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[disclaimer]

Problem Set 12

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Group 2 – Dilege Gülmez

problem number	achieved points	possible points
1	7	7
2	7	14
total		21

1 Two-particle operators in second quantization

1.1

Let \mathbb{P} be the set of all particles such that $\alpha, \beta \in \mathbb{P}$. The sum

$$\sum_{\alpha \neq \beta}$$

means that it is to be summed over all α and β but not those where they are equal. We write this more formally as

$$F = \frac{1}{2} \sum_{\alpha \in \mathbb{P}} \sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} f(\mathbf{x}_\alpha, \mathbf{x}_\beta).$$

Now we insert sets of ones.

$$= \frac{1}{2} \sum_{\alpha \in \mathbb{P}} \sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} \sum_{i,j,k,l} |i\rangle_\alpha \langle i|_\alpha |j\rangle_\beta \langle j|_\beta f(\mathbf{x}_\alpha, \mathbf{x}_\beta) |k\rangle_\alpha \langle k|_\alpha |l\rangle_\beta \langle l|_\beta \checkmark$$

We commute the bra and ket vectors of different particles which we can do since we consider the product Hilbert space of two different particles.

$$= \frac{1}{2} \sum_{\alpha \in \mathbb{P}} \sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} \sum_{i,j,k,l} |i\rangle_{\alpha} |j\rangle_{\beta} \langle i|_{\alpha} \langle j|_{\beta} f(\mathbf{x}_{\alpha}, \mathbf{x}_{\beta}) |k\rangle_{\alpha} |l\rangle_{\beta} \langle k|_{\alpha} \langle l|_{\beta}$$

We can then use the notation which corresponds to the tensor product Hilbert space of two particles.

$$= \frac{1}{2} \sum_{\alpha \in \mathbb{P}} \sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} \sum_{i,j,k,l} |i\rangle_{\alpha} |j\rangle_{\beta} \langle i, j | f(\mathbf{x}_{\alpha}, \mathbf{x}_{\beta}) |k, l\rangle \langle k|_{\alpha} \langle l|_{\beta}$$

The term in the middle is a scalar and can be moved anywhere in the product.

$$\checkmark = \frac{1}{2} \sum_{\alpha \in \mathbb{P}} \sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_{\alpha}, \mathbf{x}_{\beta}) |k, l\rangle |i\rangle_{\alpha} |j\rangle_{\beta} \langle k|_{\alpha} \langle l|_{\beta}$$

This is the desired result in equation (2) of the problem set.

1.2

We start with equation (2) from the problem set.

$$F = \frac{1}{2} \sum_{\alpha \in \mathbb{P}} \sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_{\alpha}, \mathbf{x}_{\beta}) |k, l\rangle |i\rangle_{\alpha} |j\rangle_{\beta} \langle k|_{\alpha} \langle l|_{\beta}$$

Then we change the order of the bra and ket vectors at the right side of the equation.

$$= \frac{1}{2} \sum_{\alpha \in \mathbb{P}} \sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_{\alpha}, \mathbf{x}_{\beta}) |k, l\rangle |i\rangle_{\alpha} \langle k|_{\alpha} |j\rangle_{\beta} \langle l|_{\beta}$$

We change the order of the summations such that we can plug in equation (5) from the problem set later on. The underbraces denote the outcome suggestively, we still have to work on that, though.

$$= \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_{\alpha}, \mathbf{x}_{\beta}) |k, l\rangle \underbrace{\sum_{\alpha \in \mathbb{P}} |i\rangle_{\alpha} \langle k|_{\alpha}}_{\rightsquigarrow b_k^{\dagger} b_k} \underbrace{\sum_{\beta \in \mathbb{P} \setminus \{\alpha\}} |j\rangle_{\beta} \langle l|_{\beta}}_{\rightsquigarrow b_l^{\dagger} b_l}$$

The problem is that the sum over β excludes α . Therefore, the sums are not independent and we cannot apply equation (5) yet. So we just sum over all $\beta \in \mathbb{P}$ in the sum and subtract that particular value again.

$$\checkmark = \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \sum_{\alpha \in \mathbb{P}} |i\rangle_\alpha \langle k|_\alpha \left[\sum_{\beta \in \mathbb{P}} |j\rangle_\beta \langle l|_\beta - |j\rangle_\alpha \langle l|_\alpha \right]$$

The one summation over β is now independent of α and we can use equation (5).

