Introduction to Many-body Theory

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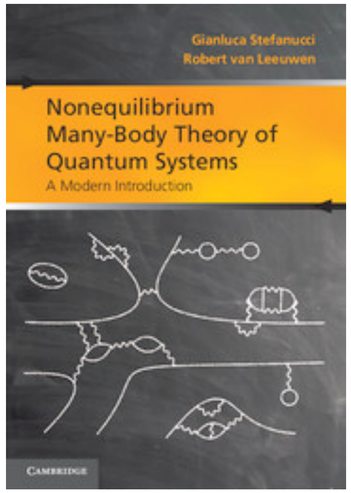
Overview



Part I : Basics

- Time-dependent Schrödinger equation
- A perturbation expansion and propagator
- Second quantisation
- Time-evolution
- The contour idea

Part II : Feynman diagrams and the Green's function

- Why Green's functions?
- Feynman diagrams and the self-energy
- Connection to TDDFT

Part III: Linear response and examples

- Conserving approximations and TDDFT
- The 2-particle Green's function
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Introduction to Many-body Theory I

Part I : Basics

- Time-dependent Schrödinger equation
- A perturbation expansion and propagator
- Second quantisation
- Time-evolution
- The contour idea

Sometimes I state things that require a few steps to work out, this is indicated by the sign

Have a coffee, take pencil and paper, and try to work out this step !

Many-particle Schrödinger equation

The dynamics of a many-electron system is governed by the time-dependent Schrödinger equation

$$i\partial_t \Psi(\underline{\mathbf{x}}, t) = \hat{H}(t)\Psi(\underline{\mathbf{x}}, t)$$

$$\Psi(\underline{\mathbf{x}}, t_0) = \Phi(\underline{\mathbf{x}})$$

initial state

$$\underline{\mathbf{x}} = (\mathbf{x}_1, \ldots, \mathbf{x}_N)$$
$$\mathbf{x} = (\mathbf{r}, \sigma)$$

in which the Hamiltonian is given by

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}$$

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2$$

kinetic energy

$$\hat{V}(t) = \sum_{i=1}^{N} v(\mathbf{x}_i, t)$$

external potential

$$\hat{W} = \sum_{i>j}^{N} w(\mathbf{x}_i, \mathbf{x}_j)$$

two-body interaction

Solving the Schrödinger equation: perturbation expansion

(details not super important now, the focus is on the general idea)

All the complications are in the two-body interactions, as we know how to solve the noninteracting problem, so let us try to expand in a perturbative parameter and study

$$i\partial_t \Psi(\underline{\mathbf{x}}, t) = (\hat{H}_0(t) + \lambda \hat{W})\Psi(\underline{\mathbf{x}}, t)$$

$$\hat{H}_0(t) = \hat{T} + \hat{V}(t)$$

$$\Psi(\underline{\mathbf{x}}, t_0) = \Phi(\underline{\mathbf{x}})$$

We take the solution to be of the form of a perturbation series

$$\Psi(\underline{\mathbf{x}}, t) = \Psi_0(\underline{\mathbf{x}}, t) + \lambda \Psi_1(\underline{\mathbf{x}}, t) + \ldots = \sum_{n=0}^{\infty} \lambda^n \, \Psi_n(\underline{\mathbf{x}}, t)$$

with initial conditions

$$\Psi_0(\underline{\mathbf{x}}, t_0) = \Phi(\underline{\mathbf{x}}) \qquad \Psi_n(\underline{\mathbf{x}}, t_0) = 0 \quad (n \geq 1)$$

Inserting our Ansatz in the Schrödinger equation gives

$$(i\partial_t - \hat{H}_0(t))\Psi(\underline{\mathbf{x}}, t) = \lambda \hat{W}\Psi(\underline{\mathbf{x}}, t)$$

$$\Rightarrow \qquad (i\partial_t - \hat{H}_0(t))(\Psi_0(\underline{\mathbf{x}}, t) + \lambda\Psi_1(\underline{\mathbf{x}}, t) + \ldots) = \lambda\hat{W}(\Psi_0(\underline{\mathbf{x}}, t) + \lambda\Psi_1(\underline{\mathbf{x}}, t) + \ldots)$$

which leads to the set of equations

$$(i\partial_t - \hat{H}_0(t))\Psi_0(\underline{\mathbf{x}}, t) = 0$$

$$(i\partial_t - \hat{H}_0(t))\Psi_1(\underline{\mathbf{x}}, t) = \hat{W}\Psi_0(\underline{\mathbf{x}}, t) \qquad \text{etcetera}$$

and generally

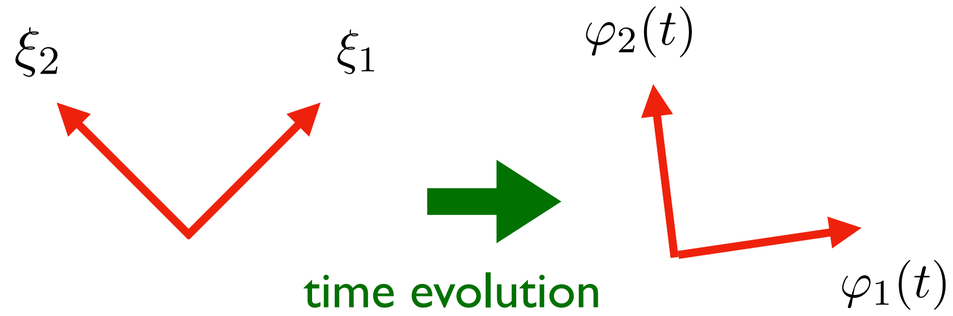
$$\boxed{(i\partial_t - \hat{H}_0(t))\Psi_n(\underline{\mathbf{x}}, t) = \hat{W}\Psi_{n-1}(\underline{\mathbf{x}}, t)} \qquad n \geq 1$$

We obtain an inhomogeneous partial differential equation that can be solved with the Green function method

The Green function or propagator

Take a complete orthonormal set of states $\{\xi_m(\underline{\mathbf{x}})\}$

$$\sum_m \xi_m(\underline{\mathbf{x}})\xi_m^*(\underline{\mathbf{y}}) = \delta(\underline{\mathbf{x}} - \underline{\mathbf{y}})$$



and propagate the set with the noninteracting Hamiltonian

$$i\partial_t \varphi_m(\underline{\mathbf{x}}, t) = \hat{H}_0(t)\varphi_m(\underline{\mathbf{x}}, t) \qquad \varphi_m(\underline{\mathbf{x}}, t_0) = \xi_m(\mathbf{x})$$

Since time evolution is unitary the orthonormality is preserved in time and we have

$$\sum_m \varphi_m(\underline{\mathbf{x}}, t)\varphi_m^*(\underline{\mathbf{y}}, t) = \delta(\underline{\mathbf{x}} - \underline{\mathbf{y}})$$

(anti-symmetrised for fermions, discussed in more detail later)

The N-particle Green function is then defined by

$$G_0(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t') = -i\theta(t - t')\sum_m \varphi_m(\underline{\mathbf{x}}, t)\varphi_m^*(\underline{\mathbf{y}}, t')$$

A quick calculation gives

$$(i\partial_t - \hat{H}_0(t))G_0(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t') = \delta(t-t')\sum_m \varphi_m(\underline{\mathbf{x}},t)\varphi_m^*(\underline{\mathbf{y}},t') + \sum_m [(i\partial_t - \hat{H}_0(t))\varphi_m(\underline{\mathbf{x}},t)]\varphi_m^*(\underline{\mathbf{y}},t')$$

= 0

$$= \delta(t-t')\delta(\underline{\mathbf{x}}-\underline{\mathbf{y}})$$

and the Green function therefore obeys the equation of motion

$$(i\partial_t - \hat{H}_0(t))G_0(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t') = \delta(t-t')\delta(\underline{\mathbf{x}}-\underline{\mathbf{y}})$$

