Week 38: Particle-hole formalism and full configuration interaction theory

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Plans for week 38

Topics to be covered:

1. Thursday: Discussion of particle-hole formalism with examples and diagrammatic representation.
2. Video of lecture
3. Whiteboard notes
4. Friday: Full configuration interaction theory
5. Lecture Material: These slides and chapters 3 and 4 of Shavitt and Bartlett covers most of the material discussed this week.
6. Fifth exercise set at https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/Exercises/2025/ExercisesWeek38.pdf
7. See also the solution of the exercises from last week. They contain also parts of the solution for the exercises this week. The solution is at https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/Exercises/2025/AnswersWeek37.pdf

Particle-hole formalism, reminder from last week

Second quantization is a useful and elegant formalism for constructing many-body states and quantum mechanical operators. One can express and translate many physical processes into simple pictures such as Feynman diagrams. Expecation values of many-body states are also easily calculated.
However, although the equations are seemingly easy to set up, from a practical point of view, that is the solution of Schroedinger's equation, there is no particular gain. The many-body equation is equally hard to solve, irrespective of representation. The cliche that there is no free lunch brings us down to earth again. Note however that a transformation to a particular basis, for cases where the interaction obeys specific symmetries, can ease the solution of Schroedinger's equation.

Redefining the reference state

But there is at least one important case where second quantization comes to our rescue. It is namely easy to introduce another reference state than the pure vacuum $|0\rangle$, where all single-particle states are active. With many particles present it is often useful to introduce another reference state than the vacuum state$|0\rangle$. We will label this state $|c\rangle$ (c for core) and as we will see it can reduce considerably the complexity and thereby the dimensionality of the many-body problem. It allows us to sum up to infinite order specific many-body correlations. The particle-hole representation is one of these handy representations.

New operators

In the original particle representation these states are products of the creation operators $a^\dagger_{\alpha_i}$ acting on the true vacuum $|0\rangle$. We have

$$|\alpha_1\alpha_2\ldots\alpha_{n-1}\alpha_n\rangle = a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\ldots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}|0\rangle \quad (1)$$

$$|\alpha_1\alpha_2\ldots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle = a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\ldots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}a^\dagger_{\alpha_{n+1}}|0\rangle \quad (2)$$

$$|\alpha_1\alpha_2\ldots\alpha_{n-1}\rangle = a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\ldots a^\dagger_{\alpha_{n-1}}|0\rangle \quad (3)$$

Reference states

If we use Eq. (1) as our new reference state, we can simplify considerably the representation of this state

$$|c\rangle \equiv |\alpha_1\alpha_2\ldots\alpha_{n-1}\alpha_n\rangle = a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\ldots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}|0\rangle \tag{4}$$

The new reference states for the $n+1$ and $n-1$ states can then be written as

$$|\alpha_1\alpha_2\ldots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle = (-1)^n a^\dagger_{\alpha_{n+1}}|c\rangle \equiv (-1)^n|\alpha_{n+1}\rangle_c \tag{5}$$

$$|\alpha_1\alpha_2\ldots\alpha_{n-1}\rangle = (-1)^{n-1}a_{\alpha_n}|c\rangle \equiv (-1)^{n-1}|\alpha_{n-1}\rangle_c \tag{6}$$

Hole and particle states

The first state has one additional particle with respect to the new vacuum state $|c\rangle$ and is normally referred to as a one-particle state or one particle added to the many-body reference state. The second state has one particle less than the reference vacuum state $|c\rangle$ and is referred to as a one-hole state. When dealing with a new reference state it is often convenient to introduce new creation and annihilation operators since we have from Eq. (6)

$$a_\alpha|c\rangle \neq 0 \tag{7}$$

since α is contained in $|c\rangle$, while for the true vacuum we have $a_\alpha|0\rangle = 0$ for all α.

