Work in progress

by

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Abstract

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Work in progress make for $w_{i \to j} \equiv w\left(i|j\right)$

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Chapter 1

1.1 Introduction

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Chapter 2

In this chapter we will list general theory regarding functions used in the methods mentioned in chapter 3 and show important properties used in later derivations.

2.1 Lagrange Multiplier Method

See [2, 3]. The optimization method of Lagrange multipliers maximizes(or minimizes) a function $f : \mathbb{R}^N \to \mathbb{R}$ with a constraint $g : \mathbb{R}^N \to \mathbb{R}$ We assume that f and g have continuous first derivatives in all variables(continuous first partial derivatives).
Given the above we can define a so-called Lagrangian $\mathcal{L}$

$$\mathcal{L}[x_1, \ldots, x_N, \lambda_1, \ldots, \lambda_M] = f(x_1, \ldots, x_N) - \lambda g(x_1, \ldots, x_N) \tag{2.1}$$

where the λ is called a Lagrange-multiplier. We now state that if $f(x_1^0, \ldots, x_N^0)$ is a maxima of $f(x_1, \ldots, x_N)$ then there exists a Lagrange-multiplier λ_0 such that $(x_1^0, \ldots, x_N^0, \lambda_0)$ is a stationary point for the Lagrangian. This then yields the $N + 1$ Lagrange-equations

$$\sum_{i=1}^{N} \frac{\partial \mathcal{L}}{\partial x_i} + \frac{\partial \mathcal{L}}{\partial \lambda} = 0 \tag{2.2}$$

to be solved for $x_1, \ldots, x_N$ and λ.

Chapter 3

Many-Body Quantum Theory

This chapter takes forth the theory regarding the basics of identical particles and *many-body quantum mechanics*. The reader is referred to [4] for an introductory text on quantum mechanics(for single particles) and also the so-called *Dirac-notation* used throughout the entire chapter. We will address » LIST METHODS « regarding computational quantum mechanics and further deepen into Hartree-Fock methods and Variational Monte Carlo method. Optimization of calculation is also given while structure of program is given in » REF TO PROGRAM STRUCTURE CHAPTER «. General statistical theory used is given in » REF TO STATISTICS CHAPTER «

3.1   The Hamiltonian and the Born-Oppenheimer Approximation

The task at hand is to solve the many-body system described by *Schrödinger's* equation

$$H \left| \Psi_i \right\rangle = E_i \left| \Psi_i \right\rangle \tag{3.1}$$

for some state $\left| \Psi_i \right\rangle$ with energy E_i. Usually the desired state is the ground-state energy E_0 of the system meaning we are primarily interested in the *ground-state* $\left| \Psi_0 \right\rangle$.

With the goal determined we can define the system to consist of N identical particles[1] with positions $\{ \boldsymbol{r}_i \}_{i=0}^{N-1}$ and A nuclei with positions $\{ \boldsymbol{R}_k \}_{k=0}^{A-1}$. The Hamiltonian H is then

$$H = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i<j} f\left(\boldsymbol{r}_j, \boldsymbol{r}_j\right) - \frac{1}{2} \sum_k \frac{\nabla_k^2}{M_k} + \sum_{k<l} g\left(\boldsymbol{R}_k, \boldsymbol{R}_l\right) + V\left(\boldsymbol{R}, \boldsymbol{r}\right) \tag{3.2}$$

The first and second terms represent the kinetic- and inter-particle interaction terms[2] for the N identical particles while the latter three represent kinetic- and interaction terms for the nuclei(with the last one being the nuclei-particle interaction). The constant M_k is the mass of nucleon k and Z_k is the corresponding atomic number.

We assume the nuclei to be much heavier than the identical particles, meaning they move much slower, at which the system can be viewed as electrons moving around the vicinity of stationary nuclei. This means the kinetic term for the nuclei vanish and the nuclei-nuclei interaction becomes a constant[3]. The approximation we end up with is the so-called *Born-Oppenheimer approximation* and the Hamiltonian is now

$$H = H_0 + H_I \tag{3.3}$$

where we have split the Hamiltonian in a *one-body* part and a *two-body* or *interaction* parts defined as

$$H_0 \equiv -\frac{1}{2} \sum_i \nabla_i^2 + V\left(\boldsymbol{R}, \boldsymbol{r}\right) \tag{3.4}$$

and

$$H_I \equiv \sum_{i<j} f\left(\boldsymbol{r}_i, \boldsymbol{r}_j\right) \tag{3.5}$$

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[1] These are in both atomic physics and in the quantum dot case always fermions or bosons.

[2] This is usually the well-known Coulomb interaction.

[3] Adding a constant to an operator does not alter the eigenvector, only the eigenvalues by the constant factor[9].

3.2   Slater Determinant and Permanent

Throughout section 3.1 we only referred to the wavefunction Ψ as a state, a function closely connected to the probabilistic nature of the quantum particles. However, we have not given it a form. One possible solution is the *Hartree product* Ψ_H defined as

$$\Psi_H = \prod_i \psi_i(\boldsymbol{r}_i) \tag{3.6}$$

with $\{\psi\}_{i=0}^N$ being the orbitals which solve the single-particle Schrödinger equation for H_0. The Hartree-product is unfortunately a poor choice since it does not solve the H_I part meaning it is not a physically valid solution. This comes from the fact that the Hartree-product does not take into account the fact that the particles in question are *identical particles*. Since the particles are identical, switching the labels on the particles shouldn't change the expectation value of some observable. If we run this remark through we end up with the conclusion that the state $|\Psi\rangle$ must be either symmetric or antisymmetric with the symmetric part being the *bosonic state* and antisymmetric being the *fermionic state*. The connection between antisymmetric states and fermions is called the *Pauli exclusion principle*.

The problem with the Hartree-product is, with the above sentiment, that it is not symmetric nor antisymmetric. However we can transform it with an operator

$$\mathcal{B} \equiv \frac{1}{N!} \sum_P \sigma_b P \tag{3.7}$$

where σ_b is defined as

$$\sigma_b \equiv \begin{cases} 1 & b \text{ represents bosonic system} \\ (-1)^p & b \text{ represents fermionic system} \end{cases} \tag{3.8}$$

P is a permutation operator that switches the labels on particles [4] and p is the parity of permutations. The operator $\mathcal{B}$ has the following properties

- Applying $\mathcal{B}$ to itself doesn't change the operator meaning $\mathcal{B}^2 = \mathcal{B}$.