The solution of our inhomogeneous equation is now given by

$$\Psi_n(\underline{\mathbf{x}},t) = \int_{t_0}^{\infty} dt' \int d\underline{\mathbf{y}}\, G_0(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t')\hat{W}(\underline{\mathbf{y}})\Psi_{n-1}(\underline{\mathbf{y}},t')$$

$$\int d\underline{\mathbf{y}} = \frac{1}{N!}\int d\mathbf{y}_1 \ldots d\mathbf{y}_N$$

$$\Psi_n(\underline{\mathbf{x}},t_0) = 0 \qquad (n \geq 1)$$

With the notation $i = (\underline{\mathbf{x}}_i, t_i)$ $\int di = \int d\underline{\mathbf{x}}_i dt_i$ we can write iteratively

$$\Psi_1(\underline{\mathbf{x}}, t) = \int d1\, G_0(\underline{\mathbf{x}}t, 1)\hat{W}(\underline{\mathbf{x}}_1)\Psi_0(1)$$

$$\Psi_2(\underline{\mathbf{x}}, t) = \int d2\, G_0(\underline{\mathbf{x}}t, 2)\hat{W}(\underline{\mathbf{x}}_2)\Psi_1(2) = \int d1d2\, G_0(\underline{\mathbf{x}}t, 2)\hat{W}(\underline{\mathbf{x}}_2)G_0(2, 1)\hat{W}(\underline{\mathbf{x}}_1)\Psi_0(1)$$

and in general

$$\Psi_n(\underline{\mathbf{x}}, t) = \int d1 \ldots dn\, G_0(\underline{\mathbf{x}}t, n)\hat{W}(\underline{\mathbf{x}}_n)G_0(n, n-1)\ldots G_0(2, 1)\hat{W}(\underline{\mathbf{x}}_1)\Psi_0(1)$$

where the solution for Ψ_0 from its homogeneous equation is given by 

$$\Psi_0(\underline{\mathbf{x}}, t) = i \int d\underline{\mathbf{y}}\, G_0(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t_0)\Phi(\underline{\mathbf{y}})$$

$$\lim_{t \to t_0^+} \Psi_0(\underline{\mathbf{x}}, t) = \int d\underline{\mathbf{y}}\delta(\underline{\mathbf{x}} - \underline{\mathbf{y}})\Phi(\underline{\mathbf{y}}) = \Phi(\underline{\mathbf{x}})$$

The solution

Going back to our expansion $$\Psi(\underline{\mathbf{x}},t) = \Psi_0(\underline{\mathbf{x}},t) + \lambda\Psi_1(\underline{\mathbf{x}},t) + \ldots = \sum_{n=0}^{\infty} \lambda^n \, \Psi_n(\underline{\mathbf{x}},t)$$

and inserting our results we find that the solution can be written as

$$\Psi(\underline{\mathbf{x}},t) = i \int d\underline{\mathbf{y}} \, G(\underline{\mathbf{x}}t,\underline{\mathbf{y}}t_0)\Phi(\underline{\mathbf{y}})$$

We act with a time propagator on the initial state

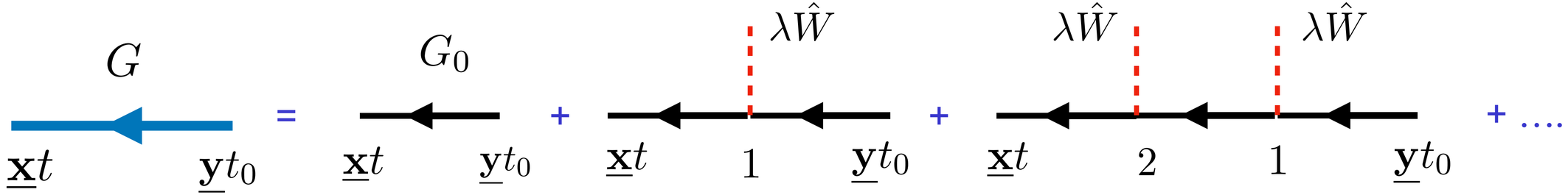
where the so-called dressed or interacting Green function or propagator is defined as

$$G(\underline{\mathbf{x}}t,\underline{\mathbf{y}}t_0) = \sum_{n=0}^{\infty} G_n(\underline{\mathbf{x}}t,\underline{\mathbf{y}}t_0)$$

$$G_n(\underline{\mathbf{x}}t,\underline{\mathbf{y}}t_0) = \lambda^n \int d1 \ldots dn \, G_0(\underline{\mathbf{x}}t,n)\hat{W}(\underline{\mathbf{x}}_n)G_0(n,n-1)\ldots G_0(2,1)\hat{W}(\underline{\mathbf{x}}_1)G_0(1,\underline{\mathbf{y}}t_0)$$

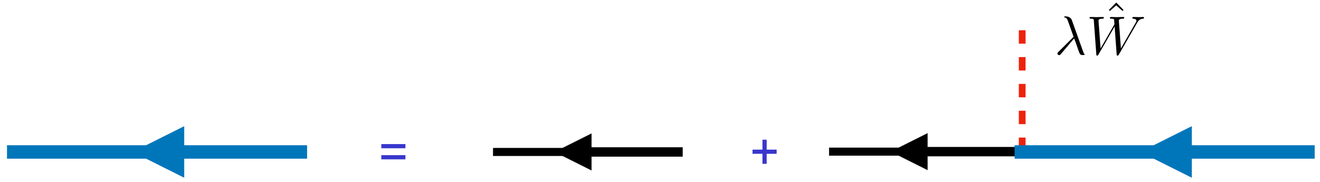
this describes a multiple scattering event with the two-body interaction

The solution has a diagrammatic representation, with a nice physical interpretation as multiple scatterings



$$G = G_0 + G_0\lambda\hat{W}G_0 + G_0\lambda\hat{W}G_0\lambda\hat{W}G_0 + \ldots$$

$$= G_0 + G_0\lambda\hat{W}(G_0 + G_0\lambda\hat{W}G_0\lambda\hat{W}G_0 + \ldots) = G_0 + G_0\lambda\hat{W}G$$

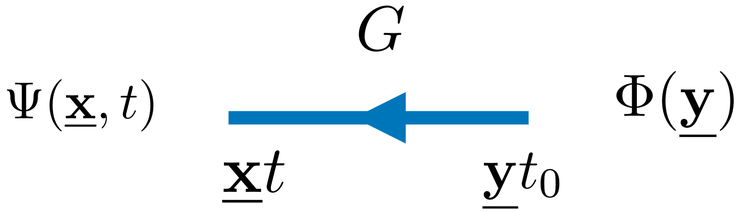


$$G = G_0 + G_0\lambda\hat{W}G$$

N-particle Dyson equation

Propagator

$$\Psi(\underline{\mathbf{x}}, t) = i \int d\underline{\mathbf{y}}\, G(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t_0)\Phi(\underline{\mathbf{y}})$$



How to solve the Schrödinger equation: summary

We conclude that one way of solving the time-dependent Schrödinger equation is to first solve the equation

$$G = G_0 + G_0 \lambda \hat{W} G$$

multiple scatterings with the 2-body interaction

and construct the wave function $\Psi(\underline{\mathbf{x}}, t)$ at a later time from the propagator equation

$$\Psi(\underline{\mathbf{x}}, t) = i \int d\underline{\mathbf{y}}\, G(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t_0)\Phi(\underline{\mathbf{y}})$$

time propagation

The problem is that here the noninteracting N-particle Green function is still a high-dimensional object

$$G_0(\underline{\mathbf{x}}t, \underline{\mathbf{y}}t') = G_0(\mathbf{x}_1, \ldots, \mathbf{x}_N, t; \mathbf{y}_1, \ldots, \mathbf{y}_N, t')$$

contains all particles

which makes the solution of the N-particle Dyson equation a very high dimensional matrix equation

