Second Quantization I

Fock Space, Creation and Annihilation Operators, Excitation Operators

Michael Papadopuolos

Presentation 3

Jan. 30, 2024

Key Points

- First quantization is "the way we have done things", with Hilbert space $\mathcal{H}$.
- Second quantization is a new way to do things, with Fock space $\mathcal{F}$.
  - Can be thought of as a sum of an arbitrarily large number of Hilbert spaces.
  - Names are historical holdovers.
- Second quantization allows us to represent the probabilities of states with various electron configurations.
  - In all; more degrees of freedom, so can represent more.

Spin Orbitals

- Four quantum numbers completely the state of an electron in an atom.
  - n, l, and m_l, which determine its spatial shell and subshell.
  - $n > 0$, $0 \leq l < n$, $-l \leq m_l \leq l$.
  - m_s, which determines its spin and may either be $\frac{1}{2}$ or $\frac{-1}{2}$.
  - You may take each state of m_s to be "spin-functions" $\alpha, \beta...$ for generality.

- Pauli Exclusion Principle: These four numbers must be unique for each electron in an atom.

Spin Orbitals

- We call these combinations of four numbers spin-orbitals.
  - Designate a spin-orbital by all its information ($\phi_{1p_z\alpha}$) or simply as the Nth spin-orbital (ϕ_0, ϕ_1...)

- If N electrons are in an atom, then N spin-orbitals are occupied, though there may be more unoccupied spin orbitals.
  - Define r_1 to represent the first electron, r_2 to represent the second, and so on.

- Then we can define states by which electrons are in which orbitals.

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

Slater Determinant Formulation

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix}$$

Figure: 2-Electron Slater Determinant

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix}$$

Figure: Generalized Slater Determinant

Fock Space

- We can define each wavefunction / determinant uniquely in Fock space, a linear vector space.

$$\mathcal{F} = \bigoplus_{M=0}^{N_B} \mathcal{H}^{(M)},$$

- The basis vectors of Fock space are occupation-number (ON) vectors. Say our system has M spin orbitals. Then we could define an ON vector as follows:
  - $|\boldsymbol{k}\rangle = |k_1, k_2, k_3, ...k_M\rangle$ where $k_P = 1$ if spin-orbital P is occupied, and 0 if it is not.

- The inner product of two ON vectors is 1 if they are the same and 0 otherwise.

Fock Space

- We can have linear combinations of ON vectors.
  - $|\boldsymbol{c}\rangle = \sum_k c_k \, |\boldsymbol{k}\rangle$
  - $\langle \boldsymbol{d}|\boldsymbol{c}\rangle = \sum_{mk} d_m^* \, \langle \boldsymbol{m}|\boldsymbol{k}\rangle \, c_k$

- Fock space $\mathcal{F}$. can be thought to have subspaces $\mathcal{F}(M)$, which includes only the ON vectors with M spin-orbitals (and therefore 2^M dimensions).
  - Additionally, it has subspaces $\mathcal{F}(M, N)$, which includes ON vectors with M spin-orbitals and N electrons (so the sum of the k_P within each ON vector equals N). These have dimension $\binom{M}{N}$.
  - The one state in $\mathcal{F}(M, 0)$ for each M is the vacuum state, sometimes written $|vac\rangle$.

Matrix Representation

- How can we connect this back to first quantization with states?
  - For each k_P in an ON vector, we can represent it as $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ if it is unoccupied and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ if it is occupied.
  - Then our whole ON vector is the outer product of all its k_P.
  - Fully occupied ON vector with 2 spin-orbitals and 2 electrons:

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

- Useful for "doing the math" of second quantization, gets unwieldy as spin-orbitals increase.

Creation & Annihilation Operators

- A Fock space $\mathcal{F}(M)$ has M creation operators $(a_1^*, a_2^*, ...a_M^*)$ and M annihilation operators $(a_1, a_2, ...a_M)$
  - They are conjugates, choice of which one is the conjugate is by convention.
  - Other terms: "raising" and "lowering" operators, "ladder" operators, etc. due to their effect on eigenfunctions.