- The Hamiltonian H and $\mathcal{B}$ *commute*, that is $[\mathcal{B}, H] = [H, \mathcal{B}]$.

- $\mathcal{B}$ is *unitary*, which means $\mathcal{B}^\dagger \mathcal{B} = \mathcal{I}$.

The solution Ψ_T to the Schrödinger equation can now be written as

$$\Psi_T(\boldsymbol{r}) = \sqrt{N!}\mathcal{B}\Psi_H(\boldsymbol{r}) \tag{3.9}$$

The antisymmetric case of $\mathcal{B}$ results in a *Slater determinant*

$$\Psi_T^{\text{AS}} = \frac{1}{\sqrt{N!}} \sum_P (-1)^p P \prod_i \psi_i \tag{3.10}$$

while the symmetric case gives the so-called *permanent*[5].

$$\Psi_T^{\text{S}} = \frac{1}{\sqrt{N!}} \sum_P P \prod_i \psi_i \tag{3.11}$$

Notice that the coordinated $\boldsymbol{r}_{i=0}^N$ is a bit of a sloppy notation as it also implicitly includes the spin orbitals discussed in » ref section on spin orbitals «.

3.3   Variational Principle

One important remark is that the Slater determinant and the permanent do not solve the interaction part, but only serves as a so-called *ansatz* or guess on the true ground-state wavefunction. This is quite useful due to the *variational principle*.
The Variational principle states that for any normalized function Ψ in Hilbert Space » REF HILBERT

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[4] $P_{ij}\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i, \ldots, \boldsymbol{r}_j, ; \boldsymbol{r}_N) = \Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_j, \ldots, \boldsymbol{r}_i, ; \boldsymbol{r}_N)$ [12].
[5] The permanent is basically just a determinant with all the negative signs replaced by positive ones.

« with a Hermitian operator H the minimum eigenvalue E_0 for H has an upper-bound given by the expectation value of H in the function Ψ. That is

$$E_0 \leq \langle H \rangle = \langle \Psi | H | \Psi \rangle = \int \Psi^* H \Psi \mathrm{d}r \tag{3.12}$$

See [4] for proof and more.

The mentioned ansatz is thereby guaranteed to give energies larger than or equal the true ground state energy meaning a minimization method is sufficient in order to get closer to this minimum.

3.4   Energy Functional

We can find a more convenient expression for this energy by using equations 3.9 and 3.12. This gives us

$$E[\Psi] = N! \langle \Psi_{\mathrm{H}} | H\mathcal{B} | \Psi_{\mathrm{H}} \rangle \tag{3.13}$$

where the hermitian and unitary property of $\mathcal{B}$ as well as the fact that $\mathcal{B}$ and H commute have been used. This energy functional(functional in the sense that it is dependant on the wave function). Applying the $\mathcal{B}$ operator to the Hartree-product, pulling the sum out of the integrals and relabeling with the following definitions

$$\langle p | h | q \rangle \equiv \langle \psi_p(\boldsymbol{r}) | h(\boldsymbol{r}) | \psi_q(\boldsymbol{r}) \rangle = \int \psi_p^*(x) h(\boldsymbol{r}) \psi_q(\boldsymbol{r}) \mathrm{d}r$$
$$\langle pq | f | rs \rangle \equiv \langle \psi_p(\boldsymbol{r}_1) \psi_q(\boldsymbol{r}_2) | f(\boldsymbol{r}_1, \boldsymbol{r}_2) | \psi_r(\boldsymbol{r}_1) \psi_s(\boldsymbol{r}_2) \rangle = \int \psi_p(\boldsymbol{r}_1) \psi_q(\boldsymbol{r}_2) f(\boldsymbol{r}_1, \boldsymbol{r}_2) \psi_r(\boldsymbol{r}_1) \psi_s(\boldsymbol{r}_2) \mathrm{d}r \tag{3.14}$$

yields in

$$E[\Psi] = \langle p | H_0 | p \rangle + \frac{1}{2} \sum_{p,q} \left[\langle pq | f_{pq} | pq \rangle \pm \langle pq | f_{pq} | qp \rangle \right] \tag{3.15}$$

The first part is written with the assumption that the single-particle wave functions $\{\psi\}$ are orthogonal and the 1/2 factor in front of the so-called *direct* and *exchange* terms[6] is due to the fact that we count the permutations twice in the sum when applying the $\mathcal{B}$ operator. The sign in the interaction term are chosen as positive for bosonic systems and negative for fermionic systems.

The expression given in equation 3.15 is the functional form we will use to derive the Hartree-fock equations in the following section.

3.5   Hartree-Fock Theory

Hartree-Fock method is a many-body method for approximating the wavefunction of a stationary many-body quantum state and thereby also obtain an estimate for the energy in this state. In this section we will derive the Hartree-Fock equations from scratch, following closely the literature by J.M Thjissen[12].

3.5.1   Assumptions

Hartree-Fock method makes the following assumptions of the system

- *The Born-Oppenheimer approximation*, see » REF BO «.

- All relativistic effects are negligible.

- The wavefunction can be described by a single *Slater determinant*.

- The *Mean Field Approximation* holds.

With these inherent approximations the last one is the most important to take into account as it can cause large deviations from test solutions (analytic solutions, experimental data etc.) since the electron correlations is in reality, for many cases, not negligible. There exists many methods that try to fix this problem » LIST METHODS «. The *Variational Monte Carlo* (or VMC) is the method for deeper explorations in this Thesis, see section 3.7 for more details.

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[6]The direct term is just due to inherent behaviour of the charge of the particles (known as the Coulomb repulsion). The exchange term is a direct consequence of the probabilistic nature of the identical particles.

