Advanced Quantum Theory (WS 21/22)
Homework no. 11 (December 20, 2021)

Please hand in your solution by Monday, January 10.

1 Two–Particle Operators in Second Quantization

Consider an operator $\hat{F}$ that can be written as a sum of two–particle operators $\hat{f}$:

$$\hat{F} = \frac{1}{2} \sum_{\alpha \neq \beta} \hat{f}(\vec{x}_\alpha, \vec{x}_\beta) \,. \tag{1}$$

Here α, β label identical particles.

1. Show that $\hat{F}$ can be written as

$$\hat{F} = \frac{1}{2} \sum_{\alpha \neq \beta} \sum_{i,j,k,l} \langle i, j | \hat{f} | k, l \rangle \; |i\rangle_\alpha |j\rangle_\beta \langle k|_\alpha \langle l|_\beta \,, \tag{2}$$

   where

$$\langle i, j | \hat{f} | k, l \rangle = \int d^3x \, d^3y \, \psi_i^*(\vec{x}) \psi_j^*(\vec{y}) \hat{f}(\vec{x}, \vec{y}) \psi_k(\vec{x}) \psi_l(\vec{y}) \,. \tag{3}$$

   Here $|i\rangle_\alpha$ means that particle α is in the single–particle state $|i\rangle$, etc. *Hint:* Compute the matrix element of $\hat{F}$ between two–particle states that can be written as products of single–particle states; this is sufficient, since all two–particle states can be written as linear superpositions of such products. **[2P]**

2. Now assume that the particles in question are fermions (the first part of this problem holds equally for bosons and fermions). Show that $\hat{F}$ can be written in terms of fermionic creation and annihilation operators:

$$\hat{F} = \frac{1}{2} \sum_{i,j,k,l} \langle i, j | \hat{f} | k, l \rangle \; \hat{b}_i^\dagger \hat{b}_j^\dagger \hat{b}_l \hat{b}_k \,. \tag{4}$$

   Hint: First, show that

$$\sum_{\mathcal{P}} (-1)^P \hat{\mathcal{P}} |i_1\rangle_1 |i_2\rangle_2 \dots |i_N\rangle_N = (-1)^{\sum_{k<j} n_k} \sum_\alpha (-1)^\alpha |j\rangle_\alpha \sum_{\mathcal{P}} (-1)^P \hat{\mathcal{P}} |i_1\rangle_1 |i_2\rangle_2 \dots |i_{N-1}\rangle_{N-1} \,,$$

   where on the rhs the permutation is only over $N-1$ elements, and it has been assumed that one of the original $|i_\alpha\rangle = |j\rangle$. Following the corresponding derivation for bosonic operators shown in class, use this relation to prove

$$\sum_\alpha |i\rangle_\alpha \langle j|_\alpha = \hat{b}_i^\dagger \hat{b}_j \,, \tag{5}$$

   which in turn can be used to prove eq.(4). **[5P]**

2 Hartree–Fock Approximation for Atoms

The formalism of second quantization can be used to derive the Hartree–Fock treatment of (possibly ionized) atoms with N electrons. The nucleus is assumed to be a fixed source (at the origin) of an external potential

$$U(\vec{x}) = -\frac{Ze^2}{|\vec{x}|} \,. \tag{6}$$

In addition, one treats the Coulomb interaction between the electrons through the two–particle potential

$$V(\vec{x}, \vec{y}) = \frac{e^2}{|\vec{x} - \vec{y}|} \,, \tag{7}$$

which is evidently a function of the difference $\vec{x} - \vec{y}$ only.

