^2|\Psi_i^2\rangle + \dots\right) \tag{3.69}$$

Regrouping in terms of orders of λ gives:

$$\begin{aligned}
n &= 0 \quad H_0|\Psi_i^0\rangle = E_i^{(0)}|\Psi_i^0\rangle \\
n &= 1 \quad H_0|\Psi_i^1\rangle + V|\Psi_i^0\rangle = E_i^{(0)}|\Psi_i^1\rangle + E_i^{(1)}|\Psi_i^0\rangle \\
n &= 2 \quad H_0|\Psi_i^2\rangle + V|\Psi_i^1\rangle = E_i^{(0)}|\Psi_i^2\rangle + E_i^{(1)}|\Psi_i^1\rangle + E_i^{(2)}|\Psi_i^0\rangle
\end{aligned}$$

Acting with $\langle\Psi_i^0|$ from the left yields:

$$\begin{aligned}
E_i^{(0)} &= \langle\Psi_i^0|H_0|\Psi_i^0\rangle \\
E_i^{(1)} &= \langle\Psi_i^0|V|\Psi_i^0\rangle \\
&\quad \hookrightarrow \text{Simple, because terms only involve } \Psi_i^0 \\
E_i^{(2)} &= \langle\Psi_i^0|V|\Psi_i^1\rangle \\
&\quad \vdots
\end{aligned}$$

For the ground state $\Psi_0^0 = \Psi_0$ and $H_0 = H_{HF}$ we get:

$$E_0^{(0)} = \langle\Psi_i^{HF}|H_{HF}|\Psi_i^{HF}\rangle = \sum_i \epsilon_i^{HF}$$

$\hookrightarrow$mean field Hamiltonian acting on Slater determinant gives sum over eigenvalues

$$\begin{aligned}
E_0^{(1)} &= \langle\Psi_0^{HF}|V|\Psi_0^{HF}\rangle \\
&\qquad \hookrightarrow = \underbrace{H_{elec}} - H_{HF} \\
&\qquad\quad = \sum_i h(i) + \frac{1}{2}\sum_{ij}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \left[\sum_i h(i) + V_{HF}(i)\right] \\
&\qquad\quad = \frac{1}{2}\sum_{ij}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - V_{HF}(i) \\
&= \underbrace{\frac{1}{2}\sum_{nm}\langle mn|mn\rangle - \langle mn|nm\rangle}_{\text{from eq. } 3.20} - \sum_{nm}\langle mn|mn\rangle - \langle mn|nm\rangle \\
&= -\frac{1}{2}\sum_{nm}\langle mn|mn\rangle - \langle mn|nm\rangle
\end{aligned}$$

$$\Longrightarrow E_{HF} = E_0^{(0)} + E_0^{(1)} \tag{3.70}$$

For 2nd order we need an expression for $|\Psi_0^1\rangle$. This we get from the expression for $n = 1$:

$$\begin{aligned}\left(E_i^{(0)} - H_0\right)|\Psi_i^1\rangle &= \left(V - E_i^{(1)}\right)|\Psi_i^0\rangle \\ &= \left(V - \langle\Psi_i^0|V|\Psi_i^0\rangle\right)|\Psi_i^0\rangle\end{aligned} \tag{3.71}$$

This is no longer an eigenvalue problem, because no eigenvalue shows up on the right. We solve it by expanding $|\Psi_i^1\rangle$ in a basis. For this we take the solutions of H_0:

$$|\Psi_i^1\rangle = \sum_n c_{in}^{(1)}|\Psi_i^0\rangle$$

$c_{in}^{(0)}$ are obtained by acting with $\langle\Psi_n^0|$ from the left:

$$\langle\Psi_n^0|\Psi_i^1\rangle = c_{in}^{(1)}$$

From intermediate normalization we know that $c_{ii}^{(1)} = 0$. Reinserting into the expansion:

$$|\Psi_i^1\rangle = \sum_{n\neq i} \Psi_n^0\rangle\langle\Psi_n^0|\Psi_i^1\rangle \tag{3.72}$$

Multiplying equation (3.71) by $\langle\Psi_n^0|$ gives:

$$\left(E_i^{(0)} - E_n^{(0)}\right)\langle\Psi_n^0|\Psi_i^0\rangle = \langle\Psi_n^0|V|\Psi_i^0\rangle \tag{3.73}$$

No we can insert eq. (3.72) and (3.73) into the expression for the 2nd order energy.

$$\begin{aligned}E_i^{(2)} &= \langle\Psi_i^0|V|\Psi_i^1\rangle \\ &= \sum_{n\neq i}\langle\Psi_i^0|V|\Psi_n^0\rangle\langle\Psi_n^0|\Psi_i^1\rangle \\ &= \sum_{n\neq i}\frac{\langle\Psi_i^0|V|\Psi_n^0\rangle\langle\Psi_n^0|V|\Psi_i^0\rangle}{E_i^{(0)} - E_n^{(0)}} \\ &= \sum_{n\neq i}\frac{\left|\langle\Psi_i^0|V|\Psi_n^0\rangle\right|^2}{E_i^{(0)} - E_n^{(0)}}\end{aligned} \tag{3.74}$$

The 2nd order energy is expressed in eigenfuntions Ψ_i^0 and eigenvalues $E_i^{(0)}$ of H_0, i represents the order of the excitation in the determinant. In other words:

- Take the eigenfuntions and eigenvalues of H_0 (the Slater determinant)
- Form the matrix elements with the pertubations operator
- Sum over expression (3.74)

If H_0 is the Hartree-Fock Hamiltonian H_{HF}, $E_0^{(2)}$ becomes (without proof):

$$E_0^{(2)} = \underbrace{\frac{1}{2}\sum_{abrs}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}}_{\text{ab ab order}} - \underbrace{\frac{1}{2}\sum_{abrs}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}}_{\text{ab ba order}} \tag{3.75}$$

This is also called the Møller-Plesset pertubation theory (MP2 energy).

4 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 is quite an unwieldy object, with 3N-many coordinates.

$$\Psi = \Psi\left(\{\mathbf{x_i}\}\right) \tag{4.1}$$

Wouldn't it be nicer to work with objects that just depend on one variable like the density.

$$n = n\left(\mathbf{r}\right)$$

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

$$n\left(\mathbf{r}\right) = N \int \mathrm{d}\sigma \int \mathrm{d}\mathbf{x_2} \dots \mathrm{d}\mathbf{x_N} \underbrace{\left|\Psi\left(\{\mathbf{x_i}\}\right)\right|^2}_{\text{normalized to 1}} \tag{4.2}$$

$$\int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right) = N \qquad \text{(gives particle number)} \tag{4.3}$$

4.1 Kohn-Sham's equations

Kohn and Sham's solution:

$\Longrightarrow$ Consider an auxiliary system of non-interacting electrons that has the same ground state density as the fully interacting system.

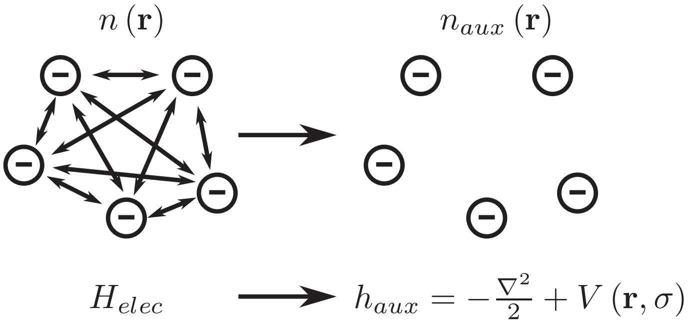


Figure 4.1: Auxiliary system with same ground state as interacting system.

$$h_{aux} = -\frac{\nabla^2}{2} + V\left(\mathbf{r},\sigma\right) \tag{4.4}$$

The non-interacting electrons move in an effective potential V_{eff} that we assune to be V-representable, but this is a problem we know, because our full Hamiltonian

$$H\left(\{\mathbf{x}_i\}\right) = \sum_i h_{aux}\left(\mathbf{x}_i\right) = H_{aux}\left(\{\mathbf{x}_i\}\right) \tag{4.5}$$

now becomes a sum over single particle Hamiltonians. These we know how to deal with from Hartree-Fock.

$$h_{aux}\varphi_i = \epsilon_i \varphi_i \qquad \text{we get a set of single-particle orbitals}$$

$\Longrightarrow$density:

$$n\left(\mathbf{r}\right) = \sum_i^{N/2} \int \mathrm{d}\sigma \left|\varphi_i\left(\mathbf{r},\sigma\right)\right|^2$$

$\Longrightarrow$This defines the classic Coulomb interaction energy:

$$E_H[n] = \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{n\left(\mathbf{r}\right)n\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|} \tag{4.6}$$

$\Longrightarrow$The kinetic energy is now also trivial:

$$T_S[n] = -\frac{1}{2}\sum_i^{N/2}\int \mathrm{d}\sigma\langle\varphi_i|\nabla^2|\varphi_i\rangle = \frac{1}{2}\sum_i^{N/2}\int \mathrm{d}\sigma\left|\nabla\varphi_i\right|^2 \tag{4.7}$$

and

$$E_{KS}[n] = T_S[n] + \underbrace{\int \mathrm{d}\mathbf{r}V_{ext}\left(\mathbf{r}\right)n\left(\mathbf{r}\right)}_{=E_{ext}} + E_H[n] + \underbrace{E_{rest}[n]}_{E_{XC}[n]\text{ for now}} \tag{4.8}$$

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

$$L[n] := E_{KS}[n] - \sum_i \epsilon_i \int \mathrm{d}\mathbf{x}\varphi_i^*\left(\mathbf{x}\right)\varphi_i\left(\mathbf{x}\right)$$

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

$$\Longrightarrow \frac{\delta T_s}{\delta\varphi_i^*} + \left[\frac{\delta E_{ext}}{\delta n} + \frac{\delta E_H}{\delta n} + \frac{\delta E_{XC}}{\delta n}\right]\frac{\delta n}{\varphi_i^*} - \epsilon_i\varphi_i = 0$$

$$\Leftrightarrow -\frac{1}{2}\nabla^2\varphi_i\left(\mathbf{x}\right)\left[v_{ext}\left(\mathbf{r}\right) + v_H\left(\mathbf{r}\right) + v_{XC}\left(\mathbf{r}\right)\right]\varphi_i\left(\mathbf{x}\right) = \epsilon_i\varphi_i\left(\mathbf{x}\right)$$

$$\Leftrightarrow \left[-\frac{1}{2}\nabla^2 + V_{KS}\left(\mathbf{r}\right)\right]\varphi_i\left(\mathbf{r}\right) = \epsilon_i\varphi_i\left(\mathbf{r}\right) \qquad \text{(only wave function depends on spin)}$$

The Kohn-Sham or effective potential is given by:

$$V_{KS}\left(\mathbf{r}\right) = V_{eff}\left(\mathbf{r}\right) = v_{ext}\left(\mathbf{r}\right) + v_H\left(\mathbf{r}\right) + v_{XC}\left(\mathbf{r}\right) \tag{4.9}$$

$$v_{XC}\left(\mathbf{r}\right) := \frac{\delta E_{XC}[n]}{\delta n\left(\mathbf{r}\right)} \tag{4.10}$$

4.2 Hohenberg-Kohn Theorem

Can we now recast

$$\begin{aligned} H_{elec}\Psi_{elec} &= E_{elec}\Psi_{elec} \\ H_{elec} &= \underbrace{-\sum_i^N \frac{\nabla_i^2}{2}} + \underbrace{\sum_i^N v_{ext}\left(\mathbf{r}_i\right)} + \underbrace{\frac{1}{2}\sum_{i\neq j}^N \frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}} \\ &= \qquad T \qquad + \qquad V_{ext} \qquad + \qquad V_{ee} \end{aligned}$$

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?

Hohenberg-Kohn Theorem I
The ground-state density $n(\mathbf{r})$ uniquely determines the potential up to an arbitrary constant.