Redefinition of creation and annihilation operators

The new reference state leads to the definition of new creation and annihilation operators which satisfy the following relations

$$b_\alpha |c\rangle = 0 \tag{8}$$

$$\{b^\dagger_\alpha, b^\dagger_\beta\} = \{b_\alpha, b_\beta\} = 0$$

$$\{b^\dagger_\alpha, b_\beta\} = \delta_{\alpha\beta} \tag{9}$$

We assume also that the new reference state is properly normalized

$$\langle c|c\rangle = 1 \tag{10}$$

Physical interpretation

The physical interpretation of these new operators is that of so-called quasiparticle states. This means that a state defined by the addition of one extra particle to a reference state $|c\rangle$ may not necesseraly be interpreted as one particle coupled to a core. We define now new creation operators that act on a state α creating a new quasiparticle state

$$b_\alpha^\dagger|c\rangle = \begin{cases} a_\alpha^\dagger|c\rangle = |\alpha\rangle, & \alpha > F \\ \\ a_\alpha|c\rangle = |\alpha^{-1}\rangle, & \alpha \leq F \end{cases} \tag{11}$$

where F is the Fermi level representing the last occupied single-particle orbit of the new reference state $|c\rangle$.

Annihilation operator

The annihilation is the hermitian conjugate of the creation operator

$$b_\alpha = (b_\alpha^\dagger)^\dagger,$$

resulting in

$$b_\alpha^\dagger = \begin{cases} a_\alpha^\dagger & \alpha > F \\ \\ a_\alpha & \alpha \leq F \end{cases} \qquad b_\alpha = \begin{cases} a_\alpha & \alpha > F \\ \\ a_\alpha^\dagger & \alpha \leq F \end{cases} \tag{12}$$

Introducing the concept of quasiparticle states

With the new creation and annihilation operator we can now construct many-body quasiparticle states, with one-particle-one-hole states, two-particle-two-hole states etc in the same fashion as we previously constructed many-particle states. We can write a general particle-hole state as

$$|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle \equiv \underbrace{b^\dagger_{\beta_1}b^\dagger_{\beta_2}\dots b^\dagger_{\beta_{n_p}}}_{>F}\underbrace{b^\dagger_{\gamma_1}b^\dagger_{\gamma_2}\dots b^\dagger_{\gamma_{n_h}}}_{\leq F}|c\rangle \tag{13}$$

We can now rewrite our one-body and two-body operators in terms of the new creation and annihilation operators.

Number operator

The number operator becomes

$$\hat{N} = \sum_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} = \sum_{\alpha > F} b_{\alpha}^{\dagger} b_{\alpha} + n_c - \sum_{\alpha \leq F} b_{\alpha}^{\dagger} b_{\alpha} \tag{14}$$

where n_c is the number of particle in the new vacuum state $|c\rangle$.
The action of $\hat{N}$ on a many-body state results in

$$N|\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle = (n_p + n_c - n_h)|\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1} \tag{15}$$

More manipulations

Here $n = n_p + n_c - n_h$ is the total number of particles in the quasi-particle state of Eq. (13). Note that $\hat{N}$ counts the total number of particles present

$$N_{qp} = \sum_{\alpha} b_{\alpha}^{\dagger} b_{\alpha}, \tag{16}$$

gives us the number of quasi-particles as can be seen by computing

$$N_{qp} = |\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle = (n_p + n_h)|\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle \tag{17}$$

where $n_{qp} = n_p + n_h$ is the total number of quasi-particles.

Onebody operator

We express the one-body operator $\hat{H}_0$ in terms of the quasi-particle creation and annihilation operators, resulting in

$$\hat{H}_0 = \sum_{\alpha\beta>F} \langle\alpha|\hat{h}_0|\beta\rangle b^\dagger_\alpha b_\beta + \sum_{\alpha>F,\beta\leq F} \left[\langle\alpha|\hat{h}_0|\beta\rangle b^\dagger_\alpha b^\dagger_\beta + \langle\beta|\hat{h}_0|\alpha\rangle b_\beta b_\alpha\right] + \sum_{\alpha\leq F} \langle\alpha|\hat{h}_0|\alpha\rangle - \sum_{\alpha\beta\leq F} \langle\beta|\hat{h}_0|\alpha\rangle b^\dagger_\alpha b_\beta \tag{18}$$

The first term gives contribution only for particle states, while the last one contributes only for holestates. The second term can create or destroy a set of quasi-particles and the third term is the contribution from the vacuum state $|c\rangle$.