A physical idea

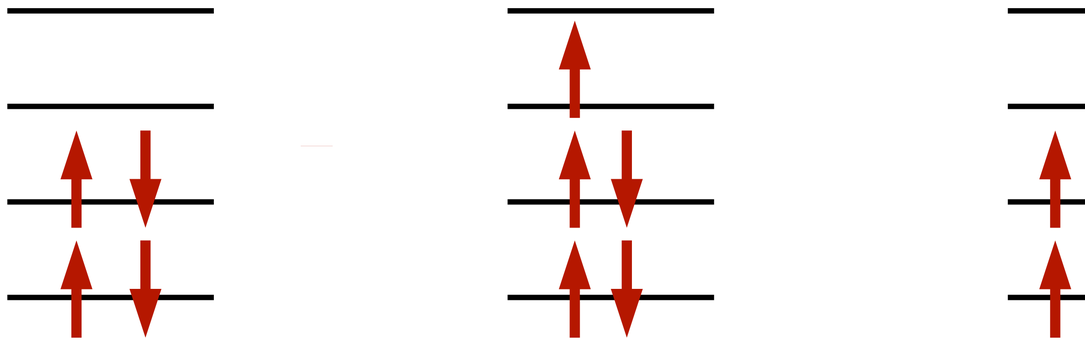
Instead of propagating an N-body object, we add or remove a particle from the system and see how the system reacts to this perturbation and derive properties of the system from this probe

The propagation of these particle and hole states are described by single particle propagators and are therefore low-dimensional objects

addition removal

energy space

Addition and removal from energy levels



These addition and removal processes have precise definitions in operator language

position space

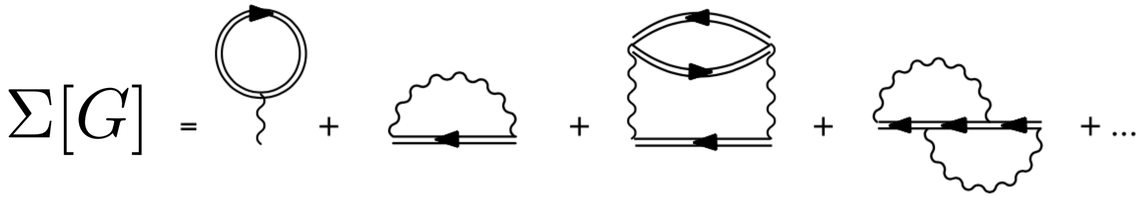
Addition and removal from spatial positions

A bit more precise

The propagation of added and removed particles are described by a Green function satisfying a Dyson equation of the form

$$G(1,2) = G_0(1,2) + \int d3d4\, G_0(1,3)\Sigma(3,4)G(4,2)$$

where the various interactions with the other particles are described by a so-called self-energy kernel



After solving the Dyson equation various observables of the many-body system can be calculated from the Green function

Explaining all this is the subject of the lectures!

Relation to TDDFT

The Green function formalism can be used to define the exchange-correlation potential of TDDFT from an integral equation involving the self-energy (the so-called Sham-Schlüter equation)

$$\int d2\, G_0(1,2)G(2,1)v_{\rm xc}(2) = \int d3d4\, G_0(1,3)\Sigma_{\rm xc}(3,4)G(4,1)$$

It can be obtained from a variational diagrammatic expression and can be constructed such that the xc-potential obtained this way automatically incorporates various conservation laws

From it we can further derive diagrammatic expansions for the xc-kernel of linear response TDDFT

These lectures will provide all the background necessary for you to understand these statements in a precise way!

Position basis

(P.A.M.Dirac, "The principles of quantum mechanics")

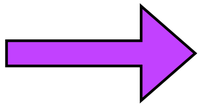
The use of a position basis is advantageous since the external potential and two-body interaction are diagonal in this basis (and DFT is naturally defined in position space)

$|\mathbf{x}\rangle = |\mathbf{r}\sigma\rangle$ = state in which there is with certainty a particle at spin-space point $\mathbf{x}$

We then have the relations

$$|\Psi\rangle = \int d\mathbf{x}\, \Psi(\mathbf{x})|\mathbf{x}\rangle$$

$$\langle \mathbf{y}|\mathbf{x}\rangle = \delta(\mathbf{y}-\mathbf{x})$$



$$\langle \mathbf{y}|\Psi\rangle = \Psi(\mathbf{y})$$

$|\Psi(\mathbf{y})|^2$ = probability to find a particle at position $\mathbf{y}$

so that

$$|\Psi\rangle = \int d\mathbf{x}|\mathbf{x}\rangle\langle\mathbf{x}|\Psi\rangle \qquad \int d\mathbf{x}\,|\mathbf{x}\rangle\langle\mathbf{x}| = 1$$

The case of two particles:

$$|\mathbf{x}_1\mathbf{x}_2\rangle = -|\mathbf{x}_2\mathbf{x}_1\rangle \quad \Rightarrow \quad |\mathbf{x}_1\mathbf{x}_1\rangle = 0$$

Pauli exclusion principle

such that in this case

$$\langle \mathbf{y}_1\mathbf{y}_2|\mathbf{x}_1\mathbf{x}_2\rangle = \delta(\mathbf{y}_1-\mathbf{x}_1)\delta(\mathbf{y}_2-\mathbf{x}_2)-\delta(\mathbf{y}_1-\mathbf{x}_2)\delta(\mathbf{y}_2-\mathbf{x}_1) = \begin{vmatrix} \delta(\mathbf{y}_1-\mathbf{x}_1) & \delta(\mathbf{y}_1-\mathbf{x}_2) \\ \delta(\mathbf{y}_2-\mathbf{x}_1) & \delta(\mathbf{y}_2-\mathbf{x}_2) \end{vmatrix}$$

$$\langle \mathbf{y}_1\mathbf{y}_2|\mathbf{x}_1\mathbf{x}_2\rangle = -\langle \mathbf{y}_2\mathbf{y}_1|\mathbf{x}_1\mathbf{x}_2\rangle = \langle \mathbf{y}_2\mathbf{y}_1|\mathbf{x}_2\mathbf{x}_1\rangle = -\langle \mathbf{y}_1\mathbf{y}_2|\mathbf{x}_2\mathbf{x}_1\rangle$$

where we used that swapping rows or columns in a determinant yields a minus sign. We have the expansion

$$|\Psi\rangle = \frac{1}{2}\int d\mathbf{x}_1 d\mathbf{x}_2 |\mathbf{x}_1\mathbf{x}_2\rangle\langle \mathbf{x}_1\mathbf{x}_2|\Psi\rangle \qquad \frac{1}{2}\int d\mathbf{x}_1 d\mathbf{x}_2 |\mathbf{x}_1\mathbf{x}_2\rangle\langle \mathbf{x}_1\mathbf{x}_2| = 1$$

Check:

$$\langle \mathbf{y}_1\mathbf{y}_2|\Psi\rangle = \frac{1}{2}\int d\mathbf{x}_1 d\mathbf{x}_2 \langle \mathbf{y}_1\mathbf{y}_2|\mathbf{x}_1\mathbf{x}_2\rangle\langle \mathbf{x}_1\mathbf{x}_2|\Psi\rangle = \frac{1}{2}\int d\mathbf{x}_1 d\mathbf{x}_2 (\delta(\mathbf{y}_1-\mathbf{x}_1)\delta(\mathbf{y}_2-\mathbf{x}_2)-\delta(\mathbf{y}_1-\mathbf{x}_2)\delta(\mathbf{y}_2-\mathbf{x}_1))\langle \mathbf{x}_1\mathbf{x}_2|\Psi\rangle$$

$$= \frac{1}{2}(\langle \mathbf{y}_1\mathbf{y}_2|\Psi\rangle - \langle \mathbf{y}_2\mathbf{y}_1|\Psi\rangle) = \langle \mathbf{y}_1\mathbf{y}_2|\Psi\rangle$$

The case of N particles:

$$|\underline{\mathbf{x}}\rangle = |\mathbf{x}_1 \dots \mathbf{x}_N\rangle$$

$$|P\underline{\mathbf{x}}\rangle = |\mathbf{x}_{P(1)} \dots \mathbf{x}_{P(N)}\rangle = (-1)^{|P|}|\mathbf{x}_1 \dots \mathbf{x}_N\rangle$$ where P is a permutation with parity |P|