Proof

- The proof proceeds by contradiction
- Let's assume non-degenerate ground states

Suppose we have two external potentials $v^1_{ext}(\mathbf{r})$ and $v^2_{ext}(\mathbf{r})$ that differ by more than a constant, but lead to the same density $n(\mathbf{r})$.

$$\begin{array}{ccl} v^1_{ext}(\mathbf{r}) \neq & v^2_{ext}(\mathbf{r}) + & \text{const.} \\ \downarrow & \downarrow & \\ H^1 & H^2 & \text{two different Hamiltonians} \\ \downarrow & \downarrow & \\ \Psi^1 & \Psi^2 & \text{two different wave-functions} \end{array}$$

Then by the variational principle we have:

$$\langle \Psi_2 | H_1 | \Psi_2 \rangle > \langle \Psi_1 | H_1 | \Psi_1 \rangle = E_1$$

as a side note:

$$\begin{aligned} \langle \Psi | V_{ext} | \Psi \rangle &= \int \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_N \sum_i v_{ext}(\mathbf{r}) \left| \Psi(\{\mathbf{x}_1 \ldots \mathbf{x}_N\}) \right|^2 \\ &= \sum_i \int \mathrm{d}\mathbf{r} \mathrm{d}\sigma \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N v_{ext}(\mathbf{r}) \left| \Psi(\mathbf{r}, \sigma, \mathbf{x}_2 \ldots \mathbf{x}_N) \right|^2 \\ &= \int \mathrm{d}\mathbf{r} v_{ext}(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

$$\langle \Psi_2 | H_1 | \Psi_2 \rangle = \langle \Psi_2 | H_2 | \Psi_2 \rangle + \langle \Psi_2 | H_1 - H_2 | \Psi_2 \rangle = E_2 + \int \mathrm{d}\mathbf{r} \left[v^1_{ext}(\mathbf{r}) - v^2_{ext}(\mathbf{r}) \right] n(\mathbf{r})$$

(T and V_{ee} give the same constant because the wave-funtion is the same)

$$\Longrightarrow E_1 < E_2 + \int \mathrm{d}\mathbf{r} \left[v^1_{ext}(\mathbf{r}) - v^2_{ext}(\mathbf{r}) \right] n(\mathbf{r})$$

but we can swap indicies 1 and 2:

$$\Longrightarrow E_2 < E_1 + \int \mathrm{d}\mathbf{r} \left[v^2_{ext}(\mathbf{r}) - v^1_{ext}(\mathbf{r}) \right] n(\mathbf{r})$$

$\Longrightarrow$ There cannot be two different v_{ext} that differ by more than a constant that give rise to the same density.

$\Longrightarrow$ This uniquely determines the external potential.

$$v_{ext}(\mathbf{r}) \Longleftrightarrow n(\mathbf{r}) \tag{4.11}$$

Corrolary:
Since the Hamiltonian is fully determined (except for a constant) the many-body wave-functions (for ground and excited states) are fully determined
$\Longrightarrow$ All properties of the system are fully determined given only the ground state density.

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 funtional, and the density that minimizes the functional is the exact ground state density.

Proof:

1. Variational space $\Longrightarrow$ restrict to v-representable densities (densities that can be represented by a potential $v(\mathbf{r})$
2. Definition of functional $\Longrightarrow$ Density determines T and V_{ee}

$$\begin{aligned} E_{HK}[n] &= \underbrace{T[n] + V_{ee}[n]} + \int \mathrm{d}\mathbf{r} v_{ext}(\mathbf{r})\, n(\mathbf{r}) \\ &= \qquad F[n] \qquad + \int \mathrm{d}\mathbf{r} v_{ext}(\mathbf{r})\, n(\mathbf{r}) \end{aligned}$$

Suppose $n_1(\mathbf{r})$ is the ground state density of $v^1_{ext}(\mathbf{r})$.

$$\Longrightarrow E_1 = E_{HK}[n_1] = \langle \Psi_1 | H_1 | \Psi_1 \rangle$$

Let's now consider a different density $n_2(\mathbf{r})$ that corresponds to a different wave-function Ψ_2.

$$E_1 = E_{HK}[n_1] = \langle \Psi_1 | H_1 | \Psi_1 \rangle < \langle \Psi_2 | H_1 | \Psi_2 \rangle = E_2$$

$\Longrightarrow$ Hohenberg-Kohn functional evaluated at ground state density gives the lowest energy

$\Longrightarrow$ 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

$\Longrightarrow$ Hohenberg-Kohn functional only gives ground state, not excited states (like e.g. Configuration Interaction)

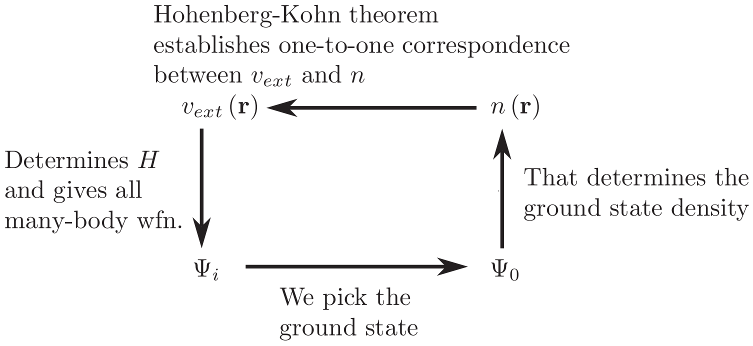


Figure 4.2: Short Summary

Problems:

- Our proofs somewhat want back to the many-body wave-function
- There exists no prescription to determine the kinetic energy from the density
- We have no prescription for generating densities

$$E_{HK}[n] = F[n] + \int \mathrm{d}\mathbf{r} v_{ext}(\mathbf{r})\, n(\mathbf{r}) \tag{4.12}$$

$$E_{KS}[n] = T_S[n] + \int \mathrm{d}\mathbf{r} v_{ext}(\mathbf{r})\, n(\mathbf{r}) + E_H(\mathbf{r}) + E_{XC}(\mathbf{r}) \tag{4.13}$$

$$\Longrightarrow E_{XC}[n] = \underbrace{T[n] - T_S[n]}_{1.} + \underbrace{V_{ee}[n] - E_H[n]}_{2.}$$

1. Difference between interacting and non-interacting kinetic energy
2. Difference between electron-electron interaction and classic Coulomb energy

- The key now is to find good approximations for $E_{XC}[n]$
- $E_{XC}[n]$ is in general small, because T_S and E_H capture a large part of T an V_{ee}
  $\Longrightarrow$ Simple approximations might already be successful
  ! Altough what matters again are energy differences and there $E_{XC}[n]$ can be decisive

4.3 The local density approximation

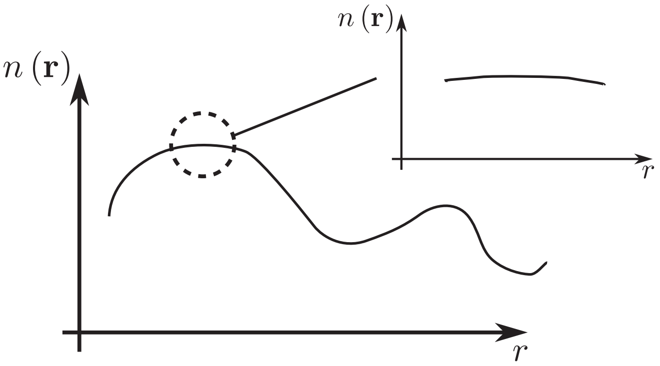


Figure 4.3: Slowly varying density.

For inhomogeneous systems that have a slowly varying density the system localy looks like the homogeneous electron gas (see fig. (4.3)).
$\Longrightarrow$ constant density n $\Longrightarrow$ constant external potential

$$\Longrightarrow E_{xc}[n] = \int \mathrm{d}\mathbf{r} n(\mathbf{r})\, \epsilon_{xc}([n], \mathbf{r}) \tag{4.14}$$

ϵ_{xc} is the energy density (i.e. the energy per electron) at point $\mathbf{r}$ in space, that depends only on the density at that point. The exchange-correlation potential v_{xc} follows straight forwardly by functional derivative:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \epsilon([n], \mathbf{r}) + n(\mathbf{r}) \frac{\delta \epsilon([n], \mathbf{r})}{\delta n(\mathbf{r})} \tag{4.15}$$

The exchange-correlation enrgy density for the homogeneous electron gas is known from accurate Quatum Monte Carlo calculations:

$$\epsilon_x[n] = \frac{3k_F}{4\pi} \quad \text{with the Fermi momentum } k_F = \left(3\pi^2 n\right)^{1/3} \tag{4.16}$$

is given exactly.

$$\begin{aligned}\implies E_{xc}[n] &= \int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right)\epsilon_{xc}\left([n],\mathbf{r}\right) = \int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right)\epsilon_{xc}\left(n\left(\mathbf{r}\right)\right)\\ &= \int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right)\frac{3}{4\pi}\left(3\pi^2 n\right)^{1/3}\\ &= \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right)^{4/3}\end{aligned}$$

and for v_x:

$$\begin{aligned}v_x[n] &= \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{1/3} + n\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\frac{1}{2}n^{-2/3}\\ &= \frac{4}{3}\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{1/3}\\ &= \left(\frac{3}{\pi}\right)^{1/3} n^{1/3}\end{aligned}$$

- Very simple expression!

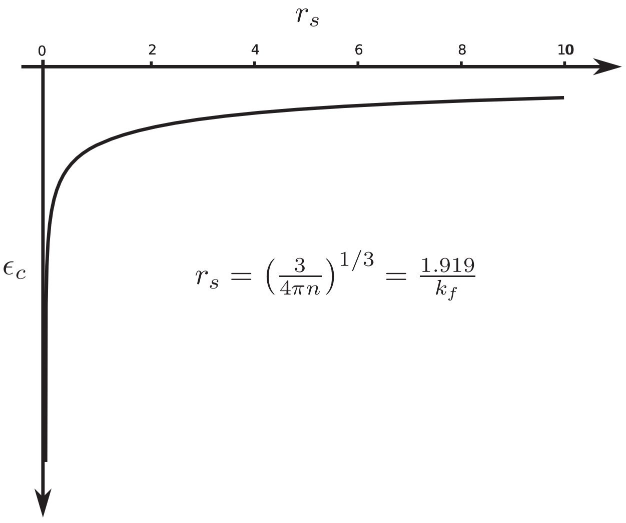


Figure 4.4: The correlation energy density of the homogenous electron gas.

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 techniques (like Configuration Interation it is a method that works directly with the many-body wave-function). An analytic expression for this behaviour (see fig. (4.4)) was first estimated by Wigner in 1938:

$$\epsilon_c[n] = -\frac{0.44}{r_s + 7.8} \tag{4.17}$$

later better parameterizations by e.g. Perdew and Zunger:

$$\epsilon_c[n] = \begin{cases} \overbrace{A\mathrm{ln}r_s + B + Cr_s\mathrm{ln}r_s + Dr_s}^{\text{Gell-Mann/Brückner}} & r_s \leq 1 \\ \dfrac{\gamma}{1+\beta_1\sqrt{r_s}+\beta_2 r_s} & r_s > 1 \end{cases} \tag{4.18}$$

(The numerical values of A, B, C, D, γ, β_1 and β_2 are given in Perdew, Zunger, Phys. Rev. B 23, 5048 (1981))

- Spin polarized extension

$$E_{xc}^{SLDA}\left[n^{\uparrow},n^{\downarrow}\right]=\int \mathrm{d}\mathbf{r}n\left(\mathbf{r}\right)\epsilon_{xc}\left(n^{\uparrow},n^{\downarrow}\right) \tag{4.19}$$

or if we introduce the spin polarization:

$$\xi\left(\mathbf{r}\right)=\frac{n^{\uparrow}\left(\mathbf{r}\right)-n^{\downarrow}\left(\mathbf{r}\right)}{n\left(\mathbf{r}\right)}$$

$$E_{xc}^{SLDA}\left[n^{\uparrow},n^{\downarrow}\right]=\int \mathrm{d}\mathbf{r}n\left(\mathbf{r}\right)\epsilon_{xc}\left(n\left(\mathbf{r}\right),\xi\left(\mathbf{r}\right)\right) \tag{4.20}$$

What we need now is reference data for the spin-polarized homogenous electron gas and appropriate paramterizations, which can also be found in Perdew, Zunger, Phys. Rev. B 23, 5048 (1981).
LDA:

- Is by construction exact for HEG
  $\Longrightarrow$ Expected to perform well for systems with slowly varying density (e.g. simple metals)
- Typically gives dissociation energies of molecules and cohesive energies of solids within 10-20%
- Bond length (lattice constant) typically within 1-2% (and typically to small)
- Problems e.g. for rapidly varying densities e.g. atoms

4.4 Generalized Gradient Approximation

Ar Atom

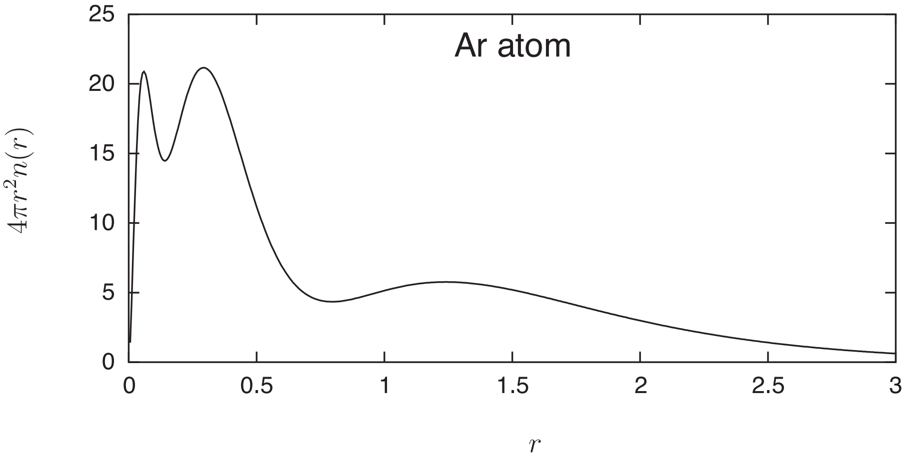


Figure 4.5: Radial density in Ar Atom, From *The ABC of Density Functional Theory* by Kieron Burke

- The shell structure is clearly visible in figure (4.5)
- The density is far from homogeneous!