3.5.2 The $\mathcal{J}$ and $\mathcal{K}$ Operators

Before we begin with the Hartree-Fock equations it is desirable to rewrite the energy function obtained in section 3.4 (form given in equation 3.15) with two operators $\mathcal{J}$ and $\mathcal{K}$ defined as

$$\mathcal{J} \equiv \sum_k \langle \psi_k^* | f_{12} | \psi_k \rangle = \int \psi_k^*(\boldsymbol{r}) f_{12} \psi_k(\boldsymbol{r}) \mathrm{d}r$$
$$\mathcal{K} \equiv \sum_k \langle \psi_k^* | f_{12} | \psi \rangle = \int \psi_k^*(\boldsymbol{r}) f_{12} \psi(\boldsymbol{r}) \mathrm{d}r$$

(3.16)

The $\mathcal{J}$ operator just gives the simple interaction-term while the $\mathcal{K}$ operator gives the exchange term with the arbitrary (notice no index) $\psi(\boldsymbol{r})$. The energy functional is thus rewritten to

$$E[\Psi] = \sum_i \left\langle \psi_i \left| h + \frac{1}{2}(\mathcal{J} \pm \mathcal{K}) \right| \psi_i \right\rangle$$

(3.17)

where the one-body Hamiltonian is split into a sum of single particle functions as $H_0 = \sum_i h(\boldsymbol{r}_i)$.

3.5.3 Hartree-Fock Equations

As a reminder. The wavefunctions $\{\psi\}$ in equation 3.17 are spin-orbitals with both a spacial part and a spin part. In order to obtain the Hartree-Fock equations we try to minimize the energy functional in order to obtain the ground-state energy for a many-body system. This is done by a variational method.

The first observation to notice is the fact that variations in the spin-orbitals $\{\psi\}$ need to respect the spin-orthogonality relation

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

(3.18)

with δ_{ij} being the well-known Kronecker-delta. This property is essentially a constraint to the minimization problem and the method to be used is the *Lagrange multiplier method*[9], with the following *Lagrangian*

$$\mathcal{L} = \delta E[\Psi] - \sum_{ij} \Lambda_{ij} \left[\langle \psi_i | \psi_j \rangle - \delta_{ij} \right]$$

(3.19)

We know then that the minimum is reached when a displacement on the spin-orbitals $\psi_i \to \psi_i + \delta\psi_i$ results in an energy variation of zero meaning $\delta E[\Psi] = 0$ in the minimum. Which giving the variational problem

$$\sum_i \langle \delta\psi_i | h + \mathcal{J} \pm \mathcal{K} | \psi_i \rangle - \sum_{ij} \Lambda_{ij} \langle \delta\psi_i | \psi_j \rangle + \mathrm{c.c} = 0$$

(3.20)

where c.c is a notation for the complex conjugate of the inner-products on its left-hand side.

The shift in the spin orbitals $\{\delta\psi\}$ is arbitrary and the constraints are symmetric[7] meaning we can with the *Fock-operator*

$$\mathcal{F} \equiv h + \mathcal{J} \pm \mathcal{K}$$

(3.21)

define the following eigenvalue problem

$$\mathcal{F}\psi_i = \sum_j \Lambda_{ij} \psi_j$$

(3.22)

Choosing the Lagrange parameter Λ_{ij} such that $\{\psi\}_{k=1}^N$ forms an orthonormal set for $\mathcal{F}$ with eigenvalues $\{\varepsilon\}_{k=1}^N$. This reduces the eigenvalue equation to

$$\mathcal{F}|\psi\rangle = \varepsilon |\psi\rangle$$

(3.23)

with $\boldsymbol{\varepsilon} = (\varepsilon_0, \ldots, \varepsilon_N)$ being the set of eigenvalues of $\mathcal{F}$ meaning we have $N+1$ equations to be solved.

If we only take the N lowest eigenfunctions into the Slater the corresponding eigenenergy is referred to as the *Hartree-Fock energy* and is the estimated ground-state energy which the Hartree-Fock method gives. We can rewrite the energy functional with the eigenenergies to

$$E[\Psi] = \sum_i \left\langle \psi_i \left| \varepsilon_i - \frac{1}{2}(\mathcal{J} \pm \mathcal{K}) \right| \psi_i \right\rangle$$

(3.24)

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[7] $\langle \psi_i | \psi_j \rangle = \langle \psi_j | \psi_i \rangle^* \Rightarrow \Lambda_{ij} = \Lambda_{ji}^*$

In the derivation of the Hartree-Fock equations we only worked with spin-orbital functions $\{\psi\}$. However it is much more convenient to rewrite these in terms of spatial orbitals $\{\phi\}$ and integrate the spin-dependant part out. There are two ways of doing this and the two different approaches give the so-called *restricted Hartree-Fock* and *unrestricted Hartree-Fock* methods.

3.6   Restricted Hartree-Fock and Roothan-Equations

The restricted spin-orbitals are paired as[8]

$$\{\psi_{2l-1}, \psi_{2l}\} = \{\phi_l(\boldsymbol{r})\alpha(s), \phi_l(\boldsymbol{r})\beta(s)\} \tag{3.25}$$

with $\alpha(s)$ and $\beta(s)$ being different spin-states (up and down). This pairing of spin-states with same and same spacial-orbitals means we can pull the spin degrees of freedom out from the $\mathcal{J}$ and $\mathcal{K}$ operators, reduce the sum to only run over half the states and multiply the entire sum by 2. The result is that the restricted energy-functional reads

$$E[\Psi] = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{\frac{N}{2}} \langle i \,|\, 2\mathcal{J} \pm \mathcal{K} \,|\, i \rangle \tag{3.26}$$

Notice that the $\mathcal{K}$ operators sum only runs up to half the number of states.