The electrons are described by single–particle states

$$|i\rangle = |\phi_i, s_i\rangle \,. \tag{8}$$

Here $\phi_i(\vec{x})$ determines the spatial distribution of the wave function of state $|i\rangle$, and $s_i = \pm\frac{1}{2}$ is the $z-$component of the electron spin. These single–particle states are generated by operators $\hat{b}_i^\dagger$. One makes the following ansatz for the $N-$electron state $|\psi\rangle$:

$$|\psi\rangle = \prod_{i=1}^{N} \hat{b}_i^\dagger |0\rangle \,, \tag{9}$$

where $|0\rangle$ is the vacuum state (without electrons). The Hamiltonian can then be written as

$$\hat{H} = \sum_{i,j} \hat{b}_i^\dagger \hat{b}_j \left(\langle i|\hat{T}|j\rangle + \langle i|U|j\rangle \right) + \frac{1}{2} \sum_{i,j,k,l} \langle i,j|V|k,l\rangle \hat{b}_i^\dagger \hat{b}_j^\dagger \hat{b}_l \hat{b}_k\rangle \,.$$

Here $\hat{T} = -\frac{\hbar^2}{2m_e}\nabla^2$ is the operator for the kinetic energy of a particle.

1. Show that

$$\langle\psi|\hat{b}_i^\dagger \hat{b}_j|\psi\rangle = \delta_{ij} \,, \tag{10}$$

   if $|j\rangle$ is one of the states appearing in the ansatz (9); for all other $\hat{b}_j$ the matrix element in eq.(10) evidently vanishes. *Hint:* You can either use the definition of how $\hat{b}_j$, $\hat{b}_i^\dagger$ act on an $N-$electron state, as given in class; or use $\hat{b}_j|0\rangle = \langle 0|\hat{b}_i^\dagger = 0$ and the anti–commutator of $\hat{b}_j$ and $\hat{b}_k^\dagger$. **[3P]**

2. Using eq.(10), show that

$$\sum_{i,j} \langle i|\hat{O}|j\rangle \langle\psi|\hat{b}_i^\dagger \hat{b}_j|\psi\rangle = \sum_{i=1}^{N} \langle i|\hat{O}|i\rangle \,, \tag{11}$$

   where $\hat{O} \in \hat{T}, U$. Note that the double sum on the left–hand side goes over *all* states, whereas the single sum on the right–hand side only goes over the N states contained in the $N-$particle state defined in eq.(9). **[1P]**

3. Similarly, show that

$$\langle\psi|\hat{b}_i^\dagger \hat{b}_j^\dagger \hat{b}_l \hat{b}_k|\psi\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}\,, \tag{12}$$

if both $|k\rangle$ and $|l\rangle$ are represented in the state $|\psi\rangle$ defined in eq.(9); otherwise the matrix element vanishes again. **[4P]**

4. Putting everything together, show that

$$\begin{aligned}\langle\psi|\hat{H}|\psi\rangle &= \sum_{i=1}^{N}\int d^3x \left(-\frac{\hbar^2}{2m_e}\phi_i^*(\vec{x})\nabla^2\phi_i(\vec{x}) + U(|\vec{x}|)\,|\phi_i(\vec{x})|^2\right) \\ &+ \frac{1}{2}\sum_{i,j=1}^{N}\int d^3x\, d^3y V(\vec{x}-\vec{y})\left[|\phi_i(\vec{x})|^2\,|\phi_j(\vec{y})|^2 - \delta_{s_i,s_j}\phi_i^*(\vec{x})\phi_j^*(\vec{y})\phi_i(\vec{y})\phi_j(\vec{x})\right]\,.\end{aligned} \tag{13}$$

Hint: Note that the matrix element $\langle i,j|V|k,l\rangle$ contains a factor $\delta_{s_i,s_k}\delta_{s_j,s_l}$, since the Coulomb interactions do not affect the spin, which is part of the definition of the single–particle states, see eq.(8). The sums in eq.(13) run over all N electrons. **[5P]**

Note: In the Hartree–Fock treatment one minimizes $\langle\psi|\hat{H}|\psi\rangle$ by appropriate choice of the single–particle wave functions $\phi_i(\vec{x})$ and spins s_i. Also, the ansatz (9) is indeed an approximation, since one writes the total wave function as a product of single–particle wave functions; the most general ansatz would involve a sum over such products with appropriate coefficients (or an integral over continuous coefficients, with a product state in the argument, as in eq.(4) on the previous HW sheet).