The idea: add gradients to E_{xc}:

$$\begin{aligned} E_{xc}^{GGA}\left[n^{\uparrow}, n^{\downarrow}\right] &= \int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right) \epsilon_{xc}\left(n^{\uparrow}, n^{\downarrow}, \left|\nabla n^{\uparrow}\right|, \left|\nabla n^{\downarrow}\right|, \ldots\right) \\ &= \int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right) \epsilon_{x}^{HEG} F_{xc}\left(n^{\uparrow}, n^{\downarrow}, \left|\nabla n^{\uparrow}\right|, \left|\nabla n^{\downarrow}\right|, \ldots\right) \end{aligned} \tag{4.21}$$

Generalized gradient expansion:
It makes sense to work with a scaled gradient

$$S\left(\mathbf{r}\right) = \frac{\left|\nabla n\left(\mathbf{r}\right)\right|}{2k_F n\left(\mathbf{r}\right)} \tag{4.22}$$

that measures the gradient on the scale of the density itself.

$$\Longrightarrow E_{xc}^{GGA}\left[n^{\uparrow}, n^{\downarrow}\right] = \int \mathrm{d}\mathbf{r} n\left(\mathbf{r}\right) \epsilon_{x}^{HEG}[n] F_{xc}\left(n^{\uparrow}, n^{\downarrow}, S^{\uparrow}, S^{\downarrow}\right) \tag{4.23}$$

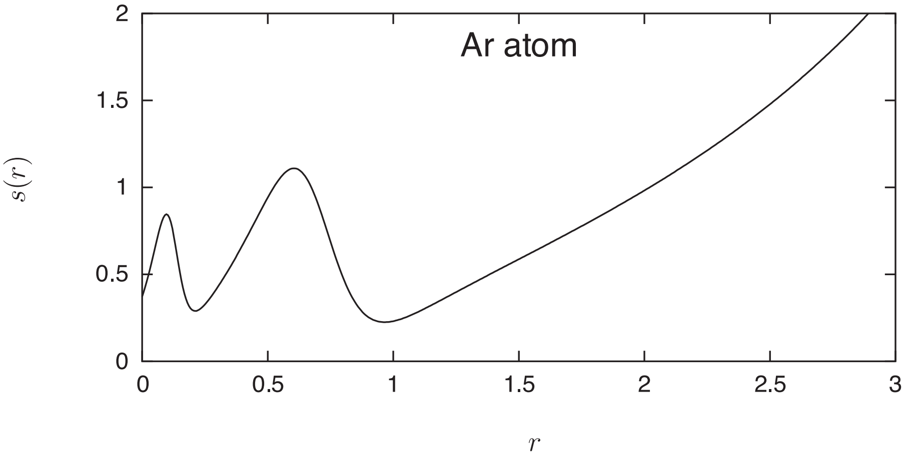


Figure 4.6: Scaled gradient for Ar Atom, From *The ABC of Density Functional Theory* by Kieron Burke

- There's no unique form or parameterization for F_{xc}
  $\Longrightarrow$ Many different parameterizations have been proposed by now that fall largely into two categories:
    - Satisfy a certain number of exact constraints
    - Are fit to benchmark sets
- GGAs usually work best in the regime for which they were designed

4.5 Self-interaction and exact-exchange

Our DFT energy expression is:

$$E_{tot}[n] = T_S[n] + E_{ext}[n] + E_H[n] + E_{xc}[n] \tag{4.24}$$

Let's recall that in E_H we summed over all single particle states in the system for convenience:

$$\begin{aligned} E_H[n] &= \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{n\left(\mathbf{r}\right) n\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|} = \frac{1}{2}\sum_{ij}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\psi_i^*\left(\mathbf{r}\right)\psi_i\left(\mathbf{r}\right)\psi_j^*\left(\mathbf{r}'\right)\psi_j\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|} \\ &= \frac{1}{2}\sum_{ij}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\left|\psi_i\left(\mathbf{r}\right)\right|^2\left|\psi_j\left(\mathbf{r}'\right)\right|^2}{\left|\mathbf{r}-\mathbf{r}'\right|} \end{aligned}$$

so when $i = j$ an electron interacts with itself $\Longrightarrow$ **self-interaction**
In Hartree-Fock this term is exacly canceld by the exchange energy:

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

For $i \neq j$ we now have terms

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

that exactly cancel those coming from E_H. However, for LDAs and GGAs this cancellation does not occur:

$$\begin{aligned}E_{xc}^{LDA/GGA} &= \int \mathrm{d}\mathbf{r}n(\mathbf{r})\,\epsilon_{xc}([n],\mathbf{r},(\nabla\mathbf{r},\ldots)) \\ &= \int \mathrm{d}\mathbf{r}\,|\psi_i(\mathbf{r})|^2\,\epsilon_{xc}([n],\mathbf{r},(\nabla\mathbf{r},\ldots))\end{aligned}$$

Perdew and Zunger (in their 1981 LDA paper) defined a 1-electron self-interaction error on this basis:

$$\delta_i = \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\frac{|\psi_i(\mathbf{r})|^2\,|\psi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} + E_{XC}\left[|\psi_i(\mathbf{r})|^2\right] \tag{4.25}$$

- δ_i is in general not zero
- As we saw earlier in section (3.1) the self-interaction error has a tendency to delocalize states

We know that Hartree-Fock removes the self-interaction error but can it be cast into the DFT framework? For that we would need the functional derivative with respect to the density:

$$E^{HF} = T_S + E_{ext} + E_H + E_x$$

The challenge is

$$v_x(\mathbf{r}) = \frac{\delta E_x}{\delta n(\mathbf{r})}; \tag{4.26}$$

all other terms are standard, but

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

$\Longrightarrow$ chain rule:

$$v_x(\mathbf{r}) = \sum_i \int \mathrm{d}\mathbf{r}'\frac{\delta E_x}{\delta\psi_i(\mathbf{r}')}\frac{\delta\psi_i(\mathbf{r}')}{\delta n(\mathbf{r})} + c.c. \tag{4.27}$$

and chain rule applied again:

$$v_x(\mathbf{r}) = \sum_i \int \mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}''\left[\frac{\delta E_x}{\delta\psi_i(\mathbf{r}')}\frac{\delta\psi_i(\mathbf{r}')}{\delta v^{KS}(\mathbf{r}'')} + c.c.\right]\frac{\delta v^{KS}(\mathbf{r}'')}{\delta n(\mathbf{r})} \tag{4.28}$$

The first term we have already encountered in the derivation of Hartree-Fock:

$$\frac{\delta E_x}{\delta\psi_i(\mathbf{r}')} = -\sum_j^{occ}\int \mathrm{d}\mathbf{r}'\frac{\psi_j^*(\mathbf{r}')\,\psi_i(\mathbf{r}')\,\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \int \mathrm{d}\mathbf{r}'\Sigma_x(\mathbf{r},\mathbf{r}')\,\psi_i(\mathbf{r}')$$

The second term

$$\frac{\delta\psi_i(\mathbf{r}')}{\delta v^{KS}(\mathbf{r}'')}$$

follows from first order pertubation theory. We recall:

$$\begin{aligned}\epsilon_i &= \epsilon_i^0 + \lambda\epsilon_i^{(1)} + \dots\\ \psi_i &= \psi_i^0 + \lambda\psi_i^{(1)} + \dots\\ v_{KS} &= v^0 + \lambda v^{(1)} + \dots\end{aligned}$$

inserting this in the Kohn-Sham equtions

$$h^{KS}\psi_i = \epsilon_i\psi_i \qquad \text{with} \qquad h^{KS} = -\frac{\nabla^2}{2} + v_{KS}$$

gives:

$$\begin{aligned}n = 0 &\qquad h_{KS}^0\psi_i^0 = \epsilon_i^0\psi_i^0\\ n = 1 &\qquad h_{KS}^0\psi_i^{(1)} + v^{(1)}\psi_i^0 = \epsilon_i^0\psi_i^{(1)} + \epsilon_i^{(1)}\psi_i^0\end{aligned}$$

now we need to get rid of $\epsilon_i^{(1)}$

$$\begin{aligned}&\Longrightarrow \text{apply } \langle\psi_j^0|\\ &\Longrightarrow \underbrace{\langle\psi_j^0|h_{KS}^0|\psi_i^{(1)}\rangle}_{\epsilon_j^0\langle\psi_j^0|\psi_i^{(1)}\rangle} + \langle\psi_j^0|v^{(1)}|\psi_i^{(0)}\rangle = \epsilon_i^0\langle\psi_j^0|\psi_i^{(1)}\rangle\\ &\Leftrightarrow \langle\psi_j^0|\psi_i^{(1)}\rangle = \frac{\langle\psi_j^0|v^{(1)}|\psi_i^{(0)}\rangle}{\epsilon_j^0 - \epsilon_i^0}\end{aligned}$$

Now we recall the expansion of $\psi_i^{(1)}$ in terms of $\{\psi_j^0\}$:

$$|\psi_i^{(1)}\rangle = \sum_{j\neq i}|\psi_j^0\rangle\langle\psi_j^0|\psi_i^{(1)}\rangle = \sum_{j\neq i}\frac{\langle\psi_j^0|v^{(1)}|\psi_i^{(0)}\rangle}{\epsilon_j^0 - \epsilon_i^0}|\psi_j^{(0)}\rangle$$

From this follows with $\delta\psi_i = |\psi_i^{(1)}\rangle$ and $\delta v_{KS} = v^{(1)}$:

$$\frac{\delta\psi_i(\mathbf{r})}{\delta v^{KS}(\mathbf{r}')} = \sum_{j\neq i}\frac{\psi_j^*(\mathbf{r}')\,\psi_j(\mathbf{r})}{\epsilon_j - \epsilon_i}\psi_i(\mathbf{r}') = G_i(\mathbf{r},\mathbf{r}')\,\psi_i(\mathbf{r}') \tag{4.29}$$

The last term

$$\frac{\delta v(\mathbf{r})}{\delta n(\mathbf{r}')}$$

is the inverse of the Kohn-Sham response function:

$$\begin{aligned}\frac{\delta n(\mathbf{r})}{\delta v(\mathbf{r}')} &= \sum_i\frac{|\psi_i(\mathbf{r})|^2}{\delta v(\mathbf{r}')} = \sum_i^N\psi_i^*(\mathbf{r}')\,G_i(\mathbf{r},\mathbf{r}')\,\psi_i(\mathbf{r}') + c.c.\\ &= \sum_i^N\sum_{j\neq i}\frac{\psi_i^*(\mathbf{r})\,\psi_j(\mathbf{r})\,\psi_j^*(\mathbf{r}')\,\psi_i(\mathbf{r}')}{\epsilon_j - \epsilon_i} + c.c.\\ &= X_S(\mathbf{r},\mathbf{r}')\end{aligned}$$

Putting this all together yields:

$$v_X(\mathbf{r}) = \sum_i\int d\mathbf{r}'\int d\mathbf{r}''\left[\int d\mathbf{r}'''\Sigma_X(\mathbf{r}',\mathbf{r}'')\,\psi_i(\mathbf{r}''')\,G_i(\mathbf{r}',\mathbf{r}'')\,\psi_i(\mathbf{r}') + c.c.\right]X_S^{-1}(\mathbf{r}'',\mathbf{r}) \tag{4.30}$$

This expression

- Is rather involved and computaionally challenging
- But it shows that a self-interaction free multiplicative potential can be constructed

This formalism is also known as OEP: optimized effective potentail approach, because v_x is the variationally best potential to E_x or E_{xx} in solids