For the overlaps we have

$$\langle \underline{\mathbf{y}}|\underline{\mathbf{x}}\rangle = \langle \mathbf{y}_1 \dots \mathbf{y}_N|\mathbf{x}_1 \dots \mathbf{x}_N\rangle = \begin{vmatrix} \delta(\mathbf{y}_1 - \mathbf{x}_1) & \dots & \delta(\mathbf{y}_1 - \mathbf{x}_N) \\ \vdots & & \vdots \\ \delta(\mathbf{y}_N - \mathbf{x}_1) & \dots & \delta(\mathbf{y}_N - \mathbf{x}_N) \end{vmatrix} = \delta(\underline{\mathbf{y}} - \underline{\mathbf{x}})$$ definition

and we find the expressions

$$|\Psi\rangle = \int d\underline{\mathbf{x}}|\underline{\mathbf{x}}\rangle\langle\underline{\mathbf{x}}|\Psi\rangle \qquad \int d\underline{\mathbf{x}}\,|\underline{\mathbf{x}}\rangle\langle\underline{\mathbf{x}}| = 1$$

where we defined

$$\int d\underline{\mathbf{x}} = \frac{1}{N!}\int d\mathbf{x}_1 \dots d\mathbf{x}_N$$

Second quantization

There is a unique operator $\hat{\psi}^\dagger(\mathbf{x})$ that generates the position basis. It is defined by

$$
\begin{aligned}
|\mathbf{x}_1\rangle &= \hat{\psi}^\dagger(\mathbf{x}_1)|0\rangle \\
|\mathbf{x}_1\,\mathbf{x}_2\rangle &= \hat{\psi}^\dagger(\mathbf{x}_2)|\mathbf{x}_1\rangle = \hat{\psi}^\dagger(\mathbf{x}_2)\hat{\psi}^\dagger(\mathbf{x}_1)|0\rangle \\
|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle &= \hat{\psi}^\dagger(\mathbf{x}_N)|\mathbf{x}_1 \ldots \mathbf{x}_{N-1}\rangle = \hat{\psi}^\dagger(\mathbf{x}_N)\ldots\hat{\psi}^\dagger(\mathbf{x}_1)|0\rangle
\end{aligned}
$$

$\hat{\psi}^\dagger(\mathbf{x})$ is called creation operator

It follows : $\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y}) = -\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{x})$

Remember that the adjoint of an operator $\hat{O}$ is defined by

$$\langle \Phi | \hat{O}^\dagger | \chi \rangle = \langle \chi | \hat{O} | \Phi \rangle^*$$

The adjoint $\hat{\psi}(\mathbf{x})$ of the creation operator therefore satisfies

$$\langle \mathbf{x}_1 \dots \mathbf{x}_{N-1} | \hat{\psi}(\mathbf{x}_N) | \mathbf{y}_1 \dots \mathbf{y}_N \rangle^* = \langle \mathbf{y}_1 \dots \mathbf{y}_N | \hat{\psi}^\dagger(\mathbf{x}_N) | \mathbf{x}_1 \dots \mathbf{x}_{N-1} \rangle$$

$$= \langle \mathbf{y}_1 \dots \mathbf{y}_N | \mathbf{x}_1 \dots \mathbf{x}_N \rangle = \begin{vmatrix} \delta(\mathbf{y}_1 - \mathbf{x}_1) & \dots & \delta(\mathbf{y}_1 - \mathbf{x}_N) \\ \vdots & & \vdots \\ \delta(\mathbf{y}_N - \mathbf{x}_1) & \dots & \delta(\mathbf{y}_N - \mathbf{x}_N) \end{vmatrix}$$

and hence, by expanding the determinant along the last column, we find 

$$\hat{\psi}(\mathbf{x}) | \mathbf{y}_1 \dots \mathbf{y}_N \rangle = \sum_{k=1}^{N} (-1)^{N-k} \, \delta(\mathbf{x} - \mathbf{y}_k) \, | \mathbf{y}_1 \dots \mathbf{y}_{k-1} \mathbf{y}_{k+1} \dots \mathbf{y}_N \rangle$$

For example:

$$
\begin{aligned}
\hat{\psi}(\mathbf{x})|0\rangle &= 0 \\
\hat{\psi}(\mathbf{x})|\mathbf{y}_1\rangle &= \delta(\mathbf{x}-\mathbf{y}_1)|0\rangle \\
\hat{\psi}(\mathbf{x})|\mathbf{y}_1\,\mathbf{y}_2\rangle &= \delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\rangle - \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\rangle \\
\hat{\psi}(\mathbf{x})|\mathbf{y}_1\,\mathbf{y}_2\,\mathbf{y}_3\rangle &= \delta(\mathbf{x}-\mathbf{y}_3)|\mathbf{y}_1\,\mathbf{y}_2\rangle - \delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\,\mathbf{y}_3\rangle + \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\,\mathbf{y}_3\rangle
\end{aligned}
$$

The operator $\hat{\psi}(\mathbf{x})$ is called annihilation operator

It follows, with anti-commutator $[A,B]_+ = AB + BA$, that 

$$
\begin{aligned}
\left[\hat{\psi}(\mathbf{x}),\hat{\psi}(\mathbf{y})\right]_+ &= \left[\hat{\psi}^\dagger(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{y})\right]_+ = 0 \\
\left[\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{y})\right]_+ &= \delta(\mathbf{x}-\mathbf{y})
\end{aligned}
$$

The density operator is defined by

$$\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})$$

and has the property

$$\hat{n}(\mathbf{x})|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle = \sum_{j=1}^{N} \delta(\mathbf{x} - \mathbf{x}_j)\,|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle$$

For example:

$$\begin{aligned}
\hat{\psi}^\dagger(\mathbf{x})\,\hat{\psi}(\mathbf{x})|\mathbf{y}_1\mathbf{y}_2\rangle &= \hat{\psi}^\dagger(\mathbf{x})\ (\delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\rangle - \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\rangle) \\
&= \delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\mathbf{x}\rangle - \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\mathbf{x}\rangle \\
&= (\delta(\mathbf{x}-\mathbf{y}_1) + \delta(\mathbf{x}-\mathbf{y}_2))|\mathbf{y}_1\mathbf{y}_2\rangle
\end{aligned}$$

The expectation value

$$n(\mathbf{x}) = \langle\Psi|\hat{n}(\mathbf{x})|\Psi\rangle$$

is the particle density of the system in state $|\Psi\rangle$

The Hamiltonian in second quantization

An operator is defined by specifying its matrix elements in a complete basis. For N particles we define the Hamiltonian by

$$\langle \underline{\mathbf{x}}|\hat{H}(t)|\underline{\mathbf{x}}'\rangle = \left(\sum_j^N -\frac{1}{2}\nabla_j^2 + v(\mathbf{x}_j,t) + \frac{1}{2}\sum_{i\neq j}^N w(\mathbf{x}_i,\mathbf{x}_j)\right)\delta(\underline{\mathbf{x}}-\underline{\mathbf{x}}')$$

potentials are diagonal in position space

The ket representation of the Schrödinger equation $i\partial_t|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle$

then becomes, when projected on a position basis,

$$i\partial_t\Psi(\underline{\mathbf{x}},t) = i\partial_t\langle\underline{\mathbf{x}}|\Psi(t)\rangle = \langle\underline{\mathbf{x}}|\hat{H}(t)|\Psi(t)\rangle = \int d\underline{\mathbf{x}}'\langle\underline{\mathbf{x}}|\hat{H}(t)|\underline{\mathbf{x}}'\rangle\langle\underline{\mathbf{x}}'|\Psi(t)\rangle$$

$$= \int d\underline{\mathbf{x}}'\left(\sum_j^N -\frac{1}{2}\nabla_j^2 + v(\mathbf{x}_j,t) + \frac{1}{2}\sum_{i\neq j}^N w(\mathbf{x}_i,\mathbf{x}_j)\right)\delta(\underline{\mathbf{x}}-\underline{\mathbf{x}}')\Psi(\underline{\mathbf{x}}',t)$$

$$= \left(\sum_j^N -\frac{1}{2}\nabla_j^2 + v(\mathbf{x}_j,t) + \frac{1}{2}\sum_{i\neq j}^N w(\mathbf{x}_i,\mathbf{x}_j)\right)\Psi(\underline{\mathbf{x}}',t)$$

