Problem 7: Single-particle-like operators in second quantization (2 points)

Consider free electrons in a box of volume V with periodic boundary conditions. Determine the momentum operator, the particle-density operator ($\delta(\vec{r} - \vec{r}_i)$ for a single particle) and the current density operator ($\frac{1}{2m} [\vec{p}_i \, \delta(\vec{r} - \vec{r}_i) + \delta(\vec{r} - \vec{r}_i) \, \vec{p}_i]$ for a single particle) in second quantization, using the single-particle energy eigenstates as single-particle basis.

Problem 8: Excited states (4 points)

In the lecture we discussed Koopmans' theorem for adding a particle to the single-Slater-determinant ground state of a N-particle system. We had assumed that the ground state $|N;\, 111\ldots100\ldots\rangle$ had been optimized within the Hartree-Fock method.

a) Prove Koopmans' theorem for particle *removal*, i. e. considering states

$$|N-1;\, m\rangle \;=\; |N-1;\, 11\ldots101\ldots1100\ldots\rangle$$

in which orbital m ($\leq N$) ist empty: show that

$$\text{(i)} \qquad \langle N-1; m|\hat{H}|N-1;\, m\rangle \;=\; E^{(\mathrm{HF})}_{N,0} \;-\; \epsilon^{(\mathrm{HF})}_{m}$$

and

$$\text{(ii)} \qquad \langle N-1;\, m|\hat{H}|N-1;\, m'\rangle \;=\; 0 \quad \text{for} \quad m \neq m' \,.$$

b) Consider particle-hole excitations

$$|N;\, m\, n\rangle \;=\; |N;\, 11\ldots101\ldots1100\ldots010\rangle$$

in which orbital $m\,(\leq N)$ is empty and orbital $n\,(> N)$ is occupied.

Show that

$$\langle N;\, m\, n|\hat{H}|N;\, m'\, n'\rangle \;=\; \left(E^{(\mathrm{HF})}_{N,0} \;+\; \epsilon_n \;-\; \epsilon_m\right) \delta_{m\, m'}\, \delta_{n\, n'} \;-\; V_{m'\, n,\, m\, n'} \;+\; V_{m'\, n,\, n'\, m} \,.$$

Problem 9: Hubbard model (4 points)

a) In the case of a single atom or ion, the most prominent physics of the electrons is often given by a (partially filled) localized orbital. This situation can often be approximated by a simplified Hubbard model of the form

$$H = \sum_{\sigma} \epsilon_0 \, \hat{c}^{\dagger}_{\sigma} \, \hat{c}_{\sigma} \;+\; U \, \hat{n}_{\uparrow} \, \hat{n}_{\downarrow} \,.$$

In here, ϵ_0 denotes the energy level of the orbital in a single-particle picture, while U indicates the extra energy which has to be invested to bring the second electron into the orbital while a first electron (repelling the second one) already occupies the orbital.

Show that the states $|N = 0\rangle$, $|N = 1;\, 10\rangle$, $|N = 1;\, 01\rangle$, and $|N = 2;\, 11\rangle$ are eigenstates of $\hat{H}$, and calculate their energies. Here, the occupation numbers $n_{\uparrow}$ and $n_{\downarrow}$ in $|N;\, n_{\uparrow}\, n_{\downarrow}\rangle$ indicate the occupation of the spin-up and spin-down state of the orbital.

b) Now consider the case of *two* such orbitals in close vicinity, i. e., on neighbouring atoms/ions. In addition to the single-site Hamiltonian, hopping is possible between the sites, yielding a Hamiltonian

$$\begin{aligned} H &= \epsilon_0 \left(\hat{c}^\dagger_{1\uparrow}\,\hat{c}_{1\uparrow} + \hat{c}^\dagger_{1\downarrow}\,\hat{c}_{1\downarrow} + \hat{c}^\dagger_{2\uparrow}\,\hat{c}_{2\uparrow} + \hat{c}^\dagger_{2\downarrow}\,\hat{c}_{2\downarrow} \right) \\ &+ t \left(\hat{c}^\dagger_{1\uparrow}\,\hat{c}_{2\uparrow} + \hat{c}^\dagger_{1\downarrow}\,\hat{c}_{2\downarrow} + \hat{c}^\dagger_{2\uparrow}\,\hat{c}_{1\uparrow} + \hat{c}^\dagger_{2\downarrow}\,\hat{c}_{1\downarrow} \right) \\ &+ U \left(\hat{n}_{1\uparrow}\,\hat{n}_{1\downarrow} + \hat{n}_{2\uparrow}\,\hat{n}_{2\downarrow} \right) \end{aligned}$$

based on the two orbitals (1) and (2) which occur as spin-up and spin-down, i. e. four single-particle states in total. Apparently, the configurations $|N;\, n_{1\uparrow}\, n_{1\downarrow}\, n_{2\uparrow}\, n_{2\downarrow}\rangle$ constitute a useful many-body basis.

i) Consider the situation of having $N = 1$ electrons in the system. Show that there are four corresponding eigenstates of H. Which is their energy?

ii) Consider the situation of having $N = 3$ electrons in the system. Show that there are four corresponding eigenstates of H. Which is their energy?

iii) Consider the situation of having $N = 2$ electrons in the system. Show that there are six corresponding eigenstates of H. Which are their energies? The lowest-energy state then constitutes the ground state for N=2.

iv) The Hamiltonian may also be treated within a mean-field approximation (often called "Hartree-Fock" approximation). Note that (without proof) this corresponds to replacing

$$\hat{n}_\uparrow\,\hat{n}_\downarrow \qquad \text{by} \qquad \langle \hat{n}_\uparrow \rangle\,\hat{n}_\downarrow + \langle \hat{n}_\downarrow \rangle\,\hat{n}_\uparrow$$

in the Hamiltonian. Note further that in the ground state (for a given N), all $\langle \hat{n}_{i,\sigma} \rangle$ are the same ($= N/4$). Calculate the mean-field ground-state energy for $N = 1$, $N = 2$ and $N = 3$ and compare your results with the exact values given above.