- $E_x$only implicitly depends on the density

$$E_x = E_x\left[\{\psi_i\}\right] = E_x\left[\{\psi_i[n]\}\right]$$

This is known as orbital functional

OEPx or EXX (see figure (4.7) and (4.8):

- Moves Hartree-Fock into the realm of DFT
- Is self-interaction free
- But includes no correlation

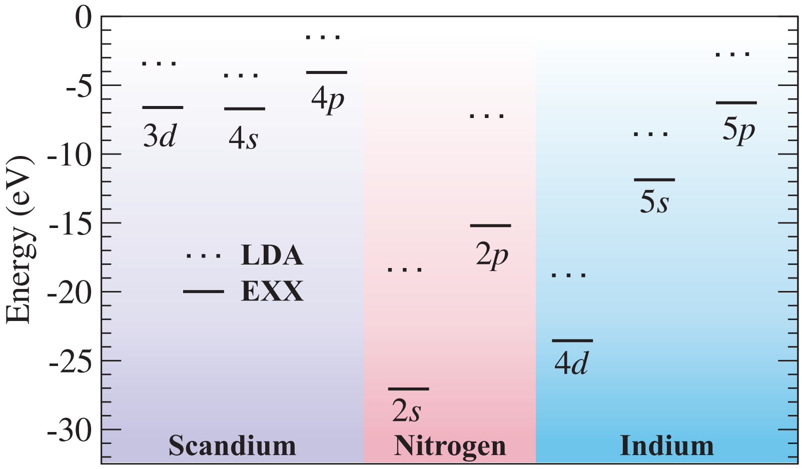


Figure 4.7: Kohn-Sham eigenvalues of the highest atomic states in LDA and EXX (≘OEPx). (from Qteish *et al. Phys. Rev. B* **74**, 245208 (2006))

4.6 Hybrid functionals

OEPx (EXX) and HF contains too much exact echange. A pragmatic solution that was adopted first in quantum chemistry was to construct a hybrid:

$$E_{xc}^{hyb} = E_{xc}^{DFT} + \alpha\left(E_x^{HF} - E_x^{DFT}\right) \tag{4.31}$$

In this simplest form a portion of DFT exchange is replaced by exact exchange, while correlations remain on the DFT level. More complex hybrids with more parameters exist (e.g. B3LYP) or where E_x^{HF} is range restricted (long, short). One of the most popular choices is $\alpha = 0.25$. Combined with PBE-exchange this functional is known as PBE0 (Perdew-Burke-Enzerhof). Contrary to common believe hybrid funtionals are not cast into the Kohn-Sham formalism of multiplicative potentials via the OEP formalism. Instead $\frac{\delta E_{XC}}{\delta \varphi_i^*}$ is performed like in HF theory, which leads to a non-local potential:

$$v_{XC}^{hyb}\left(\mathbf{r},\mathbf{r}'\right) = \left[v_{XC}^{DFT}\left(\mathbf{r}\right) - \alpha v_X^{DFT}\left(\mathbf{r}\right)\right]\delta\left(\mathbf{r}-\mathbf{r}'\right) + \alpha\Sigma_X\left(\mathbf{r},\mathbf{r}'\right) \tag{4.32}$$

The non-local potential has certain advantages over the multiplicative potential, as we will see later.

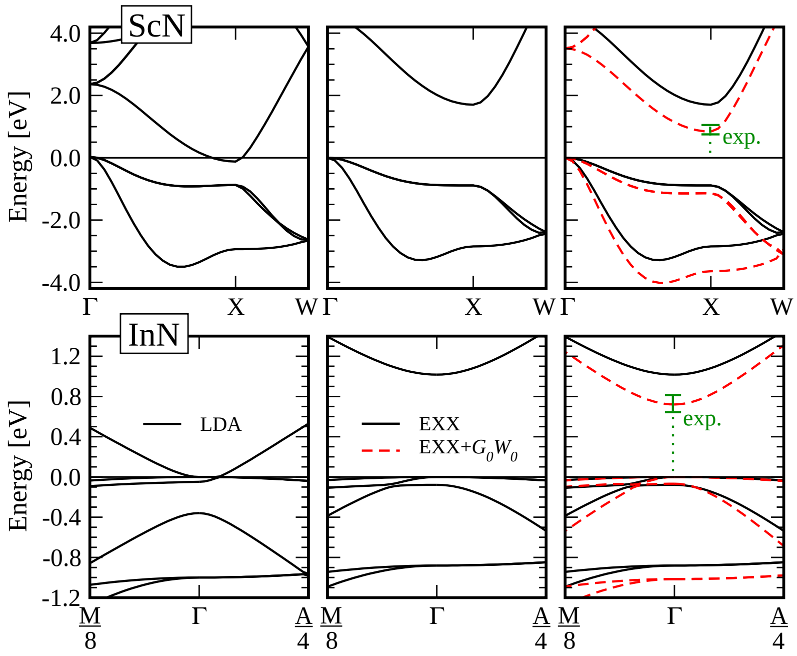


Figure 4.8: Kohn-Sham band structure of ScN and InN. In LDA ScN is a semimetal and InN a metal. EXX correctly predicts both compounds to be semiconducting. (from Rinke *et al.* phys. stat. sol. (b) **245**, 929 (2008))

4.7 DFT and excitation energies

In general, and for excitation energies in particular, it is very important to distinguish two things:

- Can a quantity in principle be calculated exactly with exact DFT?
- How do approximate funtionals perform?

Let us for now consider two different simple excitations (figure (4.9)):

$$\text{exitation energy} \qquad \epsilon_S = E^{tot}_{final} - E^{tot}_{minimal} \tag{4.33}$$

1. $\epsilon_S = E(N,s) - E(N)$
   - For a wave-function based methos (CI, Coupled Clousters, etc.) ϵ_S are the eigenvalue differences of $H\Psi = E\Psi$
2. $\epsilon_S = E(N-1,s) - E(N)$ - ionization energies
3. $\epsilon_S = E(N,s) - E(N+1,s)$ - affinities (are for some reason defined as $E_i - E_f$)

2. und 3. do not come out of $H\Psi = E\Psi$.
Where are we with our two questions? The way the excitiation energies are written they involve only differences in total energies. But remember in DFT only the ground state can be exact.

$\Longrightarrow$ only

- ionization potential $I = E(N-1) - E(N)$
- electron affinity $A = E(N) - E(N+1)$
- gap $E_{gap} = I - A$

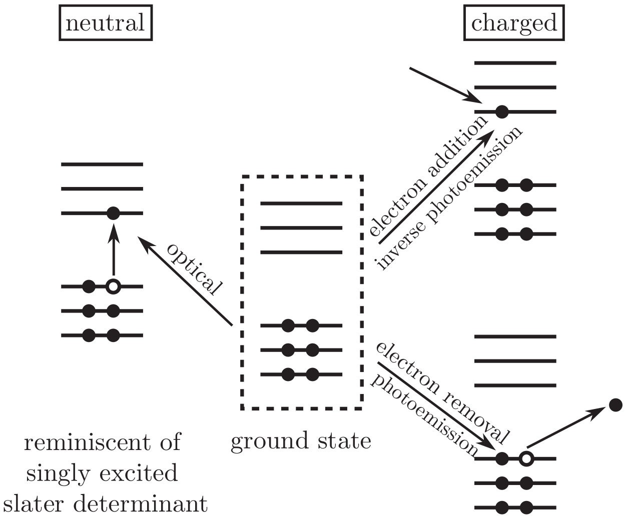


Figure 4.9: Simple excitations

could be calculated exactly in exact DFT.
All quantities involving an "s" are excited states of the system, that cannot be expressed as difference of two ground states. To mention only two problems with trying to prepare excited states $E(N,s)$ or $E(N \pm 1, s)$:

- Finding a suitable constrained to keep the system in state s may not be possible or it may not survive the self-consistency 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 Kohn-Sham eigenvalues then? In Hartree-Fock we had Koopmans' theorem:

$$-\epsilon_s^{HF} = E^*(N \pm 1, s) - E(N)$$

Where the orbitals for the calcultaion of E^* were constrained to be the ones of $E(N)$ (frozen orbitals). In DFT there is no such theorem/relation. It can, however, be proven that the highest KS eigenvalue of a finite system equals the negative of the ionization potential.

$$I = -\epsilon_N^{KS}(N) \qquad \text{in exact KS} \tag{4.34}$$

A hand-waving argument for this is:

- The asymptotic long-range density of a bound system is governed by the occupied state with highest eigenvalue
- Since the density is supposed to be exact, so must the eigenvalue be

(A more rigorous proof can be found in C. Almbladh and U. von Barth, Phys. Rev. B 31, 3231 (1985) or M. Levy, J. P. Perdew and V. Sham, Phys. Rev. A 30, 2745 (1984))

For approximate functionals this is not true, see figure (4.10)

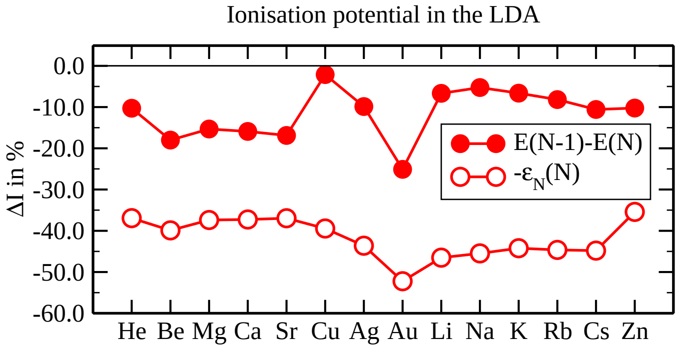


Figure 4.10: Ionization potentials of atoms calculated as total energy difference in LDA and by the LDA Kohn-Sham eigenvalue. Shown is the error with respect to the experimental ionization potential. (Reference: NIST – Atomic reference data)

Then there is Janak's theorem that establishes a connection between the KS-eigenvalues and the derivative of the total energy:

$$\frac{\partial E}{\partial n_i} = \epsilon_i \qquad \text{Janak, Phs. Rev. A 18, 7165 (1978))} \tag{4.35}$$

where n is the occupation of a given state i. For the proof we write:

$$t_i = \int d\mathbf{r}\Psi_i^* \left(-\frac{\nabla^2}{2}\right)\Psi_i = \epsilon_i - \int d\mathbf{r}\Psi_i^* \left(v_{ext} + v_H + v_{xc}\right)\Psi_i \tag{4.36}$$

$$T_S = \sum_i^N t_i$$

Then we introduce the occupation factors n_i:

$$n\left(\mathbf{r}\right) = \sum_i^N n_i \left|\Psi_i\right|^2 \quad \text{and} \quad \tilde{T} = \sum_i^N n_i t_i \tag{4.37}$$

$$\Longrightarrow \tilde{E} = \tilde{T} + E_{ext}[n] + E_H[n] + E_{xc}[n] \tag{4.38}$$

$$\frac{\partial \tilde{E}}{\partial n_i} = t_i + \sum_j n_j \frac{\partial t_j}{\partial n_i} + \int d\mathbf{r}\left(v_{ext} + v_H + v_{xc}\right)\left(\left|\Psi_i\right|^2 + \sum_j n_j \frac{\partial\left|\Psi_i\right|^2}{\partial n_i}\right)$$

Inserting the second part of eq. (4.36) into this equation cancels the first part in the integral.

$$\frac{\partial \tilde{E}}{\partial n_i} = \epsilon_i + \sum_j n_j \frac{\partial t_j}{\partial n_i} + \int d\mathbf{r} \sum_j n_j \underbrace{\frac{\partial\left|\Psi_j\right|^2}{\partial n_i}}_{\frac{\partial\Psi_j^*}{\partial n_i}\Psi_j + \frac{\partial\Psi_j}{\partial n_i}\Psi_j}$$

Now considering the first part of eq. (4.36):

$$\frac{\partial t_j}{\partial n_i} = \int d\mathbf{r}\frac{\partial \Psi_i^*}{\partial n_i}\left(-\frac{\nabla}{2}\right)\Psi_j + c.c$$

$$\begin{aligned}
\frac{\partial \tilde{E}}{\partial n_i} &= \epsilon_i + \sum_j n_j \int d\mathbf{r} \left[\frac{\partial \Psi_j^*}{\partial n_i} \underbrace{\left(-\frac{\nabla}{2} + v_{ext} + v_H + v_{xc} \right) \Psi_j}_{\epsilon_j \Psi_j} + c.c \right] \\
&= \epsilon_i + \sum_j n_j \epsilon_j \int d\mathbf{r} \left[\frac{\partial \Psi_j^*}{\partial n_i} \Psi_j + c.c \right] \\
&= \epsilon_i + \sum_j n_j \epsilon_j \underbrace{\frac{\partial}{\partial n_i} \underbrace{\int d\mathbf{r}\, |\Psi_j|^2 \cdot 2}_{=1}}_{=0} \quad \text{(wave-functions are normalized)} \\
&= \epsilon_i \quad \square
\end{aligned}$$

Rearanging Janak's theorem:

$$E(N+1,i) - E(N) = \int_0^1 dn \epsilon_i(n) \approx \epsilon(0.5) \quad \text{(mid-point approximation)} \tag{4.39}$$

In other words:

- Excitation energies are approximately given by the value of the eigenvalue of half occuption (also known as Slater-Janak's or Slater transition state)
- The problem remains, however, that for any but the highest (lowest) state occupations need to be suitably constrained.