New notations

Before we continue with the expressions for the two-body operator, we introduce a nomenclature we will use for the rest of this text. It is inspired by the notation used in quantum chemistry. We reserve the labels $i, j, k, \ldots$ for hole states and $a, b, c, \ldots$ for states above F, viz. particle states. This means also that we will skip the constraint $\leq F$ or $> F$ in the summation symbols. Our operator $\hat{H}_0$ reads now

$$\begin{aligned} \hat{H}_0 = & \sum_{ab} \langle a|\hat{h}|b\rangle b_a^\dagger b_b + \sum_{ai} \left[\langle a|\hat{h}|i\rangle b_a^\dagger b_i^\dagger + \langle i|\hat{h}|a\rangle b_i b_a \right] \\ + & \sum_{i} \langle i|\hat{h}|i\rangle - \sum_{ij} \langle j|\hat{h}|i\rangle b_i^\dagger b_j \end{aligned} \quad (19)$$

Two-particle operator

The two-particle operator in the particle-hole formalism is more complicated since we have to translate four indices $\alpha\beta\gamma\delta$ to the possible combinations of particle and hole states. When performing the commutator algebra we can regroup the operator in five different terms

$$\hat{H}_I = \hat{H}_I^{(a)} + \hat{H}_I^{(b)} + \hat{H}_I^{(c)} + \hat{H}_I^{(d)} + \hat{H}_I^{(e)} \tag{20}$$

Using anti-symmetrized matrix elements, bthe term $\hat{H}_I^{(a)}$ is

$$\hat{H}_I^{(a)} = \frac{1}{4} \sum_{abcd} \langle ab|\hat{V}|cd\rangle b_a^\dagger b_b^\dagger b_d b_c \tag{21}$$

More rewriting

The next term $\hat{H}_I^{(b)}$ reads

$$\hat{H}_I^{(b)} = \frac{1}{4}\sum_{abci}\Big(\langle ab|\hat{V}|ci\rangle b_a^\dagger b_b^\dagger b_i^\dagger b_c + \langle ai|\hat{V}|cb\rangle b_a^\dagger b_i b_b b_c\Big) \quad (22)$$

This term conserves the number of quasiparticles but creates or removes a three-particle-one-hole state. For $\hat{H}_I^{(c)}$ we have

$$\begin{aligned}\hat{H}_I^{(c)} = \; & \frac{1}{4}\sum_{abij}\Big(\langle ab|\hat{V}|ij\rangle b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger + \langle ij|\hat{V}|ab\rangle b_a b_b b_j b_i\Big) + \\ & \frac{1}{2}\sum_{abij}\langle ai|\hat{V}|bj\rangle b_a^\dagger b_j^\dagger b_b b_i + \frac{1}{2}\sum_{abi}\langle ai|\hat{V}|bi\rangle b_a^\dagger b_b. \quad (23)\end{aligned}$$

More terms

The first line stands for the creation of a two-particle-two-hole state, while the second line represents the creation to two one-particle-one-hole pairs while the last term represents a contribution to the particle single-particle energy from the hole states, that is an interaction between the particle states and the hole states within the new vacuum state.
The fourth term reads

$$\begin{aligned}\hat{H}_I^{(d)} = & \frac{1}{4}\sum_{aijk}\Big(\langle ai|\hat{V}|jk\rangle b_a^\dagger b_k^\dagger b_j^\dagger b_i + \langle ji|\hat{V}|ak\rangle b_k^\dagger b_j b_i b_a\Big) + \\ & \frac{1}{4}\sum_{aij}\Big(\langle ai|\hat{V}|ji\rangle b_a^\dagger b_j^\dagger + \langle ji|\hat{V}|ai\rangle - \langle ji|\hat{V}|ia\rangle b_j b_a\Big). \quad (24)\end{aligned}$$

Last expressions

The terms in the first line stand for the creation of a particle-hole state interacting with hole states, we will label this as a two-hole-one-particle contribution. The remaining terms are a particle-hole state interacting with the holes in the vacuum state. Finally we have

$$\hat{H}_I^{(e)} = \frac{1}{4}\sum_{ijkl}\langle kl|\hat{V}|ij\rangle b_i^\dagger b_j^\dagger b_l b_k + \frac{1}{2}\sum_{ijk}\langle ij|\hat{V}|kj\rangle b_k^\dagger b_i + \frac{1}{2}\sum_{ij}\langle ij|\hat{V}|ij\rangle \tag{25}$$

The first terms represents the interaction between two holes while the second stands for the interaction between a hole and the remaining holes in the vacuum state. It represents a contribution to single-hole energy to first order. The last term collects all contributions to the energy of the ground state of a closed-shell system arising from hole-hole correlations.