We now want to rewrite the Hamiltonian in terms of the field operators

For the 2-particle interaction we have

$$\hat{W}|\mathbf{x}_1 \dots \mathbf{x}_N\rangle = \frac{1}{2}\sum_{i\neq j}^{N} w(\mathbf{x}_i, \mathbf{x}_j)|\mathbf{x}_1 \dots \mathbf{x}_N\rangle$$

Since the density operator has the property

$$\hat{n}(\mathbf{x})|\mathbf{x}_1 \dots \mathbf{x}_N\rangle = \sum_{j=1}^{N} \delta(\mathbf{x}-\mathbf{x}_j)\,|\mathbf{x}_1 \dots \mathbf{x}_N\rangle$$

it follows that

$$\begin{aligned}
\hat{W} &= \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\hat{n}(\mathbf{x})\hat{n}(\mathbf{y}) - \frac{1}{2}\int d\mathbf{x}\, w(\mathbf{x},\mathbf{x})\hat{n}(\mathbf{x}) \\
&= \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\left(\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}) - \delta(\mathbf{x}-\mathbf{y})\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})\right) \\
&= \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x})
\end{aligned}$$

$$\hat{W} = \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x})$$

Similarly for the one-body potential

$$\hat{V}(t)|\mathbf{x}_1 \dots \mathbf{x}_N\rangle = \sum_j^N v(\mathbf{x}_j, t)|\mathbf{x}_1 \dots \mathbf{x}_N\rangle = \int d\mathbf{x}\, \hat{n}(\mathbf{x}) v(\mathbf{x}, t)|\mathbf{x}_1 \dots \mathbf{x}_N\rangle$$

$$\hat{V}(t) = \int d\mathbf{x}\, \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})\, v(\mathbf{x}, t)$$

The kinetic energy operator is only slightly more difficult. Let's illustrate it for 3 particles; remember that

$$\hat{\psi}(\mathbf{x})|\mathbf{y}_1\, \mathbf{y}_2\, \mathbf{y}_3\rangle = \delta(\mathbf{x}-\mathbf{y}_3)|\mathbf{y}_1\, \mathbf{y}_2\rangle - \delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\, \mathbf{y}_3\rangle + \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\, \mathbf{y}_3\rangle$$

$$\hat{\psi}^\dagger(\mathbf{x})\nabla^2\hat{\psi}(\mathbf{x})\,|\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle = \nabla^2\delta(\mathbf{x}-\mathbf{y}_3)|\mathbf{y}_1\, \mathbf{y}_2\, \mathbf{x}\rangle + \nabla^2\delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\mathbf{x}\, \mathbf{y}_3\rangle + \nabla^2\delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{x}\, \mathbf{y}_2\, \mathbf{y}_3\rangle$$

Such that

$$\langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3| \int d\mathbf{x}\, \hat{\psi}^\dagger(\mathbf{x})\nabla^2\hat{\psi}(\mathbf{x})\,|\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle$$

$$= \int d\mathbf{x}\, \left(\nabla^2\delta(\mathbf{x}-\mathbf{y}_3)\langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\mathbf{y}_1\, \mathbf{y}_2\, \mathbf{x}\rangle + \nabla^2\delta(\mathbf{x}-\mathbf{y}_2)\langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\mathbf{y}_1\mathbf{x}\, \mathbf{y}_3\rangle + \nabla^2\delta(\mathbf{x}-\mathbf{y}_1)\langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\mathbf{x}\, \mathbf{y}_2\, \mathbf{y}_3\rangle\right)$$

$$= (\nabla^2_{\mathbf{y}_1} + \nabla^2_{\mathbf{y}_2} + \nabla^2_{\mathbf{y}_3})\langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle$$

If we therefore define

$$\hat{T} = -\frac{1}{2}\int d\mathbf{x}\,\hat{\psi}^\dagger(\mathbf{x})\nabla^2\hat{\psi}(\mathbf{x})$$

then since T is Hermitian

$$\begin{aligned}\langle \mathbf{y}_1\mathbf{y}_2\mathbf{y}_3|\hat{T}|\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\rangle = \langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\hat{T}|\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle^* &= -\frac{1}{2}\left(\nabla^2_{\mathbf{y}_1}+\nabla^2_{\mathbf{y}_2}+\nabla^2_{\mathbf{y}_3}\right)\langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle^* \\ &= -\frac{1}{2}\left(\nabla^2_{\mathbf{y}_1}+\nabla^2_{\mathbf{y}_2}+\nabla^2_{\mathbf{y}_3}\right)\langle \mathbf{y}_1\mathbf{y}_2\mathbf{y}_3|\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\rangle\end{aligned}$$

yielding exactly the matrix element of the kinetic energy operator. Hence

$$\hat{H}(t) = \int d\mathbf{x}\,\hat{\psi}^\dagger(\mathbf{x})\left(-\frac{1}{2}\nabla^2 + v(\mathbf{x},t)\right)\hat{\psi}(\mathbf{x})$$

$$+\frac{1}{2}\int d\mathbf{x}d\mathbf{y}\,w(\mathbf{x},\mathbf{y})\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x})$$

Hamiltonian in second quantization

General basis states

We can also rewrite everything in a general basis. Let consider an orthonormal set of one-particle states $|n\rangle$

$$\langle n|m\rangle = \delta_{nm}$$

and define the spatial orbitals $\varphi_n(\mathbf{x}) = \langle \mathbf{x}|n\rangle$

Then the orbitals φ_n form an orthonormal set in the sense that

$$\int d\mathbf{x}\, \varphi_n^*(\mathbf{x})\varphi_m(\mathbf{x}) = \int d\mathbf{x}\langle n|\mathbf{x}\rangle\langle \mathbf{x}|m\rangle = \langle n|m\rangle = \delta_{nm}$$

We define the operators

$$\hat{a}_n = \int d\mathbf{x}\, \varphi_n^*(\mathbf{x})\hat{\psi}(\mathbf{x}) \qquad \hat{a}_n^\dagger = \int d\mathbf{x}\, \varphi_n(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x})$$

Let us see how these operators act

When acting on the empty state we have

$$a_n^\dagger|0\rangle = \int d\mathbf{x}\,\varphi_n(\mathbf{x})\underbrace{\hat{\psi}^\dagger(\mathbf{x})|0\rangle}_{|\mathbf{x}\rangle} = \int d\mathbf{x}|\mathbf{x}\rangle\langle\mathbf{x}|n\rangle = |n\rangle$$

and similarly we can check that $\hat{a}_m|n\rangle = \delta_{mn}|0\rangle$

Furthermore from the commutation relation of the field operators it follows immediately that

$$[\hat{a}_n, \hat{a}_m^\dagger]_+ = \delta_{nm} \qquad [\hat{a}_n, \hat{a}_m]_+ = [\hat{a}_n^\dagger, \hat{a}_m^\dagger]_+ = 0$$

In general we can generate N-particle states

$$|n_1 \dots n_N\rangle = \hat{a}_{n_N}^\dagger \dots \hat{a}_{n_1}^\dagger|0\rangle$$

which describes a state in which we have N-particles with in one-particle states $(n_1, \dots, n_N)$

