

# UNIVERSITY OF OSLO

FYS4480 Oral Exam

Quantum mechanics for many-particle  
systems

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# Notation

Here, we follow the notation of having states  $ijk \dots$  refer to occupied states, and  $abc \dots$  refer to unoccupied states, typically below and above the Fermi level, respectively. From a reference state  $|\Phi_0\rangle$  with  $N$  particles, we write a 1-particle-1-hole (1p1h) excitation as

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle, \quad (1)$$

and similarly for 2p2h, 3p3h, etc.

# Motivation

We are, in essence, interested in finding the ground state energy of a many-body system, that is, solving the eigenvalue problem

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle, \quad (2)$$

where  $\hat{H}$  is the Hamiltonian operator and  $|\Psi_0\rangle$  is the ground state wave function, such that the ground state energy  $E_0$  is minimized.

The complexity arises from the fact that the exact solution cannot typically be found for systems with more than a few particles, and we must resort to approximations.

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# Full configuration interaction theory

In full configuration interaction (FCI) theory, we seek to write the wave function as a linear combination of all possible Slater determinants, that is, all possible configurations of the system, truncated at some level.

That is, we wish to write the wave function as

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ia} C_i^a |\Phi_i^a\rangle + \sum_{ijab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots, \quad (3)$$

where the coefficients  $C$  are determined by solving the eigenvalue problem.

## Slater determinants for pairing model

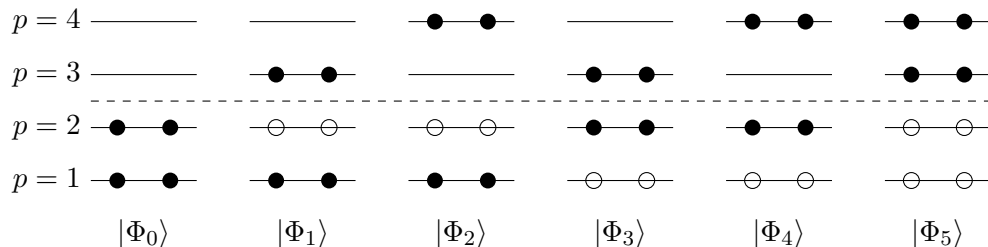


Figure: Schematic representation of the six possible Slater determinants for a system with four particles, under the constraint of no broken pairs, total spin  $S = 0$ , considering only the four lowest levels  $p = 1, 2, 3, 4$ .

## Solving the problem

In solving the system, one first has to set up the Hamiltonian matrix, with elements

$$H_{i,j} = \langle \Phi_i | \hat{H} | \Phi_j \rangle, \quad (4)$$

and then diagonalize the matrix to find the eigenvalues and eigenvectors. The ground state energy can then be found as the lowest eigenvalue, with the corresponding eigenvector giving the coefficients  $C$ .

FCI is exact, but computationally expensive, as the number of configurations grows factorially with the number of energy levels included. Approximative methods are therefore required.



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## Hartree-Fock theory

In Hartree-Fock (HF) theory, we assume that the system can be approximated by a single Slater determinant  $\Phi$ , and we seek to find the wavefunctions  $|\psi_\alpha\rangle$  that minimize the energy

$$E_0 = \langle \Phi | \hat{H} | \Phi \rangle. \quad (5)$$

This gives rise to the HF equations

$$\hat{h}^{\text{HF}} |\psi_\alpha\rangle = \varepsilon_\alpha |\psi_\alpha\rangle, \quad (6)$$

where  $\hat{h}^{\text{HF}} = \hat{t} + \hat{u}_{\text{ext}} + \hat{u}^{\text{HF}}$ , called the Fock operator, is an effective one-body operator. Here,  $\hat{u}^{\text{HF}}$  is the mean potential from the other particles, of the form

$$\langle p | \hat{u}^{\text{HF}} | q \rangle = \sum_i \langle pi | V | qi \rangle_{AS}. \quad (7)$$

## Varying the wave functions

As Eq. (7) depends on the eigenfunctions, Eq. (6) is nonlinear. We therefore solve it iteratively, until convergence is reached<sup>1</sup>. Varying the wave functions directly lead to a set of coupled integro-differential equations, wherein the integrals need to be computed at each iteration.

