# 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 $ijk\ldots$ refer to occupied states, and $abc\ldots$ 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

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle, \tag{1}$$

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

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle, \tag{2}$$

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

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

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

# Slater determinants for pairing model

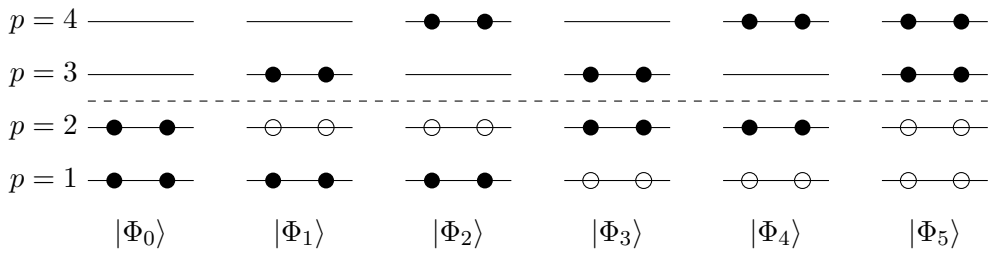


Figure: Schematic representation of the six possible Slater determinants for a system with four particles, under the constraint of no broken pairs, total spin $S = 0$, considering only the four lowest levels $p = 1, 2, 3, 4$.

# Solving the problem

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

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

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 Hatree-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

$$E_0 = \left\langle \Phi | \hat{H} | \Phi \right\rangle. \tag{5}$$

This gives rise to the HF equations

$$\hat{h}^{\mathrm{HF}} |\psi_\alpha\rangle = \varepsilon_\alpha |\psi_\alpha\rangle, \tag{6}$$

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

$$\langle p | \hat{u}^{\mathrm{HF}} | q \rangle = \sum_i \langle pi | V | qi \rangle_{AS}. \tag{7}$$

## Varying the wave functions

As Eq. (7) depends on the eigenfunctions, Eq. (6) is nonlinear. We therefore solve it iteratively, until convergence is reached[1]. 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 $p$,

$$\psi_p = \sum_\alpha C_{p\alpha}\phi_\alpha, \tag{8}$$

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

[1] If it converges at all.

# The HF equations

Varying the coefficients, we find

$$\sum_{\gamma} h^{\mathrm{HF}}_{\alpha\gamma} C_{p\gamma} = \varepsilon^{\mathrm{HF}}_{p} C_{p\alpha}, \tag{9}$$

where

$$h^{\mathrm{HF}}_{\alpha\gamma} = \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_{\beta\delta} \rho_{\beta\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \tag{10}$$

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 $h^{\mathrm{HF}}$ 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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# Derivation of the HF equations

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

$$E[\Phi] = \left\langle \Phi | \hat{H} | \Phi \right\rangle = \sum_{\alpha} \langle \alpha | \hat{h}_0 | \alpha \rangle + \frac{1}{2} \sum_{\alpha\beta} \langle \alpha\beta | V | \alpha\beta \rangle_{AS}. \tag{11}$$

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

$$\psi_p = \sum_{\alpha} C_{p\alpha} \phi_{\alpha}, \tag{12}$$

and minimizing the energy functional

$$E[\Phi^{\mathrm{HF}}] = \left\langle \Phi^{\mathrm{HF}} | \hat{H} | \Phi^{\mathrm{HF}} \right\rangle = \sum_{i} \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | V | ij \rangle_{AS} \tag{13}$$

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

## Introducing Lagrange multipliers

Defining the functional in Eq. (13) as a functional of the coefficients $C_{p\alpha}$, we have

$$E_0[C] = \sum_i \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C^*_{i\alpha} C^*_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \tag{14}$$

As we have orthonormal basis functions, we have

$$\langle i | j \rangle = \delta_{ij} = \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | \beta \rangle = \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}, \tag{15}$$

so we introduce the functional

$$F[C] = E_0[C] - \sum_i \lambda_i \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}, \tag{16}$$

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

# Minimizing $F$

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

$$\frac{\mathrm{d}F}{\mathrm{d}C^*_{i\alpha}}[C] = \frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\left[E_0[C] - \sum_j \lambda_j \sum_\alpha C^*_{j\alpha}C_{j\alpha}\right] = 0. \tag{17}$$

Term by term we have

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\sum_i\sum_{\alpha\beta} C^*_{i\alpha}C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle = \sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle \tag{18}$$

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\frac{1}{2}\sum_{ij}\sum_{\alpha\beta\gamma\delta} C^*_{i\alpha}C^*_{j\beta}C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS} = \sum_j\sum_{\beta\gamma\delta} C^*_{j\beta}C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}, \tag{19}$$

# Minimizing $F$, cont.

and finally

$$\frac{\mathrm{d}}{\mathrm{d}C_{i\alpha}^*}\sum_i \lambda_i \sum_\alpha C_{i\alpha}^* C_{i\alpha} = \lambda_i C_{i\alpha}. \tag{20}$$

Combining these terms, we have

$$\sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle + \sum_j \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS} - \lambda_i C_{i\alpha} = 0. \tag{21}$$

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

$$\sum_\gamma \left[\langle\alpha|\hat{h}_0|\gamma\rangle + \sum_j \sum_{\beta\delta} C_{j\beta}^* C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}\right] C_{p\gamma} = \varepsilon_p^{\mathrm{HF}} C_{p\alpha}. \tag{22}$$

# Hartree-Fock equations found

This finally results in the HF equations

$$\sum_{\gamma} h^{\mathrm{HF}}_{\alpha\gamma} C_{p\gamma} = \varepsilon^{\mathrm{HF}}_{p} C_{p\alpha}. \tag{23}$$