We can relate them to position basis states as follows

$$|n_1 \dots n_N\rangle = \int d\mathbf{x}_1 \dots d\mathbf{x}_N \, \varphi_{n_1}(\mathbf{x}_1) \dots \varphi_{n_N}(\mathbf{x}_N) \, \hat{\psi}^\dagger(\mathbf{x}_N) \dots \hat{\psi}^\dagger(\mathbf{x}_1)|0\rangle$$

$$= \int d\mathbf{x}_1 \dots d\mathbf{x}_N \, \varphi_{n_1}(\mathbf{x}_1) \dots \varphi_{n_N}(\mathbf{x}_N)|\mathbf{x}_1 \dots \mathbf{x}_N\rangle$$

and find that their overlaps are given by Slater determinants

$$\langle \mathbf{x}_1 \dots \mathbf{x}_N|n_1 \dots n_N\rangle = \int d\mathbf{y}_1 \dots d\mathbf{y}_N \, \varphi_{n_1}(\mathbf{y}_1) \dots \varphi_{n_N}(\mathbf{y}_N)\langle \mathbf{x}_1 \dots \mathbf{x}_N|\mathbf{y}_1 \dots \mathbf{y}_N\rangle =$$

$$= \int d\mathbf{y}_1 \dots d\mathbf{y}_N \, \varphi_{n_1}(\mathbf{y}_1) \dots \varphi_{n_N}(\mathbf{y}_N) \begin{vmatrix} \delta(\mathbf{x}_1 - \mathbf{y}_1) & \dots & \delta(\mathbf{x}_1 - \mathbf{y}_N) \\ \vdots & & \vdots \\ \delta(\mathbf{x}_N - \mathbf{y}_1) & \dots & \delta(\mathbf{x}_N - \mathbf{y}_N) \end{vmatrix}$$

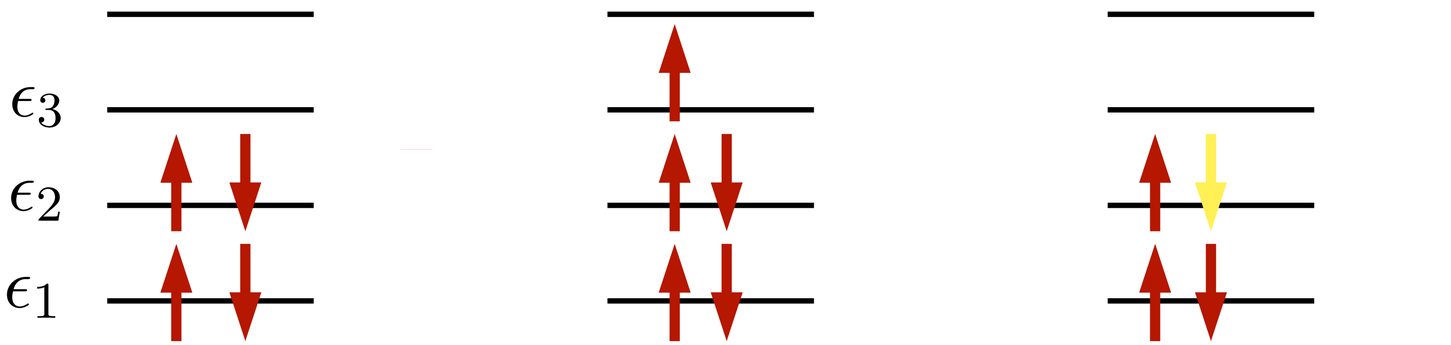
$$= \begin{vmatrix} \varphi_{n_1}(\mathbf{x}_1) & \dots & \varphi_{n_N}(\mathbf{x}_1) \\ \vdots & & \vdots \\ \varphi_{n_1}(\mathbf{x}_N) & \dots & \varphi_{n_N}(\mathbf{x}_N) \end{vmatrix}$$

The creation and annihilation operators therefore add and remove orbitals (columns) from Slater determinants

Example

addition

removal



$|1234\rangle$ $\quad$ $|12345\rangle = \hat{a}_5^\dagger |1234\rangle$ $\quad$ $|123\rangle = \hat{a}_4 |1234\rangle$

We can take the one-particle states to be eigenstates of a one-body Hamiltonian such as the Hartree-Fock or Kohn-Sham system. Then if, for example, we label

$$(1,2,3,4,5,6) = (\epsilon_1\uparrow, \epsilon_1\downarrow, \epsilon_2\uparrow, \epsilon_2\downarrow, \epsilon_3\uparrow, \epsilon_3\downarrow)$$

then

$$|12345\rangle = \hat{a}_5^\dagger |1234\rangle \qquad |123\rangle = \hat{a}_4 |1234\rangle$$

How does the Hamiltonian look like for the new operators?

$$\hat{a}_n = \int d\mathbf{x}\, \varphi_n^*(\mathbf{x})\hat{\psi}(\mathbf{x}) \quad \rightarrow \quad \hat{\psi}(\mathbf{x}) = \sum_n \varphi_n(\mathbf{x})\hat{a}_n$$

$$\hat{a}_n^\dagger = \int d\mathbf{x}\, \varphi_n(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}) \quad \rightarrow \quad \hat{\psi}^\dagger(\mathbf{x}) = \sum_n \varphi_n^*(\mathbf{x})\hat{a}_n^\dagger$$

It follows then that

$$\hat{H}_0 = \int d\mathbf{x}\, \hat{\psi}^\dagger(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 + v(\mathbf{x},t) \right) \hat{\psi}(\mathbf{x}) = \sum_{ij} h_{ij}(t)\hat{a}_i^\dagger \hat{a}_j$$

$$\hat{W} = \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\, \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x}) = \frac{1}{2}\sum_{ijkl} w_{ijkl}\, \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l$$

where

$$h_{ij}(t) = \int d\mathbf{x}\, \varphi_i^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 + v(\mathbf{x},t) \right) \varphi_j(\mathbf{x})$$

one-electron integrals

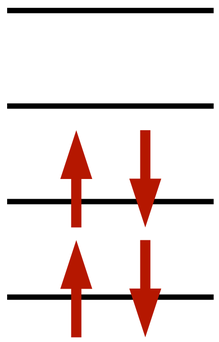
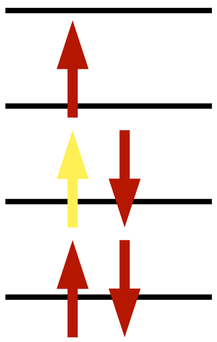
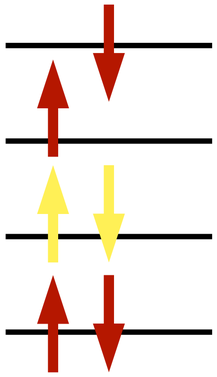
$$w_{ijkl} = \int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\, \varphi_i^*(\mathbf{x})\varphi_j^*(\mathbf{y})\varphi_k(\mathbf{y})\varphi_l(\mathbf{x})$$

two-electron integrals

The Hamiltonian in a general one-particle basis then attains the form

$$\hat{H}(t) = \sum_{ij} h_{ij}(t)\, \hat{a}_i^\dagger\, \hat{a}_j + \frac{1}{2} \sum_{ijkl} v_{ijkl}\, \hat{a}_i^\dagger\, \hat{a}_j^\dagger\, \hat{a}_k\, \hat{a}_l$$

The action of the Hamiltonian on a single Slater determinant generates an infinite number of particle-hole excitations

$\hat{H}(t)$  $= c_1(t)$  $+ c_2(t)$  $+ \ldots$

The time-evolved state is therefore, in general, a infinite expansion in Slater determinant states

Second quantization: Take home message

- Second quantisation is nothing but a convenient way to generate a many-particle basis that automatically has the correct (anti)symmetry.

  Basis states are created by (anti)-commuting operators with simple (anti)-commutation relations

- As we will see, second quantisation is very convenient in many-body theory as it allows for simple manipulation of perturbative terms without the need to deal with (anti)-symmetrised orbital products

- The derivation of the Hamiltonian in second quantisation is easy in position basis as the Hamiltonian is almost diagonal in this basis.