Summarizing and defining a normal-ordered Hamiltonian, part I

$$\Phi_{AS}(\alpha_1,\dots,\alpha_N;x_1,\dots x_N)=\frac{1}{\sqrt{A}}\sum_{\hat{P}}(-1)^P\hat{P}\prod_{i=1}^{A}\psi_{\alpha_i}(x_i),$$

which is equivalent with $|\alpha_1\dots\alpha_N\rangle = a^\dagger_{\alpha_1}\dots a^\dagger_{\alpha_N}|0\rangle$. We have also

$$a^\dagger_p|0\rangle = |p\rangle, \quad a_p|q\rangle = \delta_{pq}|0\rangle$$

$$\delta_{pq} = \left\{a_p, a^\dagger_q\right\},$$

and

$$0 = \left\{a^\dagger_p, a_q\right\} = \{a_p, a_q\} = \left\{a^\dagger_p, a^\dagger_q\right\}$$

$$|\Phi_0\rangle = |\alpha_1\dots\alpha_N\rangle, \quad \alpha_1,\dots,\alpha_N \leq \alpha_F$$

Summarizing and defining a normal-ordered Hamiltonian, part II

$$\left\{a_p^\dagger, a_q\right\} = \delta_{pq}, p, q \leq \alpha_F$$

$$\left\{a_p, a_q^\dagger\right\} = \delta_{pq}, p, q > \alpha_F$$

with $i, j, \ldots \leq \alpha_F, \quad a, b, \ldots > \alpha_F, \quad p, q, \ldots - \text{any}$

$$a_i|\Phi_0\rangle = |\Phi_i\rangle, \quad a_a^\dagger|\Phi_0\rangle = |\Phi^a\rangle$$

and

$$a_i^\dagger|\Phi_0\rangle = 0 \quad a_a|\Phi_0\rangle = 0$$

Summarizing and defining a normal-ordered Hamiltonian, part III

The one-body operator is defined as

$$\hat{F} = \sum_{pq} \langle p|\hat{f}|q\rangle a_p^\dagger a_q$$

while the two-body opreator is defined as

$$\hat{V} = \frac{1}{4}\sum_{pqrs} \langle pq|\hat{v}|rs\rangle_{AS} a_p^\dagger a_q^\dagger a_s a_r$$

where we have defined the antisymmetric matrix elements

$$\langle pq|\hat{v}|rs\rangle_{AS} = \langle pq|\hat{v}|rs\rangle - \langle pq|\hat{v}|sr\rangle.$$

Summarizing and defining a normal-ordered Hamiltonian, part III

We can also define a three-body operator

$$\hat{V}_3 = \frac{1}{36} \sum_{pqrstu} \langle pqr|\hat{v}_3|stu\rangle_{AS} a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s$$

with the antisymmetrized matrix element

$$\langle pqr|\hat{v}_3|stu\rangle_{AS} = \langle pqr|\hat{v}_3|stu\rangle + \langle pqr|\hat{v}_3|tus\rangle + \langle pqr|\hat{v}_3|ust\rangle - \langle pqr|\hat{v}_3|su$$

(26)

The Jordan-Wigner transformation, additional material and digression linking with quantum computing

For a spin-1/2 one-dimensional quantum spin-chain a fermionization procedure exists which allows the mapping between spin operators and fermionic creation-annihilation operators. The algebra governing the spin chain is the $SU(2)$ algebra, represented by the σ-matrices. The Jordan-Wigner transformation is a transformation from fermionic annihilation and creation operators to the σ-matrices of a spin-1/2 chain.

Isomorphism

There is an isomorphism between the two systems, meaning that any a or $a^\dagger$ operator can be transformed into a tensor product of σ-matrices operating on a set of qubits. The authors demonstrated, with an emphasis on single-particle fermionic operators, that the Jordan-Wigner transformation ensures efficient, i.e., not exponential complexity, simulations of a fermionic system on a quantum computer. Similar transformations must be found for other systems, in order to efficiently simulate many-body systems. We present here the various ingredients needed in order to transform a given Hamiltonian into a practical form suitable for quantum mechanical simulations.