Derivative discontinuity
Let's consider the gap of a large system (finite, but so large it could be a solid). The gap is defined as:

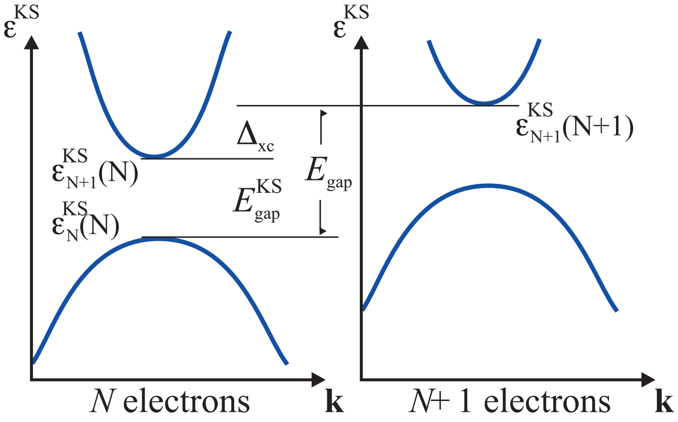


Figure 4.11: After the addition of an electron into the conduction band (right) the xc potential and the whole band-structure shift up by a quantity Δ_{xc}. Figure after R. W. Godby *et al.*, in *A Primer in DFT*, Springer 2003

$$E_{gap} = I - A = E(N+1) - 2E(N) + E(N-1) \tag{4.40}$$

But we know that the highest occupied state in exact KS is exact:

$$\begin{aligned}
E_{gap} &= \epsilon^{KS}_{N+1}(N+1) - \epsilon^{KS}_{N}(N) \\
&= \underbrace{\epsilon^{KS}_{N+1}(N+1) - \epsilon^{KS}_{N+1}(N)}_{\Delta_{xc}} + \underbrace{\epsilon^{KS}_{N+1}(N) - \epsilon^{KS}_{N}(N)}_{E^{KS}_{gap}}
\end{aligned}$$

Because our system is large we have

$$N \gg 1 \quad \Rightarrow \quad \Delta n(\mathbf{r}) \to 0 \quad \text{for} \quad N \to N+1$$

In other words, our density change is infitesimal.

$\Rightarrow$ v_H and v_{ext} will not change

$\Rightarrow$ Δ_{xc} can only come from change in v_{xc}

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

$\Rightarrow$ the derivative of E_{xc} with respect to particle number changes discontinously

$\Rightarrow$ v_{xc} changes by a constant (see figure (4.11, 4.12))

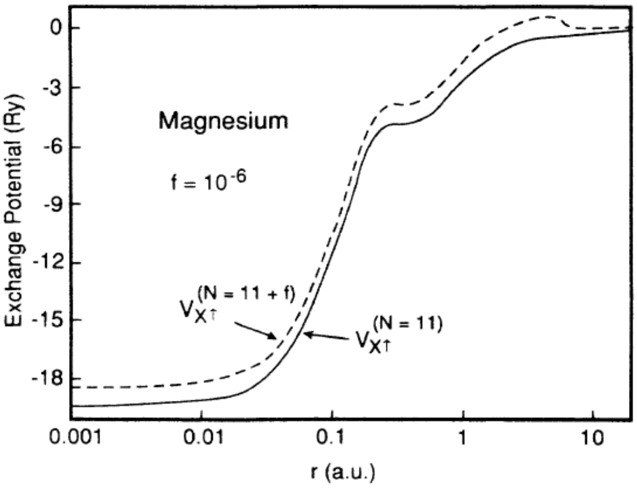


Figure 4.12: Exact-exchange potential (KLI) shifts up almost uniformily by ≈ 1 eV upon adding 10^{-6} electrons. J. B. Krieger *et al.*, Phys. Rev. A **45**, 101 (1992)

- Even exact KS calculation will not capture the derivative discontinuity and therefore will give incorrect gaps, if only KS eigenvalue differences are considered
- There is currently fierce debate about the size of the derivative discontinuity in exact KS
- The role of the kinetic energy is unclear

In summary:

- We have certain exact relations linking total energies and eigenvalues with excitation energies
- But then there is the derivative discontinuity and approximate functionals (LDAs and GGAs do not contain the discontinuity, a problem even for total energy differences and they are plagued by the self-interaction error)
- Note that non-local functionals do not really have the discontinuity problem because they are not generated from $\frac{\delta E}{\delta n}$ (see figure (4.7, 4.8, 4.10, 4.13))

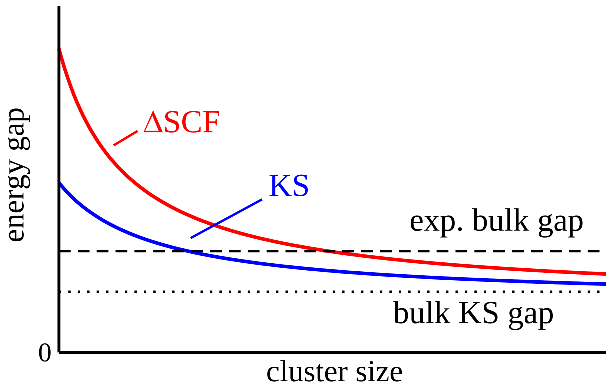


Figure 4.13: Typical behaviour of most current DFT functionals for the case of a finite system (e.g. a cluster) that approaches its bulk limit.

5 Green's function theory

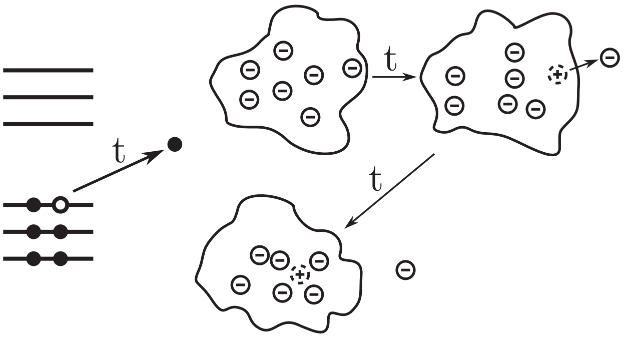


Figure 5.1: Time dependence of excitation process

- Include time dependence of excitation process
- Switch to time dependent pertubation theory
- What about total energies?

5.1 Second Quantization

In this section we introduce the method of second-quantisation, which provides an elegant, alternative to the conventional notation in quantum mechanics. In second-quantisation a physical state is represented by a state vector in Hilbert space and observables by an operator acting on this state. If the operator applied to a state reproduces the state bar a multiplicative factor, we speak of an eigenstate. The eigenstates of a Hermitian operator form a complete set. With this knowledge we can chose a suitable, complete set of states to represent the many-body problem. In the set of all Slater determinants based on a complete set of single particle functions $\varphi_k(x)$ we find a basis system and a many-body wavefunction that meet the requirements. We label this many-body state Ψ_N and use the short hand notation

$$\Psi_N = |k_1, k_2, \ldots, k_N > \tag{5.1}$$

The fermionic creation operator $a_k^\dagger$ creates a particle in state k if this has previously been unoccupied

$$a_k^\dagger |k_1, k_2, \ldots, k_N >= |k, k_1, k_2, \ldots, k_N > \tag{5.2}$$

similarly a particle is destroyed in state k by the annihilation operators a_k

$$a_k |k, k_1, k_2, \ldots, k_N >= |k_1, k_2, \ldots, k_N > \tag{5.3}$$

Based on the definitions for $a_k^\dagger$ and a_k we define the field operators $\psi^\dagger(\mathbf{x})$ and $\psi(\mathbf{x})$[1]

$$\psi^\dagger(\mathbf{x}) = \sum_k a_k^\dagger \varphi_k^*(\mathbf{x}) \tag{5.4}$$

$$\psi(\mathbf{x}) = \sum_k a_k \varphi_k(\mathbf{x}) \tag{5.5}$$

The anti commutation relations for the creation (5.2) and annihilation (5.3) operators are retained for the field operators:

$$\{\psi(\mathbf{x}), \psi^\dagger(\mathbf{x}')\} = \delta(\mathbf{x}, \mathbf{x}') \quad \wedge \quad \{\psi^\dagger(\mathbf{x}), \psi^\dagger(\mathbf{x}')\} = \{\psi(\mathbf{x}), \psi(\mathbf{x}')\} = 0 \tag{5.6}$$

In field operator notation operators of the form $O_1(\mathbf{x})$ and $O_2(\mathbf{x}')$ assume the shape

$$\hat{O}_1 = \sum_\sigma \int d\mathbf{r}\, \psi^\dagger(\mathbf{x}) O(\mathbf{x}) \psi(\mathbf{x}) \tag{5.7}$$

$$\hat{O}_2 = \sum_{\sigma\sigma'} \int d\mathbf{r} d\mathbf{r}'\, \psi^\dagger(\mathbf{x}) \psi^\dagger(\mathbf{x}') O(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}) \psi(\mathbf{x}') \tag{5.8}$$

The Hamiltonian in second quantized form

$$H = \sum_{ij} \langle i|h|j\rangle a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} \langle ij|kl\rangle a_i^\dagger a_j^\dagger a_k a_l \tag{5.9}$$

is thus transformed according to

$$H = \sum_\sigma \int d\mathbf{r}\, \psi^\dagger(\mathbf{x}) h(\mathbf{r}) \psi(\mathbf{x}) + \frac{1}{2} \sum_{\sigma\sigma'} \int \int d\mathbf{r} d\mathbf{r}'\, \psi^\dagger(\mathbf{x}) \psi^\dagger(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi(\mathbf{x}) \psi(\mathbf{x}') \tag{5.10}$$

where $h(\mathbf{r})$ is the single-particle Hamiltonian

$$h(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) \tag{5.11}$$

as always.

For the following analysis it is convenient to switch to the Heisenberg notation for the field operators

$$\psi(\mathbf{x}, t) = e^{iHt} \psi(\mathbf{x}) e^{-iHt} \tag{5.12}$$

If we now consider the N-electron ground-state, Ψ_N or in short $|N>$ and an eigenstate s of the $N+1$ particle state: $|N+1, s>$, we then obtain from (5.12)

$$\langle N|\psi(\mathbf{x}, t)|N+1, s\rangle = \langle N|e^{iHt}\psi(\mathbf{x})e^{-iHt}|N+1, s\rangle = e^{-i\epsilon_s t} f_s(\mathbf{x}) \tag{5.13}$$

with the excitation energy ϵ_s and amplitudes $f_s(\mathbf{x})$ defined by

$$\epsilon_s = E(N+1, s) - E(N), \qquad fs(\mathbf{x}) = \langle N|\psi(\mathbf{x})|N+1, s\rangle \tag{5.14}$$

From the definition of the field operators (5.4,5.5) combined with the relation (5.3) we find that $f_s(\mathbf{x})$

$$\langle N|\psi(\mathbf{x})|N+1, s\rangle = \langle N|\sum_k a_k \varphi_k(\mathbf{x})|N+1, s\rangle = \langle N|\varphi_s(\mathbf{x})|N\rangle \delta_{sk} = \varphi_s(\mathbf{x}) \tag{5.15}$$

gives the excited state wavefunction. In the next section we explore the connection between $\varphi_s(\mathbf{x})$ and the propagation of a quasiparticle is made.

---

[1] We introduce the shorthand notation x to denote the set $(\mathbf{r}, \sigma)$.

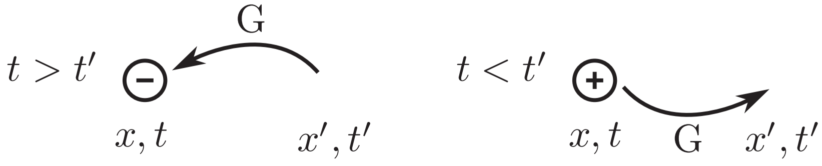


Figure 5.2: Single Particle Greensfunction for $t > t'$ and $t < t'$.