- In general one-particle basis the Hamiltonian has an intuitive interpretation as generating particle-hole excitations

Expectation values

A general expectation value is of the form

initial state

$$\langle \hat{O}(t) \rangle = \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle = \langle \Psi_0 | \hat{U}(t_0, t)\, \hat{O}(t)\, \hat{U}(t, t_0) | \Psi_0 \rangle = \langle \Psi_0 | \hat{O}_H(t) | \Psi_0 \rangle$$

where we defined the evolution operator and the operator Ô(t) in the Heisenberg picture as

$$|\Psi(t)\rangle = \hat{U}(t, t_0) |\Psi(t_0)\rangle \qquad\qquad \hat{O}_H(t) = \hat{U}(t_0, t)\, \hat{O}(t)\, \hat{U}(t, t_0)$$

It follows from the Schrödinger equation that

$$i\partial_t \hat{U}(t, t_0) = \hat{H}(t) \hat{U}(t, t_0) \qquad\qquad \hat{U}(t_0, t_0) = 1$$

In the particular case that the Hamiltonian is time-independent we have that

$$\hat{H}(t) = \hat{H} \quad \Rightarrow \quad \hat{U}(t, t_0) = e^{-i\hat{H}(t - t_0)}$$

Let us divide [t_0 ,T] into small intervals Δ then

$$\hat{U}(T,t_0) = \hat{U}(t_{n+1},t_n)\ldots\hat{U}(t_2,t_1)\hat{U}(t_1,t_0)$$

$$\hat{U}(t_{k+1},t_k) \approx e^{-i\hat{H}(t_k)\Delta}$$

$$t_{k+1} - t_k = \Delta$$

$$t_{n+1} = T$$

such that

$$|\Psi(T)\rangle \approx e^{-i\hat{H}(t_n)\Delta}\ldots e^{-i\hat{H}(t_0)\Delta}|\Psi(t_0)\rangle = \mathcal{T}\left\{e^{-i\hat{H}(t_n)\Delta}\ldots e^{-i\hat{H}(t_0)\Delta}\right\}|\Psi(t_0)\rangle$$

$$= \mathcal{T}\left\{e^{-i\sum_j^n \hat{H}(t_j)\Delta}\right\}|\Psi(t_0)\rangle$$

where $\mathcal{T}$ denotes time-ordering that orders the latest operator most left, where we used that operators commute under time-ordering

$$\mathcal{T}\left\{\hat{A}(t_1)\hat{B}(t_2)\right\} = \mathcal{T}\left\{\hat{B}(t_2)\hat{A}(t_1)\right\}$$

and hence, in particular

$$\mathcal{T}\left\{e^{\hat{A}(t_1)}e^{\hat{B}(t_2)}\right\} = \mathcal{T}\left\{e^{\hat{A}(t_1)+\hat{B}(t_2)}\right\}$$

In the limit Δ => 0 then

$$|\Psi(T)\rangle = \mathcal{T}\left\{e^{-i\int_{t_0}^{T} dt\, \hat{H}(t)}\right\}|\Psi(t_0)\rangle = \hat{U}(T,t_0)|\Psi(t_0)\rangle$$

Time-evolution operator

By a similar procedure we have

$$U(t_0,T) = e^{i\hat{H}(t_1)\Delta}e^{i\hat{H}(t_2)\Delta}\ldots e^{i\hat{H}(t_n)\Delta} = \bar{\mathcal{T}}\left\{e^{i\sum_j^n \hat{H}(t_j)\Delta}\right\}$$

$$U(t_0,T) = \bar{\mathcal{T}}\left\{e^{i\int_{t_0}^{T}\hat{H}(t)dt}\right\}$$

where $\bar{\mathcal{T}}$ denotes anti-time-ordering that orders the latest operator most right

We find therefore that the evolution operator can then be written as

$$\hat{U}(t_1,t_2) = \begin{cases} \mathcal{T} e^{-i\int_{t_1}^{t_2} dt\, \hat{H}(t)dt} & t_1 < t_2 \\ \bar{\mathcal{T}} e^{+i\int_{t_2}^{t_1} dt\, \hat{H}(t)dt} & t_2 < t_1 \end{cases}$$

and the expectation value

$$\langle \hat{O}(t) \rangle = \langle \Psi_0 | \hat{U}(t_0,t) \hat{O}(t) \hat{U}(t,t_0) | \Psi_0 \rangle$$

can therefore be written as

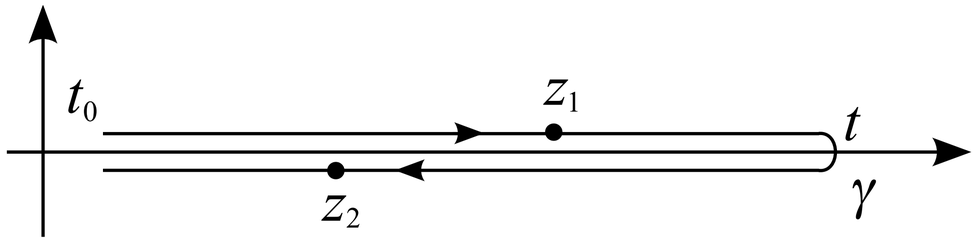
$$\langle \hat{O}(t) \rangle = \langle \Psi_0 | \, \bar{\mathcal{T}} e^{i\int_{t_0}^{t} dt\, \hat{H}(t)dt} \, \hat{O}(t) \, \mathcal{T} e^{-i\int_{t_0}^{t} dt\, \hat{H}(t)dt} \, | \Psi_0 \rangle$$

If we expand in powers of the Hamiltonian then a typical term is

$$\bar{\mathcal{T}} \left\{ \hat{H}(t_1) \ldots \hat{H}(t_n) \right\} \hat{O}(t) \, \mathcal{T} \left\{ \hat{H}(t'_1) \ldots \hat{H}(t'_n) \right\}$$

early ⟵ late late ⟵ early

A useful idea: contour ordering



$$\gamma \equiv \underbrace{(t_0, t)}_{\gamma_-} \oplus \underbrace{(t, t_0)}_{\gamma_+}$$

We define a contour γ consisting of two copies of the interval [t_0 , t]. A generic element z of γ can lie on the forward branch γ_- or the backward branch γ_+

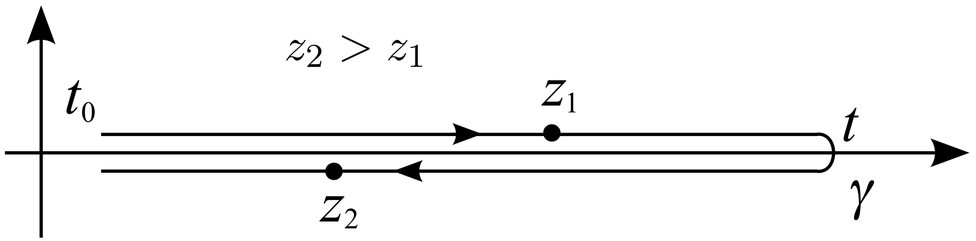
Notation

$$z = t'_- \quad \text{when} \quad z \in \gamma_- \quad \text{and its real value is} \quad t'$$

$$z = t'_+ \quad \text{when} \quad z \in \gamma_+ \quad \text{and its real value is} \quad t'$$

We can define operators on the contour

$$\hat{O}(z') = \begin{cases} \hat{O}_-(t') & z' = t'_- \\ \hat{O}_+(t') & z' = t'_+ \end{cases}$$



$$\mathcal{T}_\gamma \left\{ \hat{A}_{P(1)}(z_{P(1)}) \dots \hat{A}_{P(1)}(z_{P(1)}) \right\} = \hat{A}_1(z_1) \dots \hat{A}_n(z_n) \quad z_1 > \dots > z_n$$