Creation and annihilation operators

We begin with the fermionic creation and annihilation operators, which satisfy the following anticommutation relations

$$\{a_k, a_l\} = \{a_k^\dagger, a_l^\dagger\} = 0, \quad \{a_k^\dagger, a_l\} = \delta_{kl}. \tag{27}$$

Thereafter we define the three traceless and Hermitian generators of the $SU(2)$ group, the σ-matrices σ_x, σ_y and σ_z. Together with the identity matrix 1 they form a complete basis for all Hermitian 2×2 matrices. They can be used to write all Hamiltonians on a spin $1/2$ chain when taking sums of tensor products of these, in other words they form a product basis for the operators on the qubits.

Pauli matrices

The three σ-matrices are

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{28}$$

Raising and lowewring matrices

We define the raising and lowering matrices as

$$\sigma_+ = \frac{1}{2}(\sigma_x + i\sigma_y) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix},$$

$$\sigma_- = \frac{1}{2}(\sigma_x - i\sigma_y) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \tag{29}$$

Transformation of operators

The transformation is based on the fact that for each possible quantum state of the fermion system, there can be either one or zero fermions. Therefore we need n qubits for a system with n possible fermion states. A qubit in state $|0\rangle^i = a_i^\dagger |vacuum\rangle$ represents a state with a fermion, while $|1\rangle^i = |vacuum\rangle$ represents no fermions. Then the raising operator σ_+ changes $|1\rangle$ into $|0\rangle$ when

$$|0\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{30}$$

Creation operators in terms of Pauli matrices

This means that σ_+ acts as a creation operator, and σ_- acts as an annihilation operator. In addition, because of the anticommutation of creation(annihilation) operators for different states we have $a_1^\dagger a_2^\dagger |vacuum\rangle = -a_2^\dagger a_1^\dagger |vacuum\rangle$, meaning that for creation and annihilation operators for states higher than the state corresponding to the first qubit, we need to multiply with a σ_z-matrix on all the qubits leading up to the one in question, in order to get the correct sign in the final operation. This leads us to the Jordan-Wigner transformation

$$a_n^\dagger = \left(\prod_{k=1}^{n-1} \sigma_z^k\right) \sigma_+^n, \quad a_n = \left(\prod_{k=1}^{n-1} \sigma_z^k\right) \sigma_-^n. \tag{31}$$

The notation $\sigma_z^i \sigma_+^j$ means a tensor product of the identity matrix on all qubits other than i and j, $1 \otimes \sigma_z \otimes 1 \otimes \sigma_+ \otimes 1$, if $i < j$, with 1 being the identity matrices of appropriate dimension.

Full Configuration Interaction Theory

We have defined the ansatz for the ground state as

$$|\Phi_0\rangle = \left(\prod_{i \leq F} \hat{a}_i^\dagger \right) |0\rangle,$$

where the index i defines different single-particle states up to the Fermi level. We have assumed that we have N fermions.

One-particle-one-hole state

A given one-particle-one-hole ($1p1h$) state can be written as

$$|\Phi_i^a\rangle = \hat{a}_a^\dagger \hat{a}_i |\Phi_0\rangle,$$

while a $2p2h$ state can be written as

$$|\Phi_{ij}^{ab}\rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i |\Phi_0\rangle,$$

and a general $NpNh$ state as

$$|\Phi_{ijk\ldots}^{abc\ldots}\rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \ldots \hat{a}_k \hat{a}_j \hat{a}_i |\Phi_0\rangle.$$

Full Configuration Interaction Theory

We can then expand our exact state function for the ground state as

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ai} C_i^a|\Phi_i^a\rangle + \sum_{abij} C_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \cdots = (C_0 + \hat{C})|\Phi_0\rangle,$$

where we have introduced the so-called correlation operator

$$\hat{C} = \sum_{ai} C_i^a \hat{a}_a^\dagger \hat{a}_i + \sum_{abij} C_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \ldots$$