$$= \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \sum_{\alpha \in \mathbb{P}} |i\rangle_\alpha \langle k|_\alpha \left[b_j^\dagger b_l - |j\rangle_\alpha \langle l|_\alpha \right]$$

Now we expand the parentheses.

$$= \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_j^\dagger b_l \sum_{\alpha \in \mathbb{P}} |i\rangle_\alpha \langle k|_\alpha - \sum_{\alpha \in \mathbb{P}} |i\rangle_\alpha \langle k|_\alpha |j\rangle_\alpha \langle l|_\alpha \right]$$

We apply equation (5) once again.

$$\checkmark = \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_i^\dagger b_k b_j^\dagger b_l - \sum_{\alpha \in \mathbb{P}} |i\rangle_\alpha \langle k|_\alpha |j\rangle_\alpha \langle l|_\alpha \right]$$

This looks somewhat like equation (4) from the problem set which we should arrive at. The terms are not in the correct order yet, though. The bra-ket in the middle is just a Kronecker δ .

$$= \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_i^\dagger b_k b_j^\dagger b_l - \sum_{\alpha \in \mathbb{P}} |i\rangle_\alpha \delta_{kj} \langle l|_\alpha \right]$$

However, the Kronecker δ is also contained in the commutator of the creation and annihilation operators: $\delta_{kj} = [b_k, b_j^\dagger]_{\mp}$ (Schwabl 2005, p. 16). Since it is a plain number, we pull it out front for a step.

$$\checkmark = \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_i^\dagger b_k b_j^\dagger b_l - \delta_{kj} \sum_{\alpha \in \mathbb{P}} |i\rangle_\alpha \langle l|_\alpha \right]$$

Now we apply equation (5) from the problem set again.

$$= \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_i^\dagger b_k b_j^\dagger b_l - \delta_{kj} b_i^\dagger b_l \right]$$

Now we move the Kronecker δ in between those terms.

$$= \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_i^\dagger b_k b_j^\dagger b_l - b_i^\dagger \delta_{kj} b_l \right]$$

We expand the (anti-)commutator there.

$$= \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_i^\dagger b_k b_j^\dagger b_l - b_i^\dagger \left[b_k b_j^\dagger \mp b_k^\dagger b_j \right] b_l \right]$$

Then we expand the inner square bracket.

$$\checkmark = \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle \left[b_i^\dagger b_k b_j^\dagger b_l - b_i^\dagger b_k b_j^\dagger b_l \pm b_i^\dagger b_j^\dagger b_k b_l \right]$$

The first two terms cancel each other, so we are left with

$$\checkmark = \pm \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle b_i^\dagger b_j^\dagger b_k b_l.$$

The annihilation operators for bosons commute, the ones for fermions anticommute. So we can get rid of the \pm sign by switching the last terms.

$$\checkmark = \frac{1}{2} \sum_{i,j,k,l} \langle i, j | f(\mathbf{x}_\alpha, \mathbf{x}_\beta) | k, l \rangle b_i^\dagger b_j^\dagger b_l b_k$$

Now we still have to derive the equation (5) that we have used up to here. Say we have a state which is given in occupation number presentation,

$$|n_1, \dots\rangle.$$

Now we apply the operator $b_i^\dagger b_j$ onto that. We will get the following, assuming that the state $|j\rangle$ was occupied at least once:

$$b_i^\dagger b_j |n_1, \dots\rangle = \begin{cases} n_i |n_1, \dots\rangle & i = j \\ \sqrt{[n_i + 1]n_j} |n_1, \dots, n_i + 1, \dots, n_j - 1, \dots\rangle & \text{else} \end{cases}$$

Let us show that the same thing happens when we act with

$$\sum_\alpha |i\rangle_\alpha \langle j|_\alpha$$

on the same state. To do this, we have to decompose the occupation number representation into a product state.

$$|n_1, \dots\rangle = \prod_{k=0}^{\infty} |k\rangle^{n_k}$$

All those different $|k\rangle$ are for different particles α . In the above product, the order of the states in the product is by the value of the state, not in the order of the particle. When we order by particle, we get something like this:

$$|k_1, k_2, \dots, k_N\rangle$$

Here the i_α are allowed to appear multiple times at arbitrary positions for bosons. When we now throw that operator onto that state, like

$$\checkmark \sum_{\alpha} |k\rangle_{\alpha} \langle j|_{\alpha} |k_1, k_2, \dots, k_N\rangle,$$

it will go the particle with number α and project that part onto the state $|j\rangle$ and replace it with the state $|i\rangle$. This changed the normalization of the state.