As the title suggests we are going to end up with a set of equations referred to as the *Roothan-equations*. We start by first expanding the spacial part $\{\phi\}$ of the spin orbitals $\{\psi\}$ in some known orthonormal basis $\{\chi\}_{i=1}^{L}$

$$\phi_i(\boldsymbol{r}) = \sum_{p=1}^{L} C_{pi}\chi_p(\boldsymbol{r}) \tag{3.27}$$

and introduce the *Fock-matrix* F (associated with the Fock-operator) with elements

$$F_{pq} = h_{pq} + \sum_{pq} \rho_{pq} \left(2D_{prqs} \pm D_{prsq}\right) \tag{3.28}$$

We have here introduced a one-body matrix defined as

$$h_{pq} \equiv \langle p \,|\, h \,|\, q \rangle \tag{3.29}$$

a *density matrix* defined as[9]

$$\rho_{pq} \equiv \sum_{i=1}^{\frac{N}{2}} C_{pi}C_{qi}^* \tag{3.31}$$

and an interaction-matrix D with elements

$$D_{pqrs} \equiv \langle pq \,|\, f_{12} \,|\, rs \rangle \tag{3.32}$$

for convenience. The implicit relabeling of $\chi_p(\boldsymbol{r}) \to p$ is also present in the above expression for the Fock-matrix. The Hartree-Fock equations (equation 3.23) are then for the restricted case written as

$$F\boldsymbol{C}_i = \varepsilon S\boldsymbol{C}_i \tag{3.33}$$

with S being the overlap matrix with elements

$$S_{pq} \equiv \langle p \,|\, q \rangle \tag{3.34}$$

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[8]This is specialised for a two-spin system. For a system with more spin-states one needs to either choose different spacial-orbitals or add more such orbitals which effectively changes the energy-levels.

[9]This is just the matrix formed by

$$\sum_i |\phi_i\rangle \langle \psi_i| \tag{3.30}$$

which is in quantum mechanics defined as the so-called *density matrix*.

3.7 Quantum Monte Carlo

Quantum Monte Carlo, or QMC is a method for solving Schrödinger's equation by a statistical approach using so-called *Markov Chain* simulations (also called random walk). The nature of the wave function at hand is fundamentally a statistical model defined on a large configuration space with small areas of densities. The Monte Carlo method is perfect for solving such a system because of the non-homogeneous distribution of calculation across the space. An standard approach with equal distribution of calculation would then yield a rather poor result with respect to computation cost.

We will in this chapter address the Metropolis algorithm which is used to create a Markov chain and derive the equations used in the variational method.

The chapter will use *Dirac Notation* [4] and all equations stated assume atomic units ($\hbar = m_e = e = 4\pi\varepsilon_0$) » REF HERE ATOMIC UNITS «.

3.7.1 The Variational Principle and Expectation Value of Energy

Given a Hamiltonian $\hat{H}$ and a trial wave function $\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha})$, the variational principle [4, 8] states that the expectation value of $\hat{H}$

$$E[\psi_T] = \left\langle \hat{H} \right\rangle = \frac{\langle \psi_T | \hat{H} | \psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \tag{3.35}$$

is an upper bound to the ground state energy

$$E_0 \leq \left\langle \hat{H} \right\rangle \tag{3.36}$$

Now we can define our PDF as(see section 3.7.3 for a more detailed reasoning)

$$P(\boldsymbol{R}) \equiv \frac{|\psi_T|^2}{\langle \Psi_T | \Psi_T \rangle} \tag{3.37}$$

and with a new quantity

$$E_L(\boldsymbol{R}; \boldsymbol{\alpha}) \equiv \frac{1}{\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha})} \hat{H} \Psi_T(\boldsymbol{R}; \boldsymbol{\alpha}) \tag{3.38}$$

the so-called local energy, we can rewrite equation 3.35 as

$$E[\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha})] = \langle E_L \rangle \tag{3.39}$$

The idea now is to find the lowest possible energy by varying a set of parameters $\boldsymbol{\alpha}$. The expectation value itself is found with the Metropolis algorithm, see section 3.7.4.

An important property of the local energy is when we differentiate it with respect to one of the variational parameters $\{\alpha\}$ within the context of an expectation value. The result in this case would be zero. This is easily seen by direct calculation

$$\begin{aligned}
\left\langle \frac{\partial E_L}{\partial \alpha} \right\rangle &= \int \frac{|\psi|^2 \frac{\partial}{\partial \alpha} \left[\frac{1}{\psi} H \psi \right]}{\int |\psi|^2 \mathrm{d}r} \mathrm{d}r \\
&= \int \frac{|\psi|^2 \frac{\psi^* \frac{\partial}{\partial \alpha}(H\psi) - (H\psi^*) \frac{\partial \psi}{\partial \alpha}}{|\psi|^2}}{\int |\psi|^2 \mathrm{d}r} \mathrm{d}r \\
&= \int \frac{\psi^* H \frac{\partial \psi}{\partial \alpha} - \psi^* H \frac{\partial \psi}{\partial \alpha}}{\int |\psi|^2 \mathrm{d}r} \mathrm{d}r \\
&= 0 \tag{3.40}
\end{aligned}$$

We have used the fact that H is not dependant on any variational parameter and used the hermitian properties[4] of H to justify the movement of H within the integral.

This neat result presented in equation 3.40 will show its usefulness in the minimization when derivatives of the expectation value and variance comes into play since finding the derivative of the local energy would be much more of a hassle.[10]

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[10] The differentiation of the wavefunction is enough reduction of quality of life on its own!

3.7.2   The Trial Wave Function

The trial wave function is generally an arbitrary choice specific for the problem at hand, however it is in most cases favorable to expand the wave function in the eigenbasis (eigenstates) of the Hamiltonian since they forma complete set. This can be expressed as

$$\Psi_T(\boldsymbol{R};\boldsymbol{\alpha}) = \sum_i C_i \psi_i(\boldsymbol{R};\boldsymbol{\alpha}) \tag{3.41}$$

with the ψ_i's are the eigenstates of the Hamiltonian.

3.7.3   Use Diffusion Theory and the PDF

The statistics describing the expectation value states that any distribution may be applied in calculation, however if we take a close look at the local energy(equation 3.38) we see that for all distributions the local energy is not defined at the zeros of $\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})$. This means that an arbitrary PDF does not guarantee generation of points which makes $\psi_T = 0$. This can be overcome by introducing the square of the wave function to be defined as the distribution function as given in equation 3.37.

Because of the inherent statistical property of the wave function Quantum Mechanics can be modelled as a diffusion process, or more specifically, an *Isotropic Diffusion Process* which is essentially just a random walk model. Such a process is described by the Langevin equation with the corresponding Fokker-Planck equation describing the motion of the walkers(particles). See [5] for details.