Intermediate normalization

Since the normalization of Ψ_0 is at our disposal and since C_0 is by hypothesis non-zero, we may arbitrarily set $C_0 = 1$ with corresponding proportional changes in all other coefficients. Using this so-called intermediate normalization we have

$$\langle \Psi_0 | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1,$$

resulting in

$$|\Psi_0\rangle = (1 + \hat{C})|\Phi_0\rangle.$$

Full Configuration Interaction Theory

We rewrite

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ai} C_i^a|\Phi_i^a\rangle + \sum_{abij} C_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \ldots,$$

in a more compact form as

$$|\Psi_0\rangle = \sum_{PH} C_H^P \Phi_H^P = \left(\sum_{PH} C_H^P \hat{A}_H^P\right)|\Phi_0\rangle,$$

where H stands for $0, 1, \ldots, n$ hole states and P for $0, 1, \ldots, n$ particle states.

Compact expression of correlated part

We have introduced the operator $\hat{A}_H^P$ which contains an equal number of creation and annihilation operators.
Our requirement of unit normalization gives

$$\langle \Psi_0 | \Phi_0 \rangle = \sum_{PH} |C_H^P|^2 = 1,$$

and the energy can be written as

$$E = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \sum_{PP'HH'} C_H^{*P} \langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle C_{H'}^{P'}.$$

Full Configuration Interaction Theory

Normally

$$E = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \sum_{PP'HH'} C_H^{*P} \langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle C_{H'}^{P'},$$

is solved by diagonalization setting up the Hamiltonian matrix defined by the basis of all possible Slater determinants. A diagonalization is equivalent to finding the variational minimum of

$$\langle \Psi_0 | \hat{H} | \Psi_0 \rangle - \lambda \langle \Psi_0 | \Psi_0 \rangle,$$

where λ is a variational multiplier to be identified with the energy of the system.

Minimization

The minimization process results in

$$\delta\left[\langle\Psi_0|\hat{H}|\Psi_0\rangle - \lambda\langle\Psi_0|\Psi_0\rangle\right] = 0,$$

and since the coefficients $\delta[C_H^{*P}]$ and $\delta[C_{H'}^{P'}]$ are complex conjugates it is necessary and sufficient to require the quantities that multiply with $\delta[C_H^{*P}]$ to vanish. Varying the latter coefficients we have then

$$\sum_{P'H'}\left\{\delta[C_H^{*P}]\langle\Phi_H^P|\hat{H}|\Phi_{H'}^{P'}\rangle\, C_{H'}^{P'} - \lambda(\delta[C_H^{*P}]C_{H'}^{P'}]\right\} = 0.$$

Full Configuration Interaction Theory

This leads to

$$\sum_{P'H'} \langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle C_{H'}^{P'} - \lambda C_H^P = 0,$$

for all sets of P and H.
If we then multiply by the corresponding C_H^{*P} and sum over PH we obtain

$$\sum_{PP'HH'} C_H^{*P} \langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle C_{H'}^{P'} - \lambda \sum_{PH} |C_H^P|^2 = 0,$$

leading to the identification $\lambda = E$.

Full Configuration Interaction Theory

An alternative way to derive the last equation is to start from

$$(\hat{H} - E)|\Psi_0\rangle = (\hat{H} - E) \sum_{P'H'} C_{H'}^{P'} |\Phi_{H'}^{P'}\rangle = 0,$$

and if this equation is successively projected against all Φ_H^P in the expansion of Ψ, then the last equation on the previous slide results. As stated previously, one solves this equation normally by diagonalization. If we are able to solve this equation exactly (that is numerically exactly) in a large Hilbert space (it will be truncated in terms of the number of single-particle states included in the definition of Slater determinants), it can then serve as a benchmark for other many-body methods which approximate the correlation operator $\hat{C}$.

FCI and the exponential growth

Full configuration interaction theory calculations provide in principle, if we can diagonalize numerically, all states of interest. The dimensionality of the problem explodes however quickly. The total number of Slater determinants which can be built with say N neutrons distributed among n single particle states is

$$\left(\begin{array}{c} n \\ N \end{array} \right) = \frac{n!}{(n-N)!N!}.$$

For a model space which comprises the first for major shells only $0s$, $0p$, $1s0d$ and $1p0f$ we have 40 single particle states for neutrons and protons. For the eight neutrons of oxygen-16 we would then have

$$\left(\begin{array}{c} 40 \\ 8 \end{array} \right) = \frac{40!}{(32)!8!} \sim 10^9,$$

and multiplying this with the number of proton Slater determinants we end up with approximately with a dimensionality d of $d \sim 10^{18}$.