$$\sum_{\alpha} |i\rangle_{\alpha} \langle j|_{\alpha} |k_1, k_2, \dots, k_N\rangle = \sqrt{\frac{n_i + 1}{n_j}} \sum_{\alpha} \delta_{j_{\alpha} k_{\alpha}} |k_1, k_2, \dots, i_{\alpha}, \dots, k_N\rangle \begin{cases} 1 & i = j \\ \sqrt{\frac{n_i + 1}{n_j}} & \text{else} \end{cases}$$

So this has replaced the state that the particle α was in ($|k\rangle_{\alpha}$) with the new state ($|i\rangle_{\alpha}$) in case any of the states $k_{\alpha} = j_{\alpha}$. Otherwise, it is zero. In the case $i = j$, the state itself does not change, just like with the creation and annihilation operators above. We already assumed that the state $|j\rangle$ was in the mix at least once, so we can just take that granted. Therefore, the sum will just give us a summand for each time the state $|j\rangle$ is occupied. Combining this, we get a factor n_j from the sum.

$$\checkmark = |k_1, k_2, \dots, i_{\alpha}, \dots, k_N\rangle \begin{cases} n_i & i = j \\ n_j \sqrt{\frac{n_i + 1}{n_j}} & \text{else} \end{cases}$$

And this can be simplified to the final result.

$$= |k_1, k_2, \dots, i_{\alpha}, \dots, k_N\rangle \begin{cases} n_i & i = j \\ \sqrt{[n_i + 1]n_j} & \text{else} \end{cases}$$

2 Hartree-Fock approximation for atoms

We understand equation (8) from the problem set that there are N states occupied and those are the states with the lowest numbers from 1 to N .

2.1

Problem statement

Show that

$$\langle \psi | b_i^{\dagger} b_j | \psi \rangle = \delta_{ij}.$$

We have done this in three similar ways. We will start with the third one that we came up with because it is really succinct.

2.1.1 Third way

b_j will destroy a particle in state $|j\rangle$. b_i^\dagger will create one in the state $|i\rangle$. Since those are fermions, i has to be either the same as j or $i > N$ because there are no other free spots. If $i > N$, then this altered $|\psi\rangle$ will be orthogonal to $\langle\psi|$. If $i = j$, then the two operators are just the occupation number operator n_j . Its eigenvalue here is 1 since $j \leq N$ and fermions was assumed. $|\psi\rangle$ is left unchanged. Therefore it is δ_{ij} .

2.1.2 First way

Now we will use the Ansatz directly.

$$\langle\psi|b_i^\dagger b_j|\psi\rangle = \left[\prod_{k=1}^N b_k^\dagger |0\rangle \right]^\dagger b_i^\dagger b_j \left[\prod_{k=1}^N b_k^\dagger |0\rangle \right]$$

Now we incorporate the two stray operators into the brackets.

$$= \left[b_i \prod_{k=1}^N b_k^\dagger |0\rangle \right]^\dagger \left[b_j \prod_{k=1}^N b_k^\dagger |0\rangle \right]$$

The b anticommute with the b^\dagger like so:

$$[b_i, b_j^\dagger]_+ = \delta_{ij}$$

That means that we can move the b_j into the spot in the product over k such that we have the b_j in front of the b_j^\dagger . We will need $i - 1$ anticommutations for that. The same applies in the second bracket. We do not really like the notation with omissions, but this actually seems easier here.

$$= [-1]^{i+j-2} [b_1^\dagger b_2^\dagger \dots b_{i-1}^\dagger b_{i+1}^\dagger \dots b_N^\dagger |0\rangle]^\dagger [b_1^\dagger b_2^\dagger \dots b_{j-1}^\dagger b_{j+1}^\dagger \dots b_N^\dagger |0\rangle]$$

You can see that almost all creation operators are present, except for the ones with i and j , respectively. The states that we will get from the vacuum are then the following:

$$= [-1]^{i+j} \langle 1, 1, \dots, 1, 0, 1, \dots, 1, 0, \dots | 1, 1, \dots, 1, 0, 1, \dots, 1, 0, \dots \rangle$$

We have marked the index of the unoccupied states. This scalar product is only nonzero when $i = j$ are given. So we can write this as

$$= [-1]^{i+j} \delta_{ij}$$

And then we just have

$$= \delta_{ij}$$

because in the case of $i = j$, we have an even power of the -1 , such that does not contribute at all.