5.2 Green's function theory

5.2.1 The Single-Particle Green's Function

We will begin our introduction by defining the single particle Green's function, G, and then proceed to show that the one-particle excitation spectra is naturally contained in G.

Using the notation of second quantisation we define the single-particle Green's function as:

$$G(\mathbf{x}t, \mathbf{x}'t') = -i\langle N|\hat{T}\{\psi(\mathbf{x}, t)\psi^\dagger(\mathbf{x}', t')\}|N\rangle \tag{5.16}$$

where $\psi^\dagger(\mathbf{x}', t')$ and $\psi(\mathbf{x}, t)$ are the creation and annihilation operators of a particle, respectively, and the time ordering operator, $\hat{T}$, assures an ascending order in the set of field operators from right to left. Every pair commutation of fermionic field in Equation (5.16) operators is accompanied by a sign change and (5.16) can thus also we written as

$$\begin{aligned} G(\mathbf{x}t, \mathbf{x}'t') = &- i\langle N|\psi(\mathbf{x}, t)\psi^\dagger(\mathbf{x}', t')|N\rangle\Theta(t - t') \\ &+ i\langle N|\psi^\dagger(\mathbf{x}', t')\psi(\mathbf{x}, t)|N\rangle\Theta(t' - t) \end{aligned} \tag{5.17}$$

For times $t > t'$ the Green's function describes the creation of an additional electron at $\mathbf{x}'$ and subsequent propagation and annihilation at $\mathbf{x}$ and time t. Conversely for $t < t'$ a hole is created by extraction of an electron from the ground-state by the operation $\psi(\mathbf{x}, t)|N >$. The overlap with $\psi^\dagger(\mathbf{x}')|N >$ then gives the probability of the hole having propagated to $\mathbf{x}'$ at time t'.

Making use of the Heisenberg notation (5.12) equation (5.17) becomes

$$\begin{aligned} G(\mathbf{x}t, \mathbf{x}'t') = &- i\langle N|e^{iHt}\psi(\mathbf{x})e^{-iHt}e^{iHt'}\psi^\dagger(\mathbf{x}')e^{-iHt'}|N\rangle\Theta(t - t') \\ &+ i\langle N|e^{iHt'}\psi^\dagger(\mathbf{x}')e^{-iHt'}e^{iHt}\psi(\mathbf{x})e^{-iHt}|N\rangle\Theta(t' - t) \\ = &- i\langle N|\psi(\mathbf{x})e^{-i(H-E_N)(t-t')}\psi^\dagger(\mathbf{x}')|N\rangle\Theta(t - t') \\ &+ i\langle N|\psi^\dagger(\mathbf{x}')e^{i(H-E_N)(t-t')}\psi(\mathbf{x})|N\rangle\Theta(t' - t) \end{aligned} \tag{5.18}$$

If we insert the completeness relation in Fock-space

$$1 = |vac >< vac| + \sum_s |\Psi_s^1 >< \Psi_s^1| + \ldots \sum_s |\Psi_s^N >< \Psi_s^N| + \ldots \tag{5.19}$$

where $|\Psi_s^N >$ denote the eigenfunctions of a N-particle system $|N, s >$, equation (5.18) transforms to

$$\begin{aligned} G(\mathbf{x}t, \mathbf{x}'t') = &- i\sum_s \langle N - 1|\psi(\mathbf{x})|N, s\rangle e^{-i(E_{N-1}-E_N)(t-t')}\langle N, s|\psi^\dagger(\mathbf{x}')|N - 1\rangle\Theta(t - t') \\ &+ i\sum_s \langle N + 1|\psi^\dagger(\mathbf{x}')|N, s\rangle e^{i(E_{N+1}-E_N)(t-t')}\langle N, s|\psi(\mathbf{x})|N + 1\rangle\Theta(t' - t) \end{aligned} \tag{5.20}$$

The sum over particle number disappears because the scalar product of wavefunctions with different particle numbers vanishes. In a more compact notation the Green's function appears as

$$G(\mathbf{x}t, \mathbf{x}'t') = -i\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')e^{-i\epsilon_s(t-t')}\left[\Theta(t - t')\Theta(\epsilon_s - \mu) - \Theta(t' - t)\Theta(\mu - \epsilon_s)\right] \tag{5.21}$$

where we have defined the excitation energies ϵ_s and wave functions $f_s(\mathbf{x})$ by[2]

$$\epsilon_s = E(N+1,s) - E(N), \quad fs(\mathbf{x}) = \langle N|\psi(\mathbf{x})|N+1,s\rangle \quad \text{for} \quad \epsilon_s \geq \mu \tag{5.22}$$

$$\epsilon_s = E(N) - E(N-1,s), \quad fs(\mathbf{x}) = \langle N-1,s|\psi(\mathbf{x})|N\rangle \quad \text{for} \quad \epsilon_s < \mu \tag{5.23}$$

The energies ϵ_s correspond to the true single-particle excitation energies upon addition and removal of an electron from the system in the ground-state.

5.2.2 Spectral Representation of the Green's Function

In order to extract more physical information from the Green's function we switch to the spectral, or Lehmann, representation of G. We first note that for explicitly time-independent Hamiltonians the Green's function only dependents on the time difference $\tau = t - t'$. Secondly we need to treat the discontinuity in the time argument, brought in by the Heavyside function, carefully. We state without proof that $\Theta(\pm\tau)$ can be represented by

$$\Theta(\pm\tau) = \lim_{\eta\to 0^+} \mp\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega\tau}}{\omega \pm i\eta} \tag{5.24}$$

Inserting this equation into (5.21) we obtain

$$G(\mathbf{x},\mathbf{x}',\tau) = \lim_{\eta\to 0^+}\sum_s f_s(\mathbf{x})f_s(\mathbf{x}')\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}e^{-i(\epsilon_s+\omega)\tau}\left[\frac{\Theta(\epsilon_s-\mu)}{\omega+i\eta}+\frac{\Theta(\mu-\epsilon_s)}{\omega-i\eta}\right] \tag{5.25}$$

and with the additional substitution $\omega \equiv \epsilon_s + \omega$ we identify the Fourier transform of G to be

$$G(\mathbf{x},\mathbf{x}',\omega) = \lim_{\eta\to 0^+}\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')\left[\frac{\Theta(\epsilon_s-\mu)}{\omega-(\epsilon_s-i\eta)}+\frac{\Theta(\mu-\epsilon_s)}{\omega-(\epsilon_s+i\eta)}\right] \tag{5.26}$$

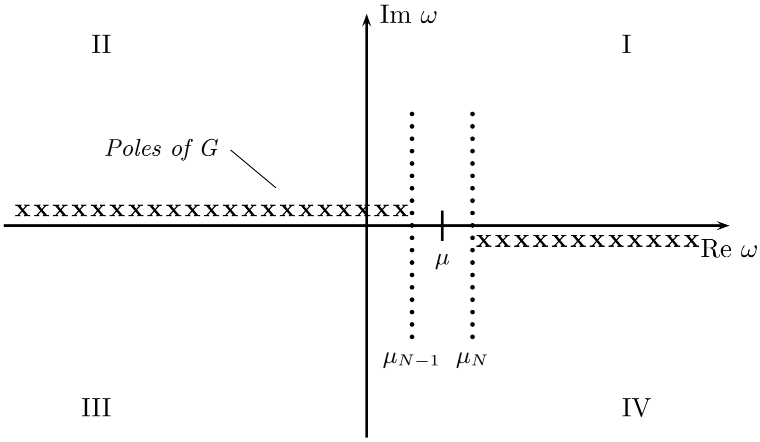


Figure 5.3: The poles of the Green's function for a finite system lie infitesimally close above the real axis for energies smaller than the chemical potential of the N-1-particle system μ_{N-1}. For energies greater than μ_N the poles fall infitesimally close below the real frequency axis. In the limit of zero temperature a single chemical potential can be defined by μ, as indicated in this figure.

From the spectral representation (5.26) we deduce, that the poles of the Green's function are the exact excitation energies (5.22) and (5.23) of the system, referenced to the chemical potential. For a finite system the energy spectrum is discrete with the poles of G lying infitesimally above the real frequency axis for energies smaller than the chemical potential and infitesimally below otherwise, as illustrated in Figure

---

[2] In principle μ has to be defined for the addition $(\mu_{(N)=E(N+1)-E(N)})$ and the removal $(\mu_{(N-1)=E(N)-E(N-1)})$ of an electron separately. We will comment on this point in Section 5.2.2

5.2.2. The Green's function is analytic in quadrant[3] I of the complex plane for energies larger than μ_{N-1} and in quadrant III for energies lower than μ_N. For an infinite system $N \approx N-1$ and the two chemical potentials merge into one. In this case the discrete series of poles form a branch cut in the complex plane, except possibly for a band gap region where there are no eigenstates.

5.2.3 Expectation value of single particle operators

According to equation (5.7) we have:

$$\hat{O}_1 = \sum_{\sigma} \int \mathrm{d}\mathbf{r}\, \psi^{\dagger}(\mathbf{x}) O(\mathbf{x}) \psi(\mathbf{x})$$

Let us write $\hat{O}_1$ with non-locality in the spin index for now:

$$\hat{O}_1 = \sum_{\alpha\beta} \int \mathrm{d}\mathbf{r}\, \psi^{\dagger}_{\beta}(\mathbf{r})\, O_{\beta\alpha'}(\mathbf{r})\, \psi_{\alpha}(\mathbf{r})$$

the expectation value is then

$$\langle N|\hat{O}_1|N\rangle = \langle N| \sum_{\alpha\beta} \int \mathrm{d}\mathbf{r}\, \psi^{\dagger}_{\beta}(\mathbf{r})\, O_{\beta\alpha'}(\mathbf{r})\, \psi_{\alpha}(\mathbf{r})\, |N\rangle \tag{5.27}$$

we now have to:

- Pull the operator out of the expectation value
- Swap the order of the field operators
- Introduce the time ordering operator

Using equation (5.4) and (5.5) we can write

$$\langle N|\psi^{\dagger}(\mathbf{x})\, \hat{O}(\mathbf{x})\, \psi(\mathbf{x})\, |N\rangle = \langle N|\psi^{\dagger}(\mathbf{x})\, \hat{O}(\mathbf{x}) \sum_{j} \varphi_j(\mathbf{x})\, a_j |N\rangle$$

We introduce an artificial $\mathbf{x}'$ dependence

$$\psi^{\dagger}(\mathbf{x}) = \lim_{x' \to x} \psi^{\dagger}(\mathbf{x}') \tag{5.28}$$

$\Longrightarrow$ now we can swap $\hat{O}$ and $\psi^{\dagger}$

$$\langle N|\psi^{\dagger}(\mathbf{x})\, \hat{O}(\mathbf{x})\, \psi(\mathbf{x})\, |N\rangle = \int \mathrm{d}\mathbf{r} \lim_{r' \to r} \sum_{\alpha\beta} O_{\alpha\beta}(\mathbf{r})\, \langle N|\psi^{\dagger}_{\beta}(\mathbf{r})\, \psi_{\alpha}(\mathbf{r})\, |N\rangle$$

Then we can employ the limit trick once more:

$$1 = \lim_{t' \to t} \mathrm{e}^{-\mathrm{i}E(t-t')} = \lim_{t' \to t} \mathrm{e}^{\mathrm{i}H(t'-t)} \tag{5.29}$$

---

[3] To be absolutely precise, it is only sensible to speak of quadrants in connection to the Green's function or the self-energy, if the chemical potential coincides with the origin of the complex plane. In the following Chapters the chemical potential is implicitly assumed to be zero unless otherwise stated.

$$
\begin{aligned}
\langle N|\psi^\dagger_\beta(\mathbf{r}')\,\psi_\alpha(\mathbf{r})\,|N\rangle &= \lim_{t'\to t} \mathrm{e}^{-\mathrm{i}E(t-t')}\langle N|\psi^\dagger_\beta(\mathbf{r}')\lim_{t'\to t}\mathrm{e}^{\mathrm{i}H(t'-t)}\psi_\alpha(\mathbf{r})\,|N\rangle \\
&= \lim_{t'\to t}\langle N|\mathrm{e}^{\mathrm{i}H(t')}\psi^\dagger_\beta(\mathbf{r}')\,\mathrm{e}^{-\mathrm{i}H(t')}\mathrm{e}^{\mathrm{i}H(t)}\psi_\alpha(\mathbf{r})\,\mathrm{e}^{-\mathrm{i}H(t)}|N\rangle \\
&= \lim_{t'\to t}\langle N|\psi^\dagger_\beta(\mathbf{r}',t')\,\psi_\alpha(\mathbf{r},t)\,|N\rangle \\
&= \lim_{t'\to t}(-1)\langle N|\psi_\alpha(\mathbf{r},t)\,\psi^\dagger_\beta(\mathbf{r}',t')\,|N\rangle \\
&= \lim_{\substack{t'\to t\\ t'>t}}(-1)\langle N|\hat{T}\psi_\alpha(\mathbf{r},t)\,\psi^\dagger_\beta(\mathbf{r}',t')\,|N\rangle \\
&= -\lim_{t'\to t}\mathrm{i}G_{\alpha\beta}(\mathbf{r},t;\ \mathbf{r}',t')
\end{aligned}
$$

Putting this together:

$$
\langle N|\hat{O}|N\rangle = -\mathrm{i}\int \mathrm{d}\mathbf{r}\lim_{r'\to r}\lim_{t'\to t}\sum_{\alpha\beta}O_{\alpha\beta}(\mathbf{r})\,G_{\alpha\beta}(\mathbf{r},t;\ \mathbf{r}',t') \tag{5.30}
$$

$$
-\mathrm{i}\int \mathrm{d}\mathbf{r}\lim_{r'\to r}\mathrm{tr}\left\{\hat{O}(\mathbf{r})\,G(\mathbf{r},t;\ \mathbf{r}',t')\right\} \tag{5.31}
$$

The expectation value of any one particle operator can be determined with the one-particle Green's function.