Another, more computationally efficient approach, is to expand the wave functions in a basis of known functions, and vary the coefficients of the expansion. We do this by a unitary transformation to a new basis  $p$ ,

$$\psi_p = \sum_{\alpha} C_{p\alpha} \phi_{\alpha}, \quad (8)$$

where we now vary the coefficients  $C_{p\alpha}$ .

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<sup>1</sup>If it converges at all.

# The HF equations

Varying the coefficients, we find

$$\sum_{\gamma} h_{\alpha\gamma}^{\text{HF}} C_{p\gamma} = \varepsilon_p^{\text{HF}} C_{p\alpha}, \quad (9)$$

where

$$h_{\alpha\gamma}^{\text{HF}} = \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_{\beta\delta} \rho_{\beta\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \quad (10)$$

Here,  $\rho_{\beta\delta}$  is the density matrix, defined as  $\rho_{\beta\delta} = \sum_i \langle \beta | i \rangle \langle i | \delta \rangle = \sum_i C_{i\beta} C_{i\delta}^*$ . Eq. (9) is in effect nothing more than an eigenvalue problem, and the HF equations are solved by diagonalizing the matrix  $h^{\text{HF}}$  repeatedly. The efficiency comes from the fact that the integrals in Eq. (10) need only be computed once, and the density matrix is updated at each iteration from the eigenvectors.

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# Many-body perturbation theory

In many-body perturbation theory (MBPT), we seek to find the ground state energy by expanding the wave function in a series of perturbations to the Hamiltonian. We assume that the exact solution can be written as

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^{\infty} C_m |\Phi_m\rangle, \quad (11)$$

and that the ground state is dominated by the reference state

$$\hat{H}_0 |\Phi_0\rangle = W_0 |\Phi_0\rangle. \quad (12)$$

## Correlation energy

The Schrödinger equation is then

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle, \quad (13)$$

which gives

$$\langle \Phi_0 | \hat{H} | \Psi_0 \rangle = E. \quad (14)$$

Combining this with

$$\langle \Psi_0 | \hat{H}_0 | \Phi_0 \rangle = W_0, \quad (15)$$

and using the fact that  $\hat{H}, \hat{H}_0$  are Hermitian, we find

$$\langle \Phi_0 | \hat{H}_I | \Psi_0 \rangle = E - W_0 = \Delta E, \quad (16)$$

where  $\Delta E$  is the correlation energy.

## Perturbed expression

Introducing the energy variable  $\omega$ , we can derive

$$\Delta E = \sum_{i=0}^{\infty} \left\langle \Phi_0 \left| \hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) \right\}^i \right| \Phi_0 \right\rangle. \quad (17)$$

This is in reality nothing more than a rewrite of Eq. (16), but serves as a starting point for the perturbation expansion. It contains the unknown energy  $E$ , as well as the variable  $\omega$ , and hence we need further assumptions to solve it.



## Brillouin-Wigner perturbation theory

In Brillouin-Wigner perturbation theory (BWPT), we assume that  $\omega = E$  in Eq. (17), and we find

$$\begin{aligned}\Delta E &= \sum_{i=0}^{\infty} \left\langle \Phi_0 \left| \hat{H}_I \left\{ \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \right\}^i \right| \Phi_0 \right\rangle \\ &= \left\langle \Phi_0 \left| \left( \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \dots \right) \right| \Phi_0 \right\rangle.\end{aligned}\tag{18}$$

The equations then become rather simple, as compared with Eq. (17), with the exception on the unknown energy  $E$ . It can however be solved iteratively, for an initial guess of  $E$ .

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## Derivation of the HF equations

In the original basis  $\alpha$  we have the energy functional

$$E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle = \sum_{\alpha} \langle \alpha | \hat{h}_0 | \alpha \rangle + \frac{1}{2} \sum_{\alpha\beta} \langle \alpha\beta | V | \alpha\beta \rangle_{AS}. \quad (19)$$

By way of varying the coefficients, the HF equations are found by introducing the new basis  $p$  defined by the unitary transformation

$$\psi_p = \sum_{\alpha} C_{p\alpha} \phi_{\alpha}, \quad (20)$$

and minimizing the energy functional

$$E[\Phi^{\text{HF}}] = \langle \Phi^{\text{HF}} | \hat{H} | \Phi^{\text{HF}} \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | V | ij \rangle_{AS} \quad (21)$$

with respect to the coefficients  $C_{p\alpha}$ .