3.7.4   Metropolis-Hastings Algorithm

The Metropolis algorithm bases itself on moves (also called transitions) as given in a Markov process. » REF THIS HERE «. This process is given by

$$w_i(t + \varepsilon) = \sum_j w_{i \to j} w_j(t) \tag{3.42}$$

where $w(j \to i)$ is just a transition from state j to state i. In order for the transition chain to reach a desired convergence while reversibility is kept, the well known condition for detailed balance must be fulfilled » REF HERE DETAILED BALANCE «. If detailed balance is true, then the following relations is true

$$w_i T_{i \to j} A_{i \to j} = w_j T_{j \to i} A_{j \to i} \Rightarrow \frac{w_i}{w_j} = \frac{T_{j \to i} A_{j \to i}}{T_{i \to j} A_{i \to j}} \tag{3.43}$$

We have here introduced two scenarios, the transition from configuration i to configuration j and the reverse process j to i. Solving the acceptance A for the two cases where the ratio in 3.43 is either 1(in which case the proposed state j is accepted and transitions is made) and when the ratio is less then 1. The Metropolis algorithm would in this case not automatically reject the latter case, but rather reject it with a proposed uniform probability. Introducing now a probability distribution function(PDF) P the acceptance A can be expressed as

$$A_{i \to j} = \min\left(\frac{P_{i \to j}}{P_{j \to i}} \frac{T_{i \to j}}{T_{j \to i}}, 1\right) \tag{3.44}$$

The so-called selection probability T is defined specifically for each problem. For our case the PDF in question is the absolute square of the wave function and the selection T is a Green's function derived in section 3.7.5. The algorithm itself would then be

(i)   Pick initial state i at random.

(ii) Pick proposed state at random in accordance to $T_{j \to i}$.

(iii) Accept state according to $A_{j \to i}$.

(iv) Jump to step (ii) until a specified number of states have been generated.

(v)   Save the state i and jump to step (ii).

3.7.5   Importance Sampling

Using the selection probability mentioned in section 3.7.4 in the Metropolis algorithm is called an *Importance sampling* because is essentially makes the sampling more concentrated around areas where the PDF has large values.

In order to derive the form of this equation we use the statements presented in section 3.7.3. With

$$\frac{\partial r}{\partial t} = DF(r(t)) + \eta \tag{3.45}$$

the *Langevin equation* »REF HERE LANGEVIN« and apply Euler's method (Euler-Maryama »REF«) and obtain the new positions

$$r^{\text{new}} = r^{\text{old}} + DF^{\text{old}}\Delta t + \xi \tag{3.46}$$

with the r's being the new and old positions in the Markov chain respectively and $F^{\text{old}} = F(r^{\text{old}})$. The quantity D is a diffusion therm equal to $1/2$ due to the kinetic energy(remind of natural units) and ξ is a Gaussian distributed random number with 0 mean and $\sqrt{\Delta t}$ variance.

As mentioned a particle is described by the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \sum_i D\frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_i} - \boldsymbol{F_i}\right)P \tag{3.47}$$

With P being the PDF(in current case the selection probability) and F being the drift therm. In order to achieve convergence, that is a stationary probability density, we need the left hand side to be zero in equation 3.47 giving the following equation

$$\frac{\partial^2 P}{\partial x_i{}^2} = P\frac{\partial \boldsymbol{F_i}}{\partial x_i} + \boldsymbol{F_i}\frac{\partial P}{\partial x_i} \tag{3.48}$$

with the drift-therm being on the form $\boldsymbol{F} = g(x)\partial P/\partial x$ we finally have that

$$\boldsymbol{F} = \frac{2}{\psi_T}\nabla\psi_T \tag{3.49}$$

This is the so-called *Quantum Force* which pushes the walkers towards regions where the wave function is large.

Chapter 4

We will in this chapter mentiond some popular basis-sets used in atomic physics and deepen into a particular set of functions called *Gaussian Type orbitals* and mimic the well known *Hermite polynomials*.

4.1 Hermite Functions

Hermite functions are functions of the following form

$$\phi_n^a(\boldsymbol{r}) \equiv \prod_d N_d H_{n_d}(\sqrt{a}x_d)\exp\left(-\frac{a}{2}x_d^2\right) \tag{4.1}$$

with $\boldsymbol{r} = \sum_d \mathbf{e}_d x_d$ and the sum over d being the sum over the number of dimensions and the H_n is the Hermite polynomial of order n. The integer n_d is the order of the function[1] while the parameter a is a scaling factor and N_d is a normalization factor. These functions show up as eigenfunctions for the *quantum harmonic oscillator system*[4] with the scaling parameter a equal to the oscillator frequency (ω) of the system.

The Hermite functions are orthogonal and give a good ansatz for the VMC method, see section 3.7, with the scaling parameter transformed with an additional variational parameter. The problem with these are however that the matrix-elements introduced in the Hartree-Fock method (section 3.5) are not solveable with the Hermite functions as basis functions. » REF FURTHER DISCUSSION «

4.2 Gaussian Type Orbitals

Gaussian Type Orbitals or GTO's are functions of the following form » REF GTO here «

$$G_n(\boldsymbol{\alpha}; \boldsymbol{r}, \boldsymbol{A}) \equiv \prod_d (x_d - A_d)^{n_d}\mathrm{e}^{-\alpha_d(x_d - A_d)^2} \tag{4.2}$$

We call α for the scaling parameter and i for the order of the GTO. The variable A is where the function is centered. These are in many literatures referred to as *primitive Gaussians* and they alone make a poor approximation to the true wave function.

In atomic physics these functions are used directly as a linear combination referred to as *contracted Gaussian functions*. These are written as

$$G_k(x, A) \equiv \sum_{a_k=0}^{P} C_{a_k} G_{a_k}(\alpha_{a_k}; x, A) \tag{4.3}$$

and are fitted[2] to *Slater-type orbitals*, which are functions with decaying properties(present in atomic systems), or found by some variational method before-hand.

These functions are unfortunately not orthogonal, but they behave nicely in integrals and actually give an analytic expression for the interaction-elements mentioned in section 3.5. For this reason we will go forth and use the Gaussian contracted functions and actually fit them to Hermite functions.

---

[1] In quantum mechanics the number n is referred to as the principal quantum number and is associated with the energy of a given orbital(energy-level) of the system.