In particular:

$$
\langle T\rangle = +\mathrm{i}\int \mathrm{d}\mathbf{r}\lim_{r'\to r}\frac{\nabla^2}{2}\mathrm{tr}\left\{G(\mathbf{r},t;\ \mathbf{r}',t')\right\} \tag{5.32}
$$

and for the density we get

$$
O_{\alpha\beta}(\mathbf{r}) = \delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}') \tag{5.33}
$$

$$
\begin{aligned}
n(\mathbf{r}) = \langle N|\hat{O}|N\rangle &= -\mathrm{i}\int \mathrm{d}\mathbf{r}\lim_{r'\to r}\sum_{\alpha\beta}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')\,G_{\alpha\beta}(\mathbf{r},t;\ \mathbf{r}',t') \\
&= -\mathrm{i}G_{\alpha\alpha}(\mathbf{r},t;\ \mathbf{r},t') = \mathrm{i}\,\mathrm{tr}\left\{G(\mathbf{r},t;\ \mathbf{r},t')\right\}
\end{aligned} \tag{5.34}
$$

what about the two particle operator, i.e. the Coulomb potential and therefore the total energy? For this we consider the equation of motion for the field operator:

$$
i\frac{\partial}{\partial t}\psi(\mathbf{x},t) = [\psi(\mathbf{x},t),H] \tag{5.35}
$$

The commutator is calculated in the Heisenberg picture ((5.12) and (5.10)). Applying the anti commutation relations (5.6) and the identity

$$
[A,BC] = \{A,B\}\,C - B\,\{C,A\} \tag{5.36}
$$

we obtain for

$$
\begin{aligned}
[\psi(\mathbf{x}), h] &= \int d\mathbf{x}' [\underbrace{\psi(\mathbf{x})}_{A}, \underbrace{\psi^\dagger(\mathbf{x}')}_{B} \underbrace{h(\mathbf{x}')\psi(\mathbf{x})}_{C}] \\
&= \int d\mathbf{x}' \left(\underbrace{\left\{\psi(\mathbf{x}), \psi^\dagger(\mathbf{x}')\right\}}_{\delta(\mathbf{x}-\mathbf{x}')} h(\mathbf{x}')\psi(\mathbf{x}') - \psi^\dagger(\mathbf{x}') \left\{h(\mathbf{x}')\psi(\mathbf{x}'), \psi(\mathbf{x})\right\} \right) \\
&= h(\mathbf{x})\psi(\mathbf{x}) - \int d\mathbf{x}'\psi^\dagger(\mathbf{x}') \left(h(\mathbf{x}')\psi(\mathbf{x}')\psi(\mathbf{x}) + \psi(\mathbf{x})h(\mathbf{x}')\psi(\mathbf{x}')\right) \\
&= h(\mathbf{x})\psi(\mathbf{x}) - \int d\mathbf{x}' \big((-1)\psi^\dagger(\mathbf{x}')h(\mathbf{x}')\psi(\mathbf{x}')\psi(\mathbf{x}) + \psi^\dagger(\mathbf{x}')\psi(\mathbf{x})h(\mathbf{x}')\psi(\mathbf{x}')\big) \\
&= h(\mathbf{x})\psi(\mathbf{x}) - \int d\mathbf{x}' \left(\underbrace{\left\{\psi^\dagger(\mathbf{x}'), \psi(\mathbf{x})\right\}}_{0} h(\mathbf{x}')\psi(\mathbf{x}') \right) \\
&= h(\mathbf{x})\psi(\mathbf{x})
\end{aligned}
\tag{5.37}
$$

For the two particle part of H we obtain an analogous expression. The equation of motion therefore reads

$$
i\frac{\partial}{\partial t}\psi(\mathbf{x}, t) = \left[\hat{h}(\mathbf{r}) + \int \psi^\dagger(\mathbf{x}', t)v(\mathbf{r}, \mathbf{r}')\psi(\mathbf{x}', t)d\mathbf{x}'\right]\psi(\mathbf{x}, t) \tag{5.38}
$$

with $v(\mathbf{r}, \mathbf{r}')$ being the Coulomb potential.
We now multiply from the left with $\psi^\dagger(\mathbf{x}', t')$ and take the ground state expectation value:

$$
(\mathrm{i}\partial_t - h(\mathbf{x})) \langle N|\psi^\dagger(\mathbf{x}', t')\psi(\mathbf{x}, t)|N\rangle = \underbrace{\int \mathrm{d}\mathbf{x}'' \langle N|\psi(\mathbf{x}', t')\psi^\dagger(\mathbf{x}'', t)V(\mathbf{r}, \mathbf{r}'))\psi(\mathbf{x}', t))\psi(\mathbf{x}, t)|N\rangle}_{\begin{array}{c}\text{integrating over } \int \mathrm{d}\mathbf{x} \text{ gives the expectation value of the two particle} \\ \text{part of the Hamiltonian in the limits } x' \to x \text{ and } t' \to t^+\end{array}} \tag{5.39}
$$

$$
\langle N|v|N\rangle = -\frac{\mathrm{i}}{2}\int \mathrm{d}\mathbf{x} \lim_{t'\to t^+} \lim_{\mathbf{x}'\to\mathbf{x}} \left(\frac{\partial}{\partial t} - h(\mathbf{x})\right) G(\mathbf{x}t, \mathbf{x}'t')
$$

where we applied the same tricks as before to turn $\langle N|\psi^\dagger(\mathbf{x}', t')\psi(\mathbf{x}, t)|N\rangle$ into the Green's function. Now we have:

$$
E_0 = \langle N|h + v|N\rangle \tag{5.40}
$$

recall that

$$
\begin{aligned}
\langle N|h|N\rangle &= \int \mathrm{d}\mathbf{x} \lim_{t'\to t^+} \lim_{\mathbf{x}'\to\mathbf{x}} h(\mathbf{x})G(\mathbf{x}t, \mathbf{x}'t') \\
\Longrightarrow E_0 &= -\frac{\mathrm{i}}{2}\int \mathrm{d}\mathbf{x} \lim_{\mathbf{x}'\to\mathbf{x}} \left[\frac{\partial}{\partial t} - h(\mathbf{x})\right] G\left(\mathbf{x}t, \mathbf{x}'t^+\right)
\end{aligned}
$$

The ground state total energy can also be calculated from the single particle Green's function!
Summary of this part:
The one-particle Green's function gives:

- Charged excitations
- The ground state total energy

What remains to be done is to find suitable approximations.

5.3 The self-energy

Before we proceed to find approximations it is useful to introduce the concept of the self-energy. Going back to the equation of motion for the field operator (eq. (5.39)).

$$(\mathrm{i}\partial_t - h(\mathbf{x}))\langle N|\psi^\dagger(\mathbf{x}',t')\psi(\mathbf{x},t)|N\rangle = \int \mathrm{d}\mathbf{x}''\langle N|\psi(\mathbf{x}',t')\psi^\dagger(\mathbf{x},t)V(\mathbf{r},\mathbf{r}'))\psi(\mathbf{x}',t))\psi(\mathbf{x},t)|N\rangle$$

We can apply similar tricks as before to write this as:

$$(\mathrm{i}\partial_t - h(\mathbf{x}))\,G(\mathbf{x}t,\mathbf{x}'t') = \delta(t-t')\,\delta(\mathbf{x}-\mathbf{x}') - \mathrm{i}\int \mathrm{d}\mathbf{x}''v(\mathbf{r},\mathbf{r}'')\underbrace{\langle N|\mathrm{T}\left\{\psi^\dagger(\mathbf{x}',t)\psi(\mathbf{x}'',t)\psi(\mathbf{x},t))\psi^\dagger(\mathbf{x}',t')\right\}|N\rangle}_{G_2(\mathbf{x}t,\mathbf{x}''t,\mathbf{x}''t^+,\mathbf{x}'t')}$$

The two particle Green's function defined as:

$$G(\mathbf{x}t,\mathbf{x}_2t_2,\mathbf{x}'t',\mathbf{x}_2't_2') = \langle N|\mathrm{T}\left\{\psi(\mathbf{x}_1,t_1)\psi(\mathbf{x}_2,t_2)\psi^\dagger(\mathbf{x}_2',t_2'))\psi^\dagger(\mathbf{x}_1',t_1')\right\}|N\rangle \tag{5.41}$$

Therefore, to calculate the one-particle Green's function requires knowledge of the two-particle green's function, which in turn will require knowledge of the three-particle Green's function and so on, It is easily seen that this builds up the full many-body Schrödinger equation. Alternatively we can here make an attempt at factorizing:

$$-\mathrm{i}\int \mathrm{d}\mathbf{x}''v(\mathbf{r},\mathbf{r}'')\,G_2\left(\mathbf{x}t,\mathbf{x}''t,\mathbf{x}''t^+,\mathbf{x}'t'\right) \equiv \int \mathrm{d}t''\mathrm{d}\mathbf{x}''M(\mathbf{x}t,\mathbf{x}''t'')\,G(\mathbf{x}''t'',\mathbf{x}'t')$$

From M we seperate out the Hatree potential.

$$v_H(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'v(\mathbf{r},\mathbf{r}')\,n(\mathbf{r}') = \int \mathrm{d}\mathbf{r}'v(\mathbf{r},\mathbf{r}')\,\langle N|\psi^\dagger(\mathbf{r}',t')\psi(\mathbf{r}',t)|N\rangle \tag{5.42}$$

So that with

$$\Sigma = M + v_H \tag{5.43}$$

we arrive at

$$\left(\mathrm{i}\frac{\partial}{\partial t} - h(\mathbf{r}) - v_H(\mathbf{r})\right)G(\mathbf{x}t,\mathbf{x}'t') = \delta(t-t')\,\delta(\mathbf{x}-\mathbf{x}') + \int \mathrm{d}t''\mathrm{d}\mathbf{x}''\Sigma(\mathbf{x}t,\mathbf{x}''t'')\,G(\mathbf{x}''t'',\mathbf{x}'t') \tag{5.44}$$

and Fourier transformed:

$$(\omega - h(\mathbf{r}) - v_H(\mathbf{r}))\,G(\mathbf{x},\mathbf{x}',\omega) - \int \mathrm{d}\mathbf{x}''\Sigma(\mathbf{x},\mathbf{x}'',\omega)\,G(\mathbf{x}'',\mathbf{x}',\omega) = \delta(\mathbf{x}-\mathbf{x}') \tag{5.45}$$

If $\Sigma(\mathbf{x},\mathbf{x}'',\omega)$ were static like in HF or local as in DFT this equation would simplify:

$$(\omega - h_0)\,G(\mathbf{x},\mathbf{x}',\omega) = \delta(\mathbf{x}-\mathbf{x}') \quad \text{where} \quad h_0 = h(\mathbf{r}) + v_H(\mathbf{r}) + \begin{cases} v_{HF}(\mathbf{r},\mathbf{r}') \\ v_{XC}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}') \end{cases} \tag{5.46}$$

$$H_0 = \sum_i^N h_0(i)$$

This is the homogenous differential equation to the Schrödinger equation

$$H_0\Psi_s = E_s^{(0)}\Psi_s \qquad h_0\varphi_s = \epsilon_s\varphi_s \tag{5.47}$$

For this system we know that $|N\rangle$ is a single slater determinant ϕ_0.

$$\begin{aligned} \Longrightarrow f_s(\mathbf{x}) &= \langle N-1,s|\psi(\mathbf{x})\,|\Phi_0\rangle \\ &= \langle N-1,s|\sum_k \varphi_k(\mathbf{x})\,a_k|\Phi_0\rangle \\ &= \sum_k \varphi_k(\mathbf{x})\underbrace{\langle N-1,s|a_k|\Phi_0\rangle}_{\delta_{sk}} = \varphi_s(\mathbf{x}) \end{aligned}$$

$$G_0\left(\mathbf{x},\mathbf{x}',\omega\right)=\lim_{\eta\to0}\sum_s\frac{\varphi_s\left(\mathbf{x}\right)\varphi_s^*\left(\mathbf{x}'\right)}{\omega-\left(\epsilon_s\pm\mathrm{i}\eta\right)}\quad\begin{cases}+&\text{for occupied}\\-&\text{for unoccupied}\end{cases}\quad\text{states}\tag{5.48}$$

So we have

$$\begin{aligned}&(\omega-h_0)G_0=\hat{I}\quad\rightarrow\quad(\omega-h_0)=G_0^{-1}\\&(\omega-h_0)G-\Sigma G=\hat{I}\\&\curvearrowright G_0^{-1}G-\Sigma G=\hat{I}\\&\Leftrightarrow\boxed{G=G_0+G_0\Sigma G}\end{aligned}$$

This is Dyson's equation!
Starting from a non-interacting Green's function, G can be obtained through Dyson's equation.

