UNIVERSITY
OF OSLO

FYS4480 Oral Exam

Quantum mechanics for
many-particle systems

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Introduction

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.

Full configuration interaction

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 with 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

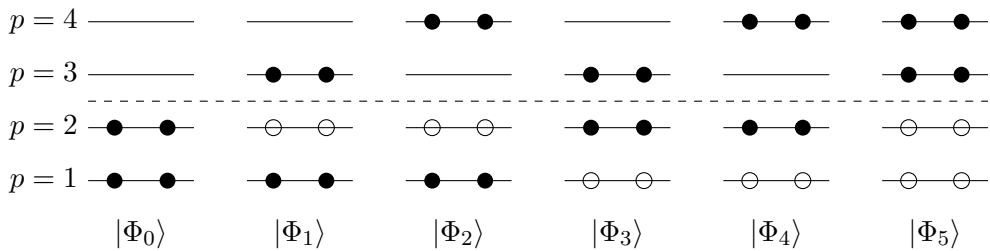

Figure: Schematic representation of the six possible Slater determinants for a system with four particles, under the constraint of no broken pairs, total spin $S = 0$, considering only the four lowest levels $p = 1, 2, 3, 4$.

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.

Hartree-Fock

Hartree-Fock theory

In Hatree-Fock (HF) theory, assume that the system can be approximated by a single Slater determinant, that is, a single configuration.

Many-body pertubation

Coupled-Clusted theory

Derivation of the HF equations

Derivation of the HF equations

In the original basis α we have the energy functional

$$E[\Phi] = \left\langle \Phi | \hat{H} | \Phi \right\rangle = \sum_{\alpha} \langle \alpha | \hat{h}_0 | \alpha \rangle + \frac{1}{2} \sum_{\alpha\beta} \langle \alpha\beta | V | \alpha\beta \rangle_{AS}. \tag{5}$$

The HF equations are found by introducing the new basis p defined by the unitary transformation

$$\psi_p = \sum_{\alpha} C_{p\alpha} \phi_{\alpha}, \tag{6}$$

and minimizing the energy functional

$$E[\Phi^{\mathrm{HF}}] = \left\langle \Phi^{\mathrm{HF}} | \hat{H} | \Phi^{\mathrm{HF}} \right\rangle = \sum_{i} \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | V | ij \rangle_{AS} \tag{7}$$

with respect to the coefficients $C_{p\alpha}$. Eq. (7)

Introducing Lagrange multipliers

Defining the functional in Eq. (7) as a functional of the coefficients $C_{p\alpha}$, we have

$$E_0[C] = \sum_i \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C^*_{i\alpha} C^*_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \tag{8}$$

As we have orthonormal basis functions, we have

$$\langle i | j \rangle = \delta_{ij} = \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | \beta \rangle = \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}, \tag{9}$$

so we introduce the functional

$$F[C] = E_0[C] - \sum_i \lambda_i \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}, \tag{10}$$

where λ_i are the Lagrange multipliers enforcing orthonormality.

Minimizing F

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

$$\frac{\mathrm{d}F}{\mathrm{d}C^*_{i\alpha}}[C] = \frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\left[E_0[C] - \sum_j \lambda_j \sum_\alpha C^*_{j\alpha}C_{j\alpha}\right] = 0. \tag{11}$$

Term by term we have

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\sum_i\sum_{\alpha\beta} C^*_{i\alpha}C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle = \sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle \tag{12}$$

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}}\frac{1}{2}\sum_{ij}\sum_{\alpha\beta\gamma\delta} C^*_{i\alpha}C^*_{j\beta}C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS} = \sum_j\sum_{\beta\gamma\delta} C^*_{j\beta}C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}, \tag{13}$$

Minimizing F, cont.

and finally

$$\frac{\mathrm{d}}{\mathrm{d}C^*_{i\alpha}} \sum_i \lambda_i \sum_\alpha C^*_{i\alpha} C_{i\alpha} = \lambda_i C_{i\alpha}. \tag{14}$$

Combining these terms, we have

$$\sum_\beta C_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_j \sum_{\beta\gamma\delta} C^*_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} - \lambda_i C_{i\alpha} = 0. \tag{15}$$

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

$$\sum_\gamma \left[\langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_j \sum_{\beta\delta} C^*_{j\beta} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS} \right] C_{p\gamma} = \varepsilon_p^{\mathrm{HF}} C_{p\alpha}. \tag{16}$$

Hartree-Fock equations found

This finally results in the HF equations

$$\sum_{\gamma} h^{\mathrm{HF}}_{\alpha\gamma} C_{p\gamma} = \varepsilon^{\mathrm{HF}}_{p} C_{p\alpha}. \tag{17}$$