2.1.3 Second way

This way uses the hint on the problem set. Basically, in the first way we have derived this hint for the special case that all the lower states are occupied. So let us use that hint in the way given on the problem set. We let b_i^\dagger act to the left, b_j to the right.

$$\langle \psi | b_i^\dagger b_j | \psi \rangle = n_i n_j [-1]^{\sum_{k < i} n_k + \sum_{k < j} n_k} \langle 1, 1, \dots, 1, 0, 1, \dots, 1, 0, \dots | 1, 1, \dots, 1, 0, 1, \dots, 1, 0, \dots \rangle$$

The sums are actually pretty straightforward, they are $i - 1$ and $j - 1$, just like above. So this comes to the desired result as well.

2.2

We just insert the result from the previous problem. The trick here is that i and j must be smaller than N as well, because only states up to N are occupied in the state $|\psi\rangle$. So we get

$$\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \langle i | O | j \rangle \langle \psi | b_i^\dagger b_j | \psi \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \langle i | O | j \rangle \delta_{ij} \theta(i - N) \theta(j - N).$$

Then this is rather straightforward. But we will include the steps in between because this problem is worth two points.

$$= \sum_{i=1}^{\infty} \langle i | O | i \rangle \theta(i - N) \theta(i - N)$$

The Heaviside step function squared it just the function itself.

$$\checkmark = \sum_{i=1}^{\infty} \langle i | O | i \rangle \theta(i - N)$$

Now we restrict the summation according to the Heaviside step function.

$$\checkmark = \sum_{i=1}^N \langle i | O | i \rangle$$

2.3

Given our in-depth coverage of the second part of this problem, we will do this one really short. Look at

$$\langle \psi | b_i^\dagger b_j^\dagger b_l b_k | \psi \rangle.$$

If we assume $j = l$ and then $i = k$, this scalar product will give us 1 because the operators will become occupation number operators which are eigenoperators of state $|\psi\rangle$. So this is the $\delta_{ik}\delta_{jl}$ term. However, we can do one anticommutation as well. We anticommute the two creation operators and get an additional minus sign: ✓

$$= -\langle \psi | b_j^\dagger b_i^\dagger b_l b_k | \psi \rangle \checkmark$$

With the same argumentation as above, we get a $-\delta_{il}\delta_{jk}$. Together we have

$$\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$$

which is the desired result. ✓

2.4

The equations are rather long here, even the result is on two lines already! We could just go landscape and plow through it like fearless theoreticians or take the more practical route and look at each summand in the Hamiltonian separately. Since we are at 8 pages already, we choose the latter way.

First we will look at the kinetic energy term. We write the matrix elements of the kinetic operator as such to avoid nesting brackets.

$$\left\langle \psi \left| \sum_{i,j} b_i^\dagger b_j T_{ij} \right| \psi \right\rangle = \sum_{i,j} \langle \psi | b_i^\dagger b_j T_{ij} | \psi \rangle$$

Because of the creation and annihilation operators, we need $i = j$ because of the reasoning we had in the previous few problems. This restricts the sum.

$$= \sum_{i=1}^N \langle \psi | b_i^\dagger b_i T_{ii} | \psi \rangle$$

Now we insert two complete sets of eigenstates, one for each particle/state.

$$= \sum_{i=1}^N \int d^3x_i d^3y_i \langle \psi | x_i \rangle \langle x_i | T_{ii} | y_i \rangle \langle y_i | \psi \rangle$$

Those scalar products are the field operators (Schwabl 2005, (1.5.3)).

$$= \sum_{i=1}^N \int d^3x_i d^3y_i \phi_i^*(x_i) \langle x_i | T_{ii} | y_i \rangle \phi_i(y_i)$$

*position eigenstates
wave functions in
position states.*

We write out the matrix element.

$$= \sum_{i=1}^N \int d^3x_i d^3y_i d^3z \phi_i^*(x_i) \delta^{(3)}(z - x_i) T_{ii}(z) \delta^{(3)}(z - y_i) \phi_i(y_i)$$

The z integration will remove one δ distribution, the y integral the other one such that the only variable left is x .

$$= \sum_{i=1}^N \int d^3x_i \phi_i^*(\mathbf{x}_i) T_{ii}(\mathbf{x}_i) \phi_i(\mathbf{x}_i)$$

As a last step we insert the kinetic energy operator.

$$= -\frac{\hbar^2}{2m} \sum_{i=1}^N \int d^3x_i \phi_i^*(\mathbf{x}_i) \Delta \phi_i(\mathbf{x}_i) \quad \checkmark$$