5.4 Hedin's equations

Without proof Hedin's equations are listed here. The derivation can be found in the appendix of Hedin's original paper: Phys. Rev. 139 A796.

$$\Sigma\left(\mathbf{x}_1t_1,\mathbf{x}_2t_2\right)=\mathrm{i}\int\mathrm{d}\mathbf{x}_3\mathrm{d}\mathbf{x}_4\mathrm{d}t_3\mathrm{d}t_4W\left(\mathbf{x}_1t_1^+,\mathbf{x}_3t_3\right)G\left(\mathbf{x}_1t_1,\mathbf{x}_4t_4\right)\Gamma\left(\mathbf{x}_4t_4,\mathbf{x}_2t_2,\mathbf{x}_3t_3\right)\tag{5.49}$$

$$W\left(\mathbf{x}_1t_1,\mathbf{x}_2t_2\right)=v\left(\mathbf{r}_1,\mathbf{r}_2\right)+\int\mathrm{d}\mathbf{x}_3\mathrm{d}\mathbf{x}_4\mathrm{d}t_3\mathrm{d}t_4W\left(\mathbf{x}_1t_1,\mathbf{x}_3t_3\right)P\left(\mathbf{x}_3t_3,\mathbf{x}_4t_4\right)v\left(\mathbf{x}_4t_4,\mathbf{x}_2t_2\right)\tag{5.50}$$

$$P\left(\mathbf{x}_1t_1,\mathbf{x}_2t_2\right)=-\mathrm{i}\int\mathrm{d}\mathbf{x}_3\mathrm{d}\mathbf{x}_4\mathrm{d}t_3\mathrm{d}t_4G\left(\mathbf{x}_2t_2,\mathbf{x}_3t_3\right)G\left(\mathbf{x}_4t_4,\mathbf{x}_2t_2\right)\Gamma\left(\mathbf{x}_3t_3,\mathbf{x}_4t_4,\mathbf{x}_1t_1\right)\tag{5.51}$$

$$\begin{aligned}\Gamma\left(\mathbf{x}_1t_1,\mathbf{x}_2t_2,\mathbf{x}_3t_3\right)=&\delta\left(\mathbf{x}_1-\mathbf{x}_2\right)\delta\left(\mathbf{x}_3-\mathbf{x}_4\right)\delta\left(t_1-t_2\right)\delta\left(t_1-t_2\right)\\&+\int\mathrm{d}\mathbf{x}_4\mathrm{d}\mathbf{x}_5\mathrm{d}\mathbf{x}_6\mathrm{d}\mathbf{x}_7\mathrm{d}t_4\mathrm{d}t_5\mathrm{d}t_6\mathrm{d}t_7\frac{\delta\Sigma\left(\mathbf{x}_1t_2,\mathbf{x}_2t_2\right)}{\delta G\left(\mathbf{x}_4t_4,\mathbf{x}_5t_5\right)}\\&\times G\left(\mathbf{x}_4t_4,\mathbf{x}_6t_6\right)G\left(\mathbf{x}_7t_7,\mathbf{x}_5t_5\right)\Gamma\left(\mathbf{x}_6t_6,\mathbf{x}_7t_7,\mathbf{x}_3t_3\right)\end{aligned}\tag{5.52}$$

With

- $W\left(\mathbf{x}_1t_1,\mathbf{x}_2t_2\right)$ - the screend Coulomb interaction
- $P\left(\mathbf{x}_1t_1,\mathbf{x}_2t_2\right)$ - the Polarisability
- $\Gamma\left(\mathbf{x}_1t_1,\mathbf{x}_2t_2,\mathbf{x}_3t_3\right)$ - the vertex function

This is an exact set of equations that expresses the many body problem in 5 quantities G, P, W, Σ and Γ. The complexity of the full many-body problem is shifted to the vertex function.
$\Longrightarrow$ find approximations for Γ
A simpe approximation is to neglect the 2nd part of Γ i.e. $\Gamma:=\hat{I}$
$\Longrightarrow$ Hedin's GW approximation

$$\Sigma\left(\mathbf{x}_1,\mathbf{x}_2,t\right)=\mathrm{i}G\left(\mathbf{x}_1,\mathbf{x}_2,t\right)W\left(\mathbf{x}_1,\mathbf{x}_2,t^+\right)\tag{5.53}$$

$$P\left(\mathbf{x}_1,\mathbf{x}_2,t\right)=-\mathrm{i}G\left(\mathbf{x}_1,\mathbf{x}_2,t\right)G\left(\mathbf{x}_2,\mathbf{x}_1,-t\right)\tag{5.54}$$

$$\text{W stays as it is}\tag{5.55}$$

The real merit of Hedin's equations lies in the fact that the bare Coulomb interaction has been replaced by the **screened Coulomb interaction**. This is important for solids and systems with large polarizability.

$$W\left(\mathbf{r},\mathbf{r}',t\right)=\int\mathrm{d}\mathbf{r}''\mathrm{d}t'\epsilon^{-1}\left(\mathbf{r},\mathbf{r}'',t-t'\right)v\left(\mathbf{r}''-\mathbf{r}\right)\tag{5.56}$$

$$\epsilon\left(\mathbf{r},\mathbf{r}',t\right)=\delta\left(\mathbf{r}-\mathbf{r}'\right)-\int\mathrm{d}\mathbf{r}''\mathrm{d}t'v\left(\mathbf{r}-\mathbf{r}''\right)P\left(\mathbf{r}'',\mathbf{r}',t-t'\right)\quad\text{(dielectric function)}\tag{5.57}$$

The procedure of a typical GW calculation is:

1. Perform a DFT calculation
2. Build Kohn Sham Green's funtion G_0
3. Calculate $P_0 = -\mathrm{i}G_0G_0$
4. Calculate $\epsilon = 1 - vP_0$
5. Invert ϵ
6. Calculate $W_0 = \epsilon^{-1}v$
7. Calculate $\sigma_0 = \mathrm{i}G_0W_0$
8. Solve Dyson's equation which can be rewritten as

$$\left(h(\mathbf{r}) + v_H(\mathbf{r})\right)\psi_s(\mathbf{r}) + \int \mathrm{d}\mathbf{r}'\Sigma_0\left(\mathbf{r},\mathbf{r}',\epsilon_s^{GW}\right)\psi_s(\mathbf{r}') = \epsilon_s^{GW}\psi_s(\mathbf{r}) \tag{5.58}$$

A typical approximation is $\psi_s(\mathbf{r}) = \psi_s^{KS}(\mathbf{r})$

$$\epsilon_s^{GW} = \epsilon_s^{KS} + \langle s|\sigma_0\left(\epsilon_s^{GW}\right) - v_{xc}|s\rangle \tag{5.59}$$

The performace of the GW approximation is compared to HF and LDA with respect to band structure and band gap in figures (5.4) and (5.5).

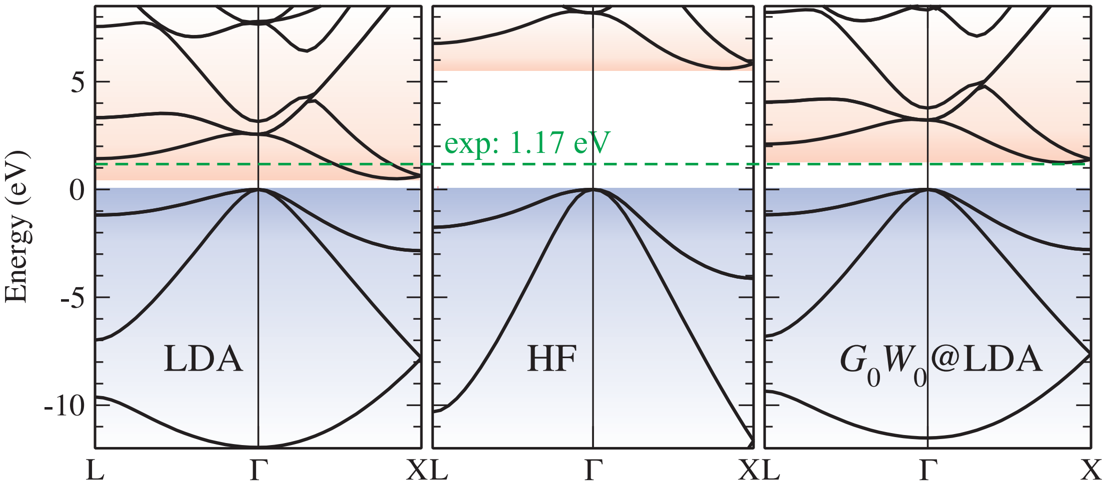


Figure 5.4: Band structure of silicon.

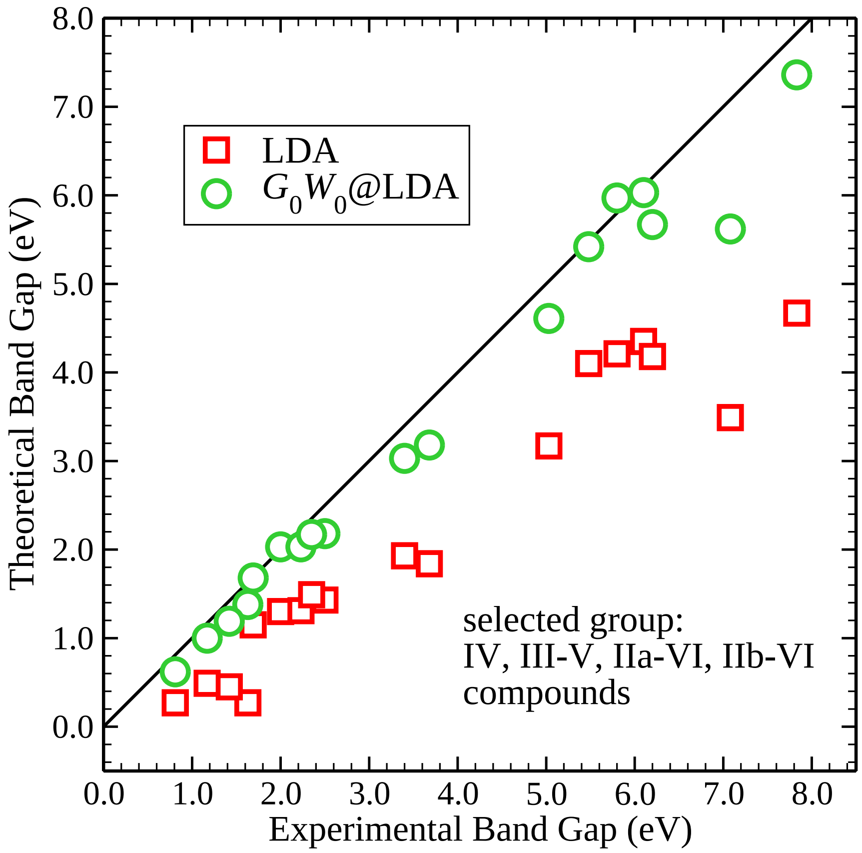


Figure 5.5: Band gaps of selected compounds compared to experimental values.