With this definition we can write

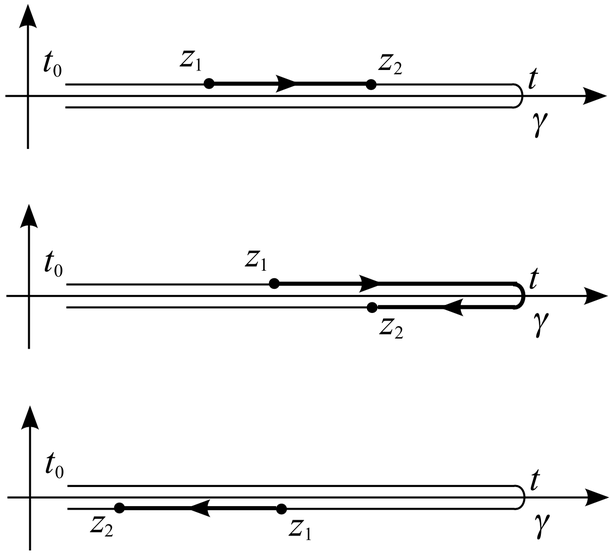
$$\bar{\mathcal{T}} \left\{ \hat{H}(t_1) \dots \hat{H}(t_n) \right\} \hat{O}(t) \mathcal{T} \left\{ \hat{H}(t'_1) \dots \hat{H}(t'_n) \right\}$$

$$= \mathcal{T}_\gamma \left\{ \hat{H}(t_{1+}) \dots \hat{H}(t_{n+}) \hat{O}(t) \hat{H}(t'_{1-}) \dots \hat{H}(t'_{n-}) \right\}$$

where

$$\hat{H}(z = t'_\pm) = \hat{H}(t')$$

With this trick we can write the expectation value in a compact way



$$\int_{z_1}^{z_2} d\bar{z}\, \hat{A}(\bar{z}) = \begin{cases} \int_{t_1}^{t_2} d\bar{t}\, \hat{A}_-(\bar{t}) & \text{if } z_1 = t_{1-} \text{ and } z_2 = t_{2-} \\ \int_{t_1}^{t} d\bar{t}\, \hat{A}_-(\bar{t}) + \int_{t}^{t_2} d\bar{t}\, \hat{A}_+(\bar{t}) & \text{if } z_1 = t_{1-} \text{ and } z_2 = t_{2+} \\ \int_{t_1}^{t_2} d\bar{t}\, \hat{A}_+(\bar{t}) & \text{if } z_1 = t_{1+} \text{ and } z_2 = t_{2+} \end{cases}$$

The expectation value can then be written as

$$\langle \hat{O}(t) \rangle = \langle \Psi_0 | \mathcal{T}_\gamma \left\{ e^{-i \int_{\gamma_+} \hat{H}(\bar{z}) d\bar{z}}\, \hat{O}(t_\pm)\, e^{-i \int_{\gamma_-} \hat{H}(\bar{z}) d\bar{z}} \right\} | \Psi_0 \rangle$$

and since the operators commute under the time-ordering we obtain the elegant expression

$$\langle \hat{O}(t) \rangle = \langle \Psi_0 | \mathcal{T}_\gamma \left\{ e^{-i \int_{\gamma} \hat{H}(\bar{z}) d\bar{z}}\, \hat{O}(t_\pm) \right\} | \Psi_0 \rangle$$

It will be useful to extend the concept of expectation value to ensembles

$$\langle \hat{O}_H(t) \rangle = \sum_n w_n \langle \Psi_n | \hat{O}_H(t) | \Psi_n \rangle = \mathrm{Tr} \left\{ \hat{\rho}\, \hat{O}_H(t) \right\}$$

$$\hat{\rho} = \sum_n w_n |\Psi_n\rangle\langle\Psi_n| \qquad \sum_n w_n = 1 \qquad w_m \geq 0$$

probability distribution of initial states

A very common relevant case is that of the grand canonical ensemble, which describes a system at initial equilibrium at a given temperature and chemical potential

$$w_n = \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} \qquad \hat{H}^M |\Psi_n\rangle = E_n |\Psi_n\rangle \qquad \hat{H}^M = \hat{H}(t_0) - \mu \hat{N}$$

$$\beta = \frac{1}{k_B T}$$

$$\hat{\rho} = \sum_n w_n |\Psi_n\rangle\langle\Psi_n| = \frac{e^{-\beta \hat{H}^M}}{\mathrm{Tr} \left\{ e^{-\beta \hat{H}^M} \right\}}$$

initial Hamiltonian

The density operator can be viewed as a time-propagation in imaginary time

$$e^{-\beta \hat{H}^M} = e^{-i[(t_0 - i\beta) - t_0]\hat{H}^M} = \hat{U}(t_0 - i\beta, t_0)$$

If we therefore define

$$\hat{H}(z) = \begin{cases} \hat{H}(t) & z \in [t_0, \infty[\\ \hat{H}^M & z \in [t_0, t_0 - i\beta] \end{cases}$$

then we can write

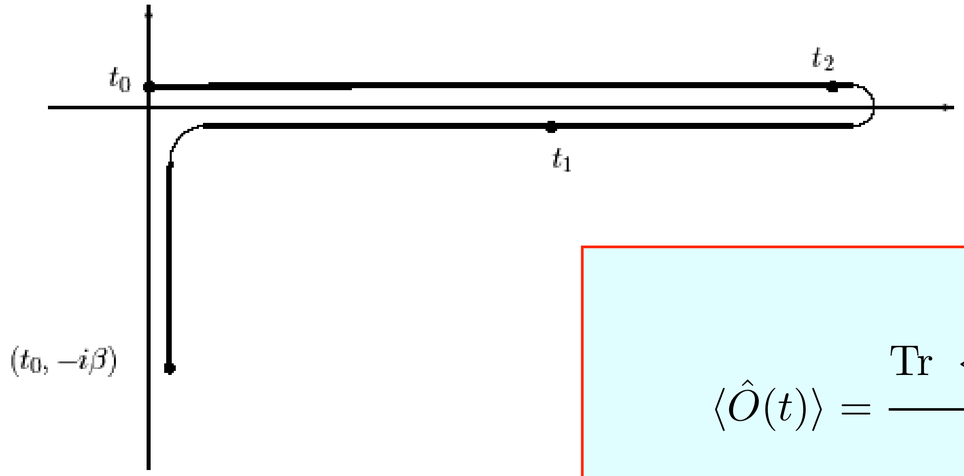
$$\langle \hat{O}(t) \rangle = \frac{\mathrm{Tr}\ \left\{ \hat{U}(t_0 - i\beta, t_0) \hat{U}(t_0, t) \hat{O}(t) \hat{U}(t, t_0) \right\}}{\mathrm{Tr}\ \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}}$$

Now we can gain apply our contour trick, in which we add a vertical track to our contour that describes the initial ensemble

Expectation values as contour orderings

(L.V.Keldysh, Sov.Phys.JETP20, 1018 (1965),
Konstantinov, Perel', JETP12,142 (1961))

The final result is now that we can regard expectation values as contour orderings. This considerably simplifies the subsequent formalism which will be valid for general time-dependent systems



$$\langle \hat{O}(t) \rangle = \frac{\mathrm{Tr}\ \left\{ \hat{U}(t_0 - i\beta, t_0) \hat{U}(t_0, t) \hat{O}(t) \hat{U}(t, t_0) \right\}}{\mathrm{Tr}\ \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}}$$

$$\langle \hat{O}(t) \rangle = \frac{\mathrm{Tr}\ \mathcal{T} \left\{ e^{-i \int_\gamma dz\, \hat{H}(z)} \hat{O}(t) \right\}}{\mathrm{Tr}\ \mathcal{T} \left\{ e^{-i \int_\gamma dz\, \hat{H}(z)} \right\}}$$

Time ordering is now defined along the extended contour

Time-ordering: Take home message

- Time-ordering is a direct consequence of the structure of time-dependent Schrödinger equation.

- Expectation values consist of a time-ordered evolution operator for the ket state and an anti-time-ordering for the bra state

- The expectation of any operator value can be rewritten in terms of a single time-ordered exponential by introducing contour ordering

- In case of systems prepared in an initial ensemble the expectation value can be rewritten as a time-ordering on a contour with an additional vertical track