That was fun, let us do it again. The exact same steps can be done for the scalar potential U . So we will have this:

$$\left\langle \psi \left| \sum_{i,j} b_i^\dagger b_j U_{ij} \right| \psi \right\rangle = \sum_{i,j} \int d^3x \phi_i^*(\mathbf{x}) U(\mathbf{x}) \phi_j(\mathbf{x}) \quad \checkmark$$

The new thing here is that U is just a regular function, not an operator. Therefore it commutes with the field operators and we get a modulus squared.

$$= \sum_{i,j} \int d^3x U(\mathbf{x}) |\phi_i(\mathbf{x})|^2$$

For the last part, the equations got so long that we had to use landscape paper for that either way. So see you after the page break. 😊

Now the stage is set for the last part, the interaction between different electrons. H_{IV} is supposed to be a shorthand for the summand of the Hamiltonian which contains V . It is merely introduced for alignment purposes. This time we did not avoid the nested bracket.

$$\langle \psi | H_{IV} | \psi \rangle = \langle \psi | \frac{1}{2} \sum_{i,j,k,l} \langle i, j | V | k, l \rangle b_i^\dagger b_j^\dagger b_l b_k | \psi \rangle$$

We pull out the sum.

$$= \frac{1}{2} \sum_{i,j,k,l} \langle \psi | \langle i, j | V | k, l \rangle b_i^\dagger b_j^\dagger b_l b_k | \psi \rangle$$

We can already replace the creation and annihilation operators with Kronecker δ s again.

$$= \frac{1}{2} \sum_{i,j,k,l} [\delta_{ji} \delta_{ik} - \delta_{il} \delta_{jk}] \langle \psi | \langle i, j | V | k, l \rangle | \psi \rangle$$

We again insert a bunch of space eigenstates to get more integration variables and field operators. Each is associated with a particular state.

$$= \frac{1}{2} \sum_{i,j,k,l} [\delta_{ji} \delta_{ik} - \delta_{il} \delta_{jk}] \int d^3x d^3y d^3z d^3w \langle \psi | x, y \rangle \langle y, z | V_{ijkl} | z, w \rangle \langle z, w | \psi \rangle$$

Now we introduce the field operators.

$$= \frac{1}{2} \sum_{i,j,k,l} [\delta_{ji} \delta_{ik} - \delta_{il} \delta_{jk}] \int d^3x d^3y d^3z d^3w \phi_i^*(x) \phi_j^*(y) \langle x, y | V_{ijkl} | z, w \rangle \phi_k(z) \phi_l(w)$$

Like before, the δ distributions in the matrix element around the interaction term V will identify \mathbf{x} and \mathbf{y} with \mathbf{z} and \mathbf{w} . Then the interaction term can be written in position space simply. We still have to integrate that factor $\delta_{s_i, s_k} \delta_{s_j, s_l}$ from the matrix element of V into this.

$$\checkmark = \frac{1}{2} \sum_{i,j,k,l=1}^N [\delta_{jl} \delta_{ik} - \delta_{il} \delta_{jk}] \int d^3x d^3y V(\mathbf{x} - \mathbf{y}) \delta_{s_i, s_k} \delta_{s_j, s_l} \phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{x}) \phi_k(\mathbf{y}) \phi_l(\mathbf{y})$$

Now we execute the Kronecker δ s that have been waiting for their turn.

$$= \frac{1}{2} \sum_{i,j=1}^N \int d^3x d^3y V(\mathbf{x} - \mathbf{y}) [\delta_{s_i, s_i} \delta_{s_j, s_j} \phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{y}) \phi_i(\mathbf{x}) \phi_j(\mathbf{y}) - \delta_{s_i, s_j} \delta_{s_i, s_j} \phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{y}) \phi_j(\mathbf{x}) \phi_i(\mathbf{y})]$$

The spins in the same state are equal, so we can just drop this. The second summand has the δ twice, so we just remove one of them.

$$\checkmark = \frac{1}{2} \sum_{i,j=1}^N \int d^3x d^3y V(\mathbf{x} - \mathbf{y}) [\phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{y}) \phi_i(\mathbf{x}) \phi_j(\mathbf{y}) - \delta_{s_i, s_j} \phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{y}) \phi_j(\mathbf{x}) \phi_i(\mathbf{y})]$$

When all three terms are added up, it is the desired equation from the problem set.

References

Schwabl, Franz (2005). *Quantenmechanik für Fortgeschrittene*. 4. Berlin: Springer. ISBN: 978-3-540-25904-6.