[2] Meaning we find the parameters C_{a_k}. and α_{a_k}

4.3   Fitting GTO's to Hermite Functions with Least-Squares

Looking at equations 4.1 and 4.2 we see that both functions are separable in the different dimensions. For this reason we simplify to only work in one dimensions with label x for the positions and omit the subscript d. We will also specialize to the quantum dot case where the imagined nuclei is centered in origo for all orbitals. The functions will hereby be written as

$$\phi_n(x) = N H_n(\sqrt{\omega}x)\mathrm{e}^{-\frac{\omega}{2}x^2}$$
$$G_n(x, A) = \sum_{b_n=0}^{n+1} C_{b_n} G_{b_n}(\alpha; x, A) \tag{4.4}$$

First observation here is that we choose the scaling parameter in the GTO to be equal to the oscillator frequency ω halved. We then only have 1 set of coefficients to determine, namely the $\{C\}_{a_k}^P$. Note also that the sum in the contracted function runs to $n+1$, we will show later that this is sufficient to approximate the Hermite of order n.

A Least-Squares problem for a continuous set $x \in \mathbb{R}$ is defined to be of form

$$\min_{\{a\}} \left| \int (f(x) - \sum_j a_j g_j(x))\mathrm{d}x \right|^2 \quad \forall \ x \in \mathbb{R} \tag{4.5}$$

where we minimize with respect to a set of parameters $\{a\}$. The stationary point in the parameters space of the a's is reached when all partial derivatives of $\{a\}$ is zero. This can be expressed as a linear system

$$\boldsymbol{X}\boldsymbol{a} = \boldsymbol{b} \tag{4.6}$$

with the matrix $\boldsymbol{X}$ having elements

$$X_{ij} \equiv \int g_i(x)g_j(x)\mathrm{d}x \tag{4.7}$$

and the vector $\boldsymbol{b}$

$$b_i \equiv \int g_i(x)f(x)\mathrm{d}x \tag{4.8}$$

Inserting the Hermite function for f and the GTO for g the integrands (see Appendix B) we get

$$X_{ij} = \int x^i N_i N_j \mathrm{e}^{\frac{\omega}{2}x^2} x^j \mathrm{e}^{\frac{\omega}{2}x^2} \mathrm{d}x$$
$$b_i = \int N_i x^i \mathrm{e}^{\frac{\omega}{2}x^2} \left(2^n n! \sqrt{\frac{\pi}{\omega}}\right)^{-\frac{1}{2}} H_n(\sqrt{\omega}x)\mathrm{e}^{\frac{\omega}{2}x^2} \mathrm{d}x \tag{4.9}$$

We can solve this by hand, but it is desirable to solve it using Sympy. See »REF IMPLEMENTATION CHAPTER «.

4.4   Integral Elements

In the Hartree-Fock scheme described in chapter 3 we need to calculate the integrals which define the different matrix elements. The integrals to be found are of the following form

$$\langle i|j \rangle = \int_{-\infty}^{\infty} g_i(\alpha_i; r, A)g_j(\alpha_j; r, B)\mathrm{d}\boldsymbol{r}$$

$$\langle i| x_d^k |j \rangle = \int_{-\infty}^{\infty} g_i(\alpha_i; r, A)r^k g_j(\alpha_j; r, B)\mathrm{d}\boldsymbol{r}$$

$$\langle i| \nabla^2 |j \rangle = \int_{-\infty}^{\infty} g_i(\alpha_i; r, A)\nabla^2 g_j(\alpha_j; r, B)\mathrm{d}\boldsymbol{r} \tag{4.10}$$

$$\langle ij| r^{-1} |kl \rangle = \int_{-\infty}^{\infty} g_i(\alpha_i; r_1, A)g_j(\alpha_j; r_2, B)\frac{1}{r_{12}}g_k(\alpha_k; r_1, C)g_l(\alpha_l; r_2, D)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2$$

where $\mathrm{d}\boldsymbol{r}$ means integration over all dimensions and with the g's being the usual *Hermite-Gaussians* defined as

$$g_n(\alpha; \boldsymbol{r}, \boldsymbol{A}) = \prod_d (x_d - A_d)^{n_d} \mathrm{e}^{-\alpha(x_d - A_d)^2} \tag{4.11}$$

We will in this chapter limit ourselves to work with isotropic gaussians (meaning α_d is the same for all dimensions) as this will yield a simpler closed-form solution to the integrals. » Ref non-isotropic «.
The approach given further follows closely the excellent text by Helgaker »REF«, who calculates the integral elements in 3 dimensions.

Before we throw ourselves out into the integrals, let us first express the Hermite-Gaussians in a more convenient way » REF HELGAKER «. The Gaussians can be expressed as

$$g_n(\alpha; \boldsymbol{r}, \boldsymbol{A}) = \prod_d \left(\frac{\partial}{\partial A_{x_d}}\right)^{n_d} \mathrm{e}^{-\alpha(x_d - A_d)^2} = \prod_d \left(\frac{\partial}{\partial A_{x_d}}\right)^{n_d} g_0(\alpha; \boldsymbol{r}, \boldsymbol{A}) \tag{4.12}$$

Since the derivatives are with respect to the center variables we may pull them out of the integration meaning the integrals will only be over s-type Gaussians, greatly simplifying the calculations. With the mentioned simplification in mind, the problem is to find a closed-form expression for the integrals over s-type Gaussians. We proceed with the overlap element first.

