Second Quantization

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The long awaited sequel

First Quantization vs. Second Quantization

- Change in notation
- Wavefunction focus vs. Operator focus
- Trajectories vs. Fields

For our purposes, its just a name to separate 2 formalisms with equivalent meaning

Occupation Number (ON) Formalism

Representation of Slater Determinant using molecular orbitals

$$\Psi = \phi_1 \phi_2 \ldots \phi_n$$

Representation of Slater Determinant using occupation of spin orbitals

$$|\boldsymbol{n}\rangle = |n_1 n_2 \ldots\rangle$$

$$|\phi_1 \phi_2 \phi_4 \phi_7\rangle = |11010010 \ldots\rangle$$

$$\langle \boldsymbol{n} | \boldsymbol{m} \rangle = \delta_{\boldsymbol{nm}} = \prod_i \delta_{n_i m_i}$$

Relevant Operators for ON

Annihilation Operators

$$\hat{a}_p|\dots n_p \dots\rangle = \begin{cases} (-1)^m|\dots 0 \dots\rangle & n_p = 1 \\ 0 & n_p = 0 \end{cases}$$

Creation Operators

$$\hat{a}^\dagger{}_p|\dots n_p \dots\rangle = \begin{cases} 0 & n_p = 1 \\ (-1)^m|\dots 1 \dots\rangle & n_p = 0 \end{cases}$$

m is the number of occupations preceding p: $m = \sum_{k=1}^{p-1} n_k$

Relevant Operators for ON

Creation/Annihilation operators work like this due to Fermion properties

$$\hat{a}_2|\phi_1\phi_2\phi_3\rangle = -\hat{a}_2|\phi_2\phi_1\phi_3\rangle = -|\phi_1\phi_3\rangle$$

$$\hat{a}_1^\dagger\hat{a}_2^\dagger|0\rangle = \hat{a}_1^\dagger|\phi_2\rangle = |\phi_1\phi_2\rangle$$

$$\hat{a}_2^\dagger\hat{a}_1^\dagger|0\rangle = \hat{a}_2^\dagger|\phi_1\rangle = |\phi_2\phi_1\rangle = -|\phi_1\phi_2\rangle$$

$$\hat{a}|0\rangle = \hat{a}_p^\dagger|\phi_p\rangle = 0$$

Relevant Operators for ON

Some relations

$$(\hat{a})^\dagger = \hat{a}^\dagger$$

$$\left(\hat{a}_p \middle| \ldots n_p \ldots \right\rangle\Big)^\dagger = \langle \ldots n_p \ldots | \hat{a}^\dagger$$

$$N_p = \hat{a}_p^\dagger \hat{a}_p$$

$$\left(\hat{a}_p\right)^2 = \left(\hat{a}_p^\dagger\right)^2 = 0$$

Relevant Operators for ON

Anticommutation relations: $\{a, b\} = ab + ba$

$$\hat{a}_i \hat{a}_j = -\hat{a}_j \hat{a}_i \qquad \{\hat{a}_i, \hat{a}_j\} = 0$$

$$\hat{a}_i^\dagger \hat{a}_j^\dagger = -\hat{a}_j^\dagger \hat{a}_i^\dagger \qquad \left\{\hat{a}_i^\dagger, \hat{a}_j^\dagger\right\} = 0$$

$$\hat{a}_i \hat{a}_j^\dagger = \begin{cases} -\hat{a}_j^\dagger \hat{a}_i & i \neq j \\ 1 - \hat{a}_i^\dagger \hat{a}_i & i = j \end{cases} \qquad \left\{\hat{a}_i, \hat{a}_j^\dagger\right\} = \delta_{i,j}$$

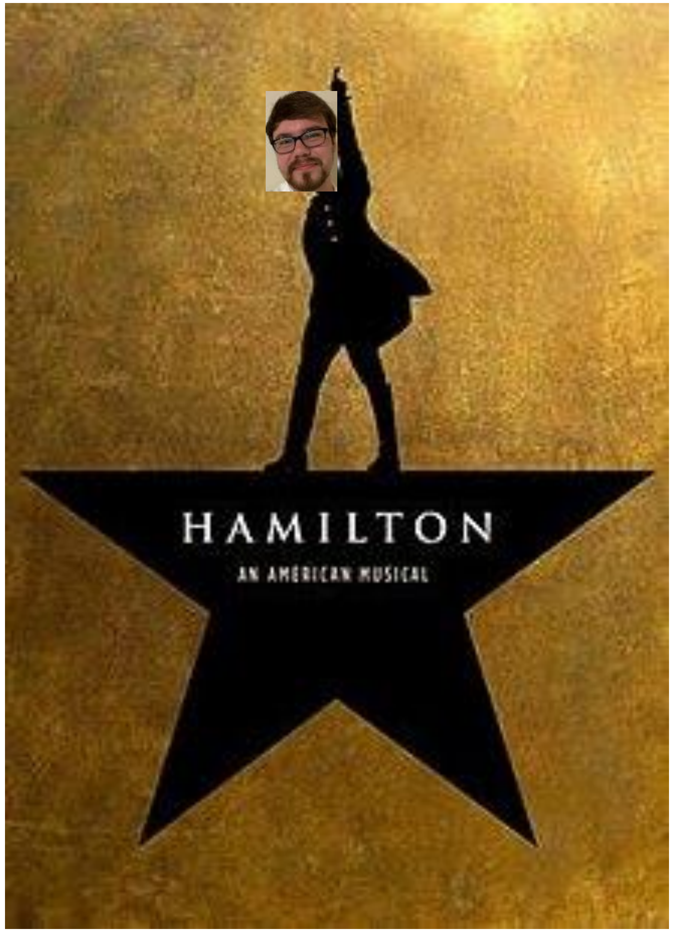
All together now

All determinants can be expressed as creation operators acting on the *true vacuum* state

$$|0\rangle = |000\ldots\rangle$$

$$|00\ldots1\ldots1\ldots00\rangle = \hat{a}^{\dagger}{}_{p}\hat{a}^{\dagger}{}_{q}|0\rangle$$

$$\Psi = \prod \hat{a}^{\dagger}\,|0\rangle$$



Second quantized Hamiltonian

$$\hat{H} = \sum_{pq} \langle p|\hat{h}|q\rangle\, \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2}\sum_{pqrs} \langle pq|\hat{g}|rs\rangle\, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

$$\hat{H} = \sum_{pq} \langle p|\hat{h}|q\rangle\, \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle\, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

… and more

Particle-Hole formalism / Fermi Vacuum

$$|111000\rangle \rightarrow |000000\rangle$$

Normal Ordering

$$n\left[\hat{a}_p a_q^\dagger\right] = a_q^\dagger \hat{a}_p$$

Wick's Theorem

$$x_1 \ldots x_m = n[x_1 \ldots x_m] + \sum\nolimits_{a.c} n\overline{[x_1 \ldots x_m]}$$

Kutzelnigg*-Mukherjee Notation

$$a_p^\dagger \rightarrow \; a^p \qquad\qquad a^{p_1 \ldots p_m} a_{q_1 \ldots q_m} \; = a^{p_1 \ldots p_m}_{q_1 \ldots . q_m}$$

$\tilde{a}^p_q$ (Normal Ordered)

$$\langle p|\hat{h}|q\rangle = h_p^q \qquad \langle p|\hat{h}|q\rangle + \sum_i \langle pi||qi\rangle = f_p^q$$

$$\langle pq|rs\rangle = g_{pq}^{rs} \qquad \langle pq||rs\rangle = \bar{g}_{pq}^{rs}$$

*Jonathon’s nemesis