Exponential wall

This number can be reduced if we look at specific symmetries only. However, the dimensionality explodes quickly!

- For Hamiltonian matrices of dimensionalities which are smaller than $d \sim 10^5$, we would use so-called direct methods for diagonalizing the Hamiltonian matrix
- For larger dimensionalities iterative eigenvalue solvers like Lanczos' method are used. The most efficient codes at present can handle matrices of $d \sim 10^{10}$.

A non-practical way of solving the eigenvalue problem

To see this, we look at the contributions arising from

$$\langle \Phi_H^P | = \langle \Phi_0 |,$$

that is we multiply with $\langle \Phi_0 |$ from the left in

$$(\hat{H} - E) \sum_{P'H'} C_{H'}^{P'} | \Phi_{H'}^{P'} \rangle = 0.$$

Using the Condon-Slater rule

If we assume that we have a two-body operator at most, using the Condon-Slater rule gives then an equation for the correlation energy in terms of C_i^a and C_{ij}^{ab} only. We get then

$$\langle\Phi_0|\hat{H}-E|\Phi_0\rangle+\sum_{ai}\langle\Phi_0|\hat{H}-E|\Phi_i^a\rangle C_i^a+\sum_{abij}\langle\Phi_0|\hat{H}-E|\Phi_{ij}^{ab}\rangle C_{ij}^{ab}=0,$$

or

$$E-E_0=\Delta E=\sum_{ai}\langle\Phi_0|\hat{H}|\Phi_i^a\rangle C_i^a+\sum_{abij}\langle\Phi_0|\hat{H}|\Phi_{ij}^{ab}\rangle C_{ij}^{ab},$$

where the energy E_0 is the reference energy and ΔE defines the so-called correlation energy. The single-particle basis functions could be the results of a Hartree-Fock calculation or just the eigenstates of the non-interacting part of the Hamiltonian.

A non-practical way of solving the eigenvalue problem

To see this, we look at the contributions arising from

$$\langle \Phi_H^P | = \langle \Phi_0 |,$$

that is we multiply with $\langle \Phi_0 |$ from the left in

$$(\hat{H} - E) \sum_{P'H'} C_{H'}^{P'} | \Phi_{H'}^{P'} \rangle = 0.$$

A non-practical way of solving the eigenvalue problem

If we assume that we have a two-body operator at most, Slater's rule gives then an equation for the correlation energy in terms of C_i^a and C_{ij}^{ab} only. We get then

$$\langle \Phi_0 | \hat{H} - E | \Phi_0 \rangle + \sum_{ai} \langle \Phi_0 | \hat{H} - E | \Phi_i^a \rangle C_i^a + \sum_{abij} \langle \Phi_0 | \hat{H} - E | \Phi_{ij}^{ab} \rangle C_{ij}^{ab} = 0.$$

Slight rewrite

Which we can rewrite

$$E - E_0 = \Delta E = \sum_{ai} \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle C_i^a + \sum_{abij} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle C_{ij}^{ab},$$

where the energy E_0 is the reference energy and ΔE defines the so-called correlation energy. The single-particle basis functions could be the results of a Hartree-Fock calculation or just the eigenstates of the non-interacting part of the Hamiltonian.

Rewriting the FCI equation

In our discussions of the Hartree-Fock method planned for week 39, we are going to compute the elements $\langle\Phi_0|\hat{H}|\Phi_i^a\rangle$ and $\langle\Phi_0|\hat{H}|\Phi_{ij}^{ab}\rangle$. If we are using a Hartree-Fock basis, then these quantities result in $\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = 0$ and we are left with a *correlation energy* given by

$$E - E_0 = \Delta E^{HF} = \sum_{abij}\langle\Phi_0|\hat{H}|\Phi_{ij}^{ab}\rangle C_{ij}^{ab}.$$

Rewriting the FCI equation

Inserting the various matrix elements we can rewrite the previous equation as

$$\Delta E = \sum_{ai} \langle i|\hat{f}|a\rangle C_i^a + \sum_{abij} \langle ij|\hat{v}|ab\rangle C_{ij}^{ab}.$$

This equation determines the correlation energy but not the coefficients C.