Since we only work with s-types when integrating we introduce a new notation

$$\langle A| \hat{O} |B\rangle \equiv \int g_0(\alpha; \boldsymbol{r}, \boldsymbol{A}) \hat{O} g_0(\beta; \boldsymbol{r}, \boldsymbol{B}) \mathrm{d}\boldsymbol{r}$$

$$\langle AB| \hat{O} |CD\rangle \equiv \int g_0(\alpha; \boldsymbol{r_1}, \boldsymbol{A}) g_0(\beta; \boldsymbol{r_2}, \boldsymbol{B}) \hat{O} g_0(\gamma; \boldsymbol{r_1}, \boldsymbol{C}) g_0(\delta; \boldsymbol{r_2}, \boldsymbol{D}) \mathrm{d}\boldsymbol{r_1} \mathrm{d}\boldsymbol{r_2} \tag{4.13}$$

with $\hat{O}$ being We also introduce the *Gaussian product rule*[3] which basically states that the product of two Gaussian functions is just a third Gaussian centered between the center of the two. The expressions give

$$g_0(\alpha; \boldsymbol{r}, \boldsymbol{A}) g_0(\beta; \boldsymbol{r}, \boldsymbol{B}) = K_{AB} \exp\left(-(\alpha + \beta)\boldsymbol{r}_s^2\right) \tag{4.14}$$

where

$$\begin{aligned} K_{AB} &\equiv \exp\left(-\frac{\alpha\beta}{\alpha + \beta} R_{AB}^2\right) \\ R_{AB} &= |\boldsymbol{A} - \boldsymbol{B}| \\ \boldsymbol{r_s} &= \boldsymbol{r} - \boldsymbol{P} \\ \boldsymbol{P} &= \frac{\alpha(\boldsymbol{r} - \boldsymbol{A}) + \beta(\boldsymbol{r} - \boldsymbol{B})}{\alpha + \beta} \end{aligned} \tag{4.15}$$

the vector $\boldsymbol{r}_S$ is just somewhere between $\boldsymbol{A}$ and $\boldsymbol{B}$(We will see that r_S disappears when the integration is done). The Gaussian product rule greatly simplifies the integral over two Gaussian functions since we can just pull K_{AB} out of the integration since it is a constant.

With The simplification to s-types and the product rule, the integration may begin. Starting with the overlap $\langle A|B\rangle$ and applying the Gaussian product rule(equation 4.14) [4]

$$\begin{aligned} \langle A|B\rangle &= \int\limits_{-\infty}^{\infty} g_0(\alpha; \boldsymbol{r}, \boldsymbol{A}) g_0(\beta; \boldsymbol{r}, \boldsymbol{B}) \mathrm{d}\boldsymbol{r} \\ &= K_{AB} \int\limits_{-\infty}^{\infty} \exp\left(-(\alpha + \beta)\boldsymbol{r}_s^2\right) \mathrm{d}\boldsymbol{r} \\ &= K_{AB} \left(\frac{\pi}{\alpha + \beta}\right)^{\frac{d}{2}} \end{aligned} \tag{4.16}$$

The power $d/2$ comes from splitting the integral into the d dimensions. The component-wise factors from the splitting are also substituted(i.e $u = x - P_x$)

---

[3]Still in the isotropic case.

[4]And using the following integral $\int\limits_{-\infty}^{\infty} \mathrm{e}^{-\lambda x^2} = \sqrt{\frac{\pi}{\lambda}}, \quad \lambda > 0$. »REF ROTTMANN«

The second integral with the x_d^k part shows up in the external potential part of the Hamiltonian and again with the Gaussian product rule the expression gives

$$
\begin{aligned}
\langle A|\, x_d^k\, |B\rangle &= \int\limits_{-\infty}^{\infty} g_0(\alpha_i; r, A)\, x_d^k\, g_0(\alpha_j; r, B)\mathrm{d}\boldsymbol{r} \\
&= K_{AB} \int\limits_{-\infty}^{\infty} x_d^k \exp\!\big(-(\alpha+\beta)\boldsymbol{r}_s^2\big)\mathrm{d}\boldsymbol{r} \\
&= K_{AB} \left(\frac{\pi}{\alpha+\beta}\right)^{\frac{D-1}{2}} \int\limits_{-\infty}^{\infty} (u + P_d)^k \exp\!\big(-(\alpha+\beta)u^2\big)\mathrm{d}u \\
&= K_{AB} \left(\frac{\pi}{\alpha+\beta}\right)^{\frac{D-1}{2}} \sum_{l=0}^{k} \binom{k}{l} P_d^{k-l} \int\limits_{-\infty}^{\infty} u^l \exp\!\big(-(\alpha+\beta)u^2\big)\mathrm{d}u \\
&= K_{AB} \left(\frac{\pi}{\alpha+\beta}\right)^{\frac{D-1}{2}} \sum_{l=0}^{k} \binom{k}{l} \frac{P_d^{k-l}}{2(\alpha+\beta)^{\frac{l}{2}}} \left((-1)^l + 1\right) \Gamma\!\left(\frac{l+1}{2}\right) \qquad (4.17)
\end{aligned}
$$

The integrals are split in each dimension and the dimensions not equal to d (in x_d^k) are pulled out and the approach in equation 4.16 is applied. The integral over dimension d is then substituted with $u = x_d + P_d$. In line four $(u + P_d)^k$ is rewritten with the *binomial expansion*[5].

The third integral with the Laplacian operator arises in the kinetic part of the Hamiltonian. This integral can be expressed in terms of equation 4.16, the overlap integral, however the Laplacian applied to a Hermite-Gaussian has to be calculated first

$$
\begin{aligned}
\nabla^2 g_i(\alpha; \boldsymbol{r}, \boldsymbol{A}) &= \sum_d \frac{\partial^2}{\partial x_d^{\,2}} \left(\prod_{d'} (x - A_{d'})^{i_{d'}}_{d'} \exp\!\Big(-\alpha\,(x_{d'} - A_{d'})^2\Big) \right) \\
&= \sum_d \prod_{d'\neq d} g_{i,d'} \frac{\partial^2}{\partial x_d^{\,2}} \Big((x_d - A_d)^{i_d} \exp\!\big(-\alpha\,(x_d - A_d)^2\big) \Big) \\
&= \sum_d \prod_{d'\neq d} g_{i,d'}\, g_{i,d} \left(4\alpha^2 (x_d - A_d)^{i_d+2} - 2\alpha\,(2i_d+1)(x_d - A_d)^{i_d} + i_d(i_d-1)(x_d - A_d)^{i_d-2} \right) \\
&= g_i(\alpha; , \boldsymbol{r}, \boldsymbol{A}) \sum_d \left(4\alpha^2 (x_d - A_d)^{i_d+2} - 2\alpha\,(2i_d+1)(x_d - A_d)^{i_d} + i_d(i_d-1)(x_d - A_d)^{i_d-2} \right)
\end{aligned}
$$
$$(4.18)$$

[5] The integral $\int\limits_{-\infty}^{\infty} x^n \mathrm{e}^{-ax^2}\mathrm{d}x = \frac{1}{2} a^{-\frac{n}{2}} \Gamma\!\left(\frac{k+1}{2}\right), \quad n > -1, n$ even, » REF THIS «< is used as well.