Creation Operator

- $a_P^* \left|\boldsymbol{k}\right\rangle = a_P^* \left|k_1, ...k_P, ...k_M\right\rangle = ?$
  - If $k_P = 0$, $a_P^* \left|\boldsymbol{k}\right\rangle = \Gamma_P^{\boldsymbol{k}} \left|k_1, ...1_P, ...k_M\right\rangle$
  - If $k_P = 1$, $a_P^* \left|\boldsymbol{k}\right\rangle = 0$
  - So in all, $a_P^* \left|\boldsymbol{k}\right\rangle = \delta_{k_P,0} \Gamma_P^{\boldsymbol{k}} \left|k_1, ...1_P, ...k_M\right\rangle$
  - $(a_P^*)^2 = 0$

- $\Gamma_P^{\boldsymbol{k}} = (-1)^{\sum_{i=1}^{P-1} k_i}$. It is a phase factor necessary for representation.

- We can also see how all ON vectors may be represented as a string of creation operators acting on $\left|vac\right\rangle$.

Creation Operator Anticommutation

- We are working with fermions, so we care about anticommutation. (One could also define bosonic Fock space, but we work with fermionic.)

- $[a_P^*, a_Q^*]_+ = 0$ when $P \neq Q$, in part due to Γ.
  - $[A, B]_+ = AB + BA$

Annihilation Operator

- a_P is simple from here! Properties are exactly what you expect from being the conjugate of the creation operator.
  - $a_P \left|\boldsymbol{k}\right\rangle = \delta_{k_P,1}\Gamma_P^{\boldsymbol{k}} \left|k_1, ...0_P, ...k_M\right\rangle$
  - $[a_P, a_Q]_+ = 0$
  - $[a_P^*, a_Q]_+ = [a_P, a_Q^*]_+ = 0$ for $P \neq Q$.

- $[a_P^*, a_P] = \mathbf{1}$. Consider $\left(a_P a_P^* + a_P^* a_P\right)\left|\boldsymbol{k}\right\rangle$.

Creation & Annihilation Matrix Notation

- $a = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$.
- $a_P = \sigma_{z_1} \otimes \sigma_{z_2} \otimes ... \otimes \sigma_{z_{P-1}} \otimes a \otimes I_{P+1} \otimes ... \otimes I_M$
- $a_P^* = \sigma_{z_1} \otimes \sigma_{z_2} \otimes ... \otimes \sigma_{z_{P-1}} \otimes a^* \otimes I_{P+1} \otimes ... \otimes I_M$
- This matrix representation can be used for clearly manipulating small ON vectors, or proving the anticommutation relations.

More Operators: ON Operator

- Creation and annihilation operators change $\mathcal{F}(M, N)$. Let's look at operators that preserve this subspace.
- $N_P = a_P^* a_P$. So clearly, $N_P \left|\boldsymbol{k}\right\rangle = k_P \left|\boldsymbol{k}\right\rangle$.
- ON Operator is Hermitian, idempotent, commutes with other ON Operators and all operators X_Q where $P \neq Q$.
  - $[N_P, a_P] = -a_P$, $[N_P, a_P^*] = a_P^*$, etc.

More Operators: ON Operator

- ON vectors are the simultaneous eigenvectors of the set of Hermitian operators N_P.
- ON vectors are completely characterized by which ON operators they are eigenvectors of.
  - This is a one-to-one mapping.

More Operators: Number Operator

- $N|\boldsymbol{k}\rangle = n|\boldsymbol{k}\rangle$, where $n = \sum_{i=1}^{M} k_i$
- Counts the number of electrons in the state.
- Commutes with "number-conserving" operators.
  - a_P^* is not number-conserving.
  - $a_Q a_P^*$ is number-conserving.
  - Needs to maintain $\mathcal{F}(M, N)$.

More Operators: Excitation Operator

- $X = a_P^* a_Q$, where $P \neq Q$
- "Excites" an electron from one spin-orbital to another.
  - Some formulations only allow you to go up which is why this is "excitation".
  - In this formulation, going in either direction is OK.
- Note that this maintains $\mathcal{F}(M, N)$.

Why Second Quantization?

- Consider resolving $\langle ij|kl\rangle$. (Probability of finding a 2-electron state in a 2-electron state).
- First quantization: Requires numerous matrix multiplications that bring it to $\mathcal{O}(n^3)$.
- Second quantization: Inherent information of our new representation allows for methods (covered next time) that bring it to $\mathcal{O}(1)$.