## Introducing Lagrange multipliers

Defining the functional in Eq. (21) as a functional of the coefficients  $C_{p\alpha}$ , we have

$$E_0[C] = \sum_i \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \quad (22)$$

As we have orthonormal basis functions, we have

$$\langle i | j \rangle = \delta_{ij} = \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \beta \rangle = \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}, \quad (23)$$

so we introduce the functional

$$F[C] = E_0[C] - \sum_i \lambda_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}, \quad (24)$$

where  $\lambda_i$  are the Lagrange multipliers enforcing orthonormality.

# Minimizing $F$

Minimizing  $F$  with respect to  $C_{i\alpha}^*$ , we wish to solve

$$\frac{dF}{dC_{i\alpha}^*}[C] = \frac{d}{dC_{i\alpha}^*} \left[ E_0[C] - \sum_j \lambda_j \sum_{\alpha} C_{j\alpha}^* C_{j\alpha} \right] = 0. \quad (25)$$

Term by term we have

$$\frac{d}{dC_{i\alpha}^*} \sum_i \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle = \sum_{\beta} C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \quad (26)$$

$$\frac{d}{dC_{i\alpha}^*} \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} = \sum_j \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}, \quad (27)$$

Minimizing  $F$ , cont.

and finally

$$\frac{d}{dC_{i\alpha}^*} \sum_i \lambda_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha} = \lambda_i C_{i\alpha}. \quad (28)$$

Combining these terms, we have

$$\sum_{\beta} C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_j \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} - \lambda_i C_{i\alpha} = 0. \quad (29)$$

Recognizing  $\lambda_i$  as the eigenvalues  $\varepsilon_i^{\text{HF}}$ , we can write this as

$$\sum_{\gamma} \left[ \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_j \sum_{\beta\delta} C_{j\beta}^* C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} \right] C_{p\gamma} = \varepsilon_p^{\text{HF}} C_{p\alpha}. \quad (30)$$

## Hartree-Fock equations found

This finally results in the HF equations

$$\sum_{\gamma} h_{\alpha\gamma}^{\text{HF}} C_{p\gamma} = \varepsilon_p^{\text{HF}} C_{p\alpha}. \quad (31)$$



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# Derivation of many-body perturbation expansion

We have

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle \quad (32)$$

$$(\hat{H}_0 + \hat{H}_I)|\Psi_0\rangle = E|\Psi_0\rangle \quad (33)$$

$$-\hat{H}_0|\Psi_0\rangle = (-E + \hat{H}_I)|\Psi_0\rangle \quad (34)$$

$$(\omega - \hat{H}_0)|\Psi_0\rangle = (\omega - E + \hat{H}_I)|\Psi_0\rangle, \quad (35)$$

where  $\omega$  is an energy variable dependent on the expansion method. Assuming the resolvent of  $(\omega - \hat{H}_0)$  exists, we can then rewrite the Schrödinger equation as

$$|\Psi_0\rangle = \frac{1}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I)|\Psi_0\rangle. \quad (36)$$

## Combining with projection operators

With the projection operators

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0|, \quad \text{and} \quad \hat{Q} = \sum_{m=1}^{\infty} |\Phi_m\rangle\langle\Phi_m|, \quad (37)$$

we can then write

$$\begin{aligned} |\Psi_0\rangle &= (\hat{P} + \hat{Q}) |\Psi_0\rangle = |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle \\ &= |\Phi_0\rangle + \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) |\Psi_0\rangle. \end{aligned} \quad (38)$$

Solving this in an iterative fashion, with an initial guess for  $|\Psi_0\rangle = |\Phi_0\rangle$ , we have

$$|\Psi_0\rangle = \sum_{i=0}^{\infty} \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) \right\}^i |\Phi_0\rangle \quad (39)$$