Appendix A

A.1 Interaction-Term in Fock-Operator

Introducing the so-called permutation operator P which interchanges the labels of particles meaning we can define

$$A \equiv \frac{1}{N!} \sum_p (-1)^p P \tag{A.1}$$

the so-called *antisymmetrization* operator. This operator has the following traits

- The Hamiltonian H and A commute since the Hamiltonian is invariant under permutation.
- A applied on itself (that is A^2) is equal to itself since permuting a permuted state reproduces the state.

We can now express our Slater Ψ_T in terms of A as

$$\Psi_T = \sqrt{N!} A \prod_{i,j} \psi_{ij} \tag{A.2}$$

where $\psi_{ij} = \psi_j(\boldsymbol{r}_i)$ is element i,j of the Slater matrix (the matrix associated with the Slater determinant Ψ_T).

The interaction part of H is then

$$\langle \Psi_T | H_I | \Psi_T \rangle = N! \prod_{i,j} \langle \psi_{ij} | A H_I A | \psi_{ij} \rangle \tag{A.3}$$

The interaction H_I and A commute since A commutes with H giving

$$A H_I A | \psi_{ij} \rangle = \frac{1}{N!^2} \sum_{i<j} \sum_p (-1)^{2p} f_{ij} P | \psi_{ij} \rangle \tag{A.4}$$

$$= \frac{1}{N!^2} \sum_{i<j} f_{ij} (1 - P_{ij}) | \psi_{ij} \rangle \tag{A.5}$$

The factor $1 - P_{ij}$ comes from the fact that contributions with $i \neq j$ vanishes due to orthogonality when P is applied. The final expression for the interaction term is thus

$$\langle \Psi_T | H_I | \Psi_T \rangle = \sum_{i<j} \prod_{k,l} [\langle \psi_{kl} | f_{ij} | \psi_{kl} \rangle - \langle \psi_{kl} | f_{ij} | \psi_{lk} \rangle] \tag{A.6}$$

Writing out the product and realizing the double summation over pairs of states we end up with

$$\langle \Psi_T | H_I | \Psi_T \rangle = \frac{1}{2} \sum_{i,j} [\langle \psi_{ij} \psi_{ji} | f_{ij} | \psi_{ij} \psi_{ji} \rangle - \langle \psi_{ij} \psi_{ji} | f_{ij} | \psi_{ji} \psi_{ij} \rangle] \tag{A.7}$$

More comprehensive details and derivations are given in [6, 12].

A.2 Interaction-Matrix Elements

The integrals involved in the matrix-elements of the Fock-matrix in section 3.5 is calculated as follows

$$D_{pqrs} = \langle pq \,|\, f_{12} \,|\, rs \rangle = \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \chi_p(\boldsymbol{r}_1) \chi_q(\boldsymbol{r}_2) \frac{1}{r_{12}} \chi_r(\boldsymbol{r}_1) \chi_s(\boldsymbol{r}_2) \mathrm{d}r_1 \mathrm{d}r_2 \tag{A.8}$$

Appendix B

B.1 Integral-elements in Least-Squares Fitting

The integral elements are as follows

$$
\begin{aligned}
X_{ij} &= \int g_i(x)g_j(x)\mathrm{d}x \\
&= \int x^i N_i N_j \mathrm{e}^{\frac{\omega}{2}x^2} x^j \mathrm{e}^{\frac{\omega}{2}x^2} \mathrm{d}x
\end{aligned}
\tag{B.1}
$$

and

$$
\begin{aligned}
b_i &= \int g_i(x)f(x)\mathrm{d}x \\
&= \int N_i x^i \mathrm{e}^{\frac{\omega}{2}x^2} \left(2^n n! \sqrt{\frac{\pi}{\omega}}\right)^{-\frac{1}{2}} H_n(\sqrt{\omega}x)\mathrm{e}^{\frac{\omega}{2}x^2} \mathrm{d}x
\end{aligned}
\tag{B.2}
$$

We dont contract the expressions further in favor of reusing the normalization factors.

B.2 Derivative of Energy and Variance

The derivative with respect to a general variational parameter α of the energy expectation value $\langle E \rangle$ is

$$
\begin{aligned}
\frac{\partial \langle E \rangle}{\partial \alpha} &= 2\left\langle \frac{E_L}{\psi}\frac{\partial \psi}{\partial \alpha} \right\rangle + \left\langle \frac{\partial E_L}{\partial \alpha} \right\rangle - 2\left\langle \frac{\langle E \rangle}{\psi}\frac{\partial \psi}{\partial \alpha} \right\rangle \\
&= 2\left(\left\langle \frac{E_L}{\psi}\frac{\partial \psi}{\partial \alpha} \right\rangle - \langle E \rangle \left\langle \frac{1}{\psi}\frac{\partial \psi}{\partial \alpha} \right\rangle \right)
\end{aligned}
\tag{B.3}
$$

by using the hermiticity of the Hamiltonian (contained in the local energy E_L).
The derivative of the variance is » REF THIS STARTER «

$$
\begin{aligned}
\frac{\partial \sigma^2}{\partial \alpha} &= 2\left\langle \left(\frac{\partial E_L}{\partial \alpha} - \frac{\partial \langle E \rangle}{\partial \alpha} \right)(E_L - \langle E \rangle) \right\rangle \\
&= 2\left(\left\langle E_L \frac{\partial E_L}{\partial \alpha} \right\rangle - \langle E \rangle \left\langle \frac{\partial E_L}{\partial \alpha} \right\rangle + \left\langle \frac{\partial \langle E \rangle}{\partial \alpha}(\langle E \rangle - E_L) \right\rangle \right) \\
&= 2\langle E \rangle \left(\frac{\partial \langle E \rangle}{\partial \alpha} - 1 \right)
\end{aligned}
\tag{B.4}
$$

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