Rewriting the FCI equation, does not stop here

We need more equations. Our next step is to set up

$$\langle \Phi_i^a | \hat{H} - E | \Phi_0 \rangle + \sum_{bj} \langle \Phi_i^a | \hat{H} - E | \Phi_j^b \rangle C_j^b + \sum_{bcjk} \langle \Phi_i^a | \hat{H} - E | \Phi_{jk}^{bc} \rangle C_{jk}^{bc} + \sum_{bcdjkl} \langle \Phi_i^a | \hat{H}$$

Finding the coefficients

This equation will allow us to find an expression for the coefficents C_i^a since we can rewrite this equation as

$$\langle i|\hat{f}|a\rangle + \langle \Phi_i^a|\hat{H}|\Phi_i^a\rangle C_i^a + \sum_{bj\neq ai} \langle \Phi_i^a|\hat{H}|\Phi_j^b\rangle C_j^b + \sum_{bcjk} \langle \Phi_i^a|\hat{H}|\Phi_{jk}^{bc}\rangle C_{jk}^{bc} + \sum_{bcdjkl} \langle \Phi_i^a|$$

Rewriting the FCI equation

We see that on the right-hand side we have the energy E. This leads to a non-linear equation in the unknown coefficients. These equations are normally solved iteratively (that is we can start with a guess for the coefficients C_i^a). A common choice is to use perturbation theory for the first guess, setting thereby

$$C_i^a = \frac{\langle i|\hat{f}|a\rangle}{\epsilon_i - \epsilon_a}.$$

Rewriting the FCI equation, more to add

The observant reader will however see that we need an equation for C_{jk}^{bc} and C_{jkl}^{bcd} as well. To find equations for these coefficients we need then to continue our multiplications from the left with the various Φ_H^P terms.
For C_{jk}^{bc} we need then

$$\langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_0 \rangle + \sum_{kc} \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_k^c \rangle C_k^c +$$

$$\sum_{cdkl} \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_{kl}^{cd} \rangle C_{kl}^{cd} + \sum_{cdeklm} \langle \Phi_{ij}^{ab} | \hat{H} - E | \Phi_{klm}^{cde} \rangle C_{klm}^{cde} + \sum_{cdefklmn} \langle \Phi_{ij}^{ab} | \hat{H} - E |$$

and we can isolate the coefficients C_{kl}^{cd} in a similar way as we did for the coefficients C_i^a.

Rewriting the FCI equation, more to add

A standard choice for the first iteration is to set

$$C_{ij}^{ab} = \frac{\langle ij|\hat{v}|ab\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}.$$

At the end we can rewrite our solution of the Schroedinger equation in terms of n coupled equations for the coefficients C_H^P. This is a very cumbersome way of solving the equation. However, by using this iterative scheme we can illustrate how we can compute the various terms in the wave operator or correlation operator $\hat{C}$. We will later identify the calculation of the various terms C_H^P as parts of different many-body approximations to full CI. In particular, we can relate this non-linear scheme with Coupled Cluster theory and many-body perturbation theory.

Summarizing FCI and bringing in approximative methods

If we can diagonalize large matrices, FCI is the method of choice since:

- It gives all eigenvalues, ground state and excited states
- The eigenvectors are obtained directly from the coefficients C_H^P which result from the diagonalization
- We can compute easily expectation values of other operators, as well as transition probabilities
- Correlations are easy to understand in terms of contributions to a given operator beyond the Hartree-Fock contribution.

Definition of the correlation energy

The correlation energy is defined as, with a two-body Hamiltonian,

$$\Delta E = \sum_{ai} \langle i|\hat{f}|a\rangle C_i^a + \sum_{abij} \langle ij|\hat{v}|ab\rangle C_{ij}^{ab}.$$

The coefficients C result from the solution of the eigenvalue problem.

Ground state energy

The energy of say the ground state is then

$$E = E_{ref} + \Delta E,$$

where the so-called reference energy is the energy we obtain from a Hartree-Fock calculation, that is

$$E_{ref} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle.$$