Second quantization

The wavefunction is fully represented by a linear combination of Slater determinants

$$|\Psi\rangle = \sum_{p_1 < \cdots < p_N} c_p \, |\Phi_{p_1 \cdots p_N}\rangle$$

$$E = \langle \Phi | \sum_i \hat{h}(i) + \sum_{i<j} \hat{g}(i,j) | \Phi \rangle$$

- System dependent representation
- Have to keep track of anti-symmetry properties

What do we need to know to uniquely define a determinant?

$$\Phi_{p_1 \cdots p_N}$$

- We need to know which spin-orbitals are occupied in our basis (indices $p_1 \ldots p_N$)
- Assign an occupation number (ON) to each spin orbital: 1 for occupied, 0 for unoccupied

$$|\mathbf{n}\rangle = |n_1 \, n_2 \, \cdots \, n_p \, \cdots n_M\rangle$$

- ON vector follows vector algebra

Operators in the ON formalism

$$m = \sum_{k=1}^{p-1} n_k$$

- Annihilation operator

$$a_p \left|\cdots n_p \cdots\right\rangle = (-1)^m n_p \left|\cdots (1-n_p) \cdots\right\rangle$$

  - Annihilation operator acting on a single particle state gives the true vacuum

- Creation operator

$$a_p^\dagger \left|\cdots n_p \cdots\right\rangle = (-1)^m (1-n_p) \left|\cdots (1-n_p) \cdots\right\rangle$$

Relating the determinant and ON formalism

- For ordered indices:

$$|\Phi_{p_1 \cdots p_N}\rangle = |\mathbf{n}_{p_1 \cdots p_N}\rangle = |\cdots\ n_p\ \cdots\rangle$$

$$n_p = 0 \text{ if } p \notin \{p_1 \cdots p_N\}$$

$$n_p = 1 \text{ if } p \in \{p_1 \cdots p_N\}$$

- For arbitrary indices:

$$|\Phi_{p_1 \cdots p_N}\rangle = (-1)^R\, |\mathbf{n}_{p_1 \cdots p_N}\rangle$$

Anticommutation relations

$$\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$$

$$\{a_p, a_q\} = 0$$

$$\{a_p^\dagger, a_q^\dagger\} = 0$$

$$\boxed{\{a_p^\dagger, a_q\} = \delta_{pq}}$$

Operators acting on the determinant

$$a_p \Phi_{(p_1 \cdots p_N)} = (-)^{k-1} \Phi_{(p_1 \cdots \cancel{p_k} \cdots p_N)} \text{ if } p = p_k \in (p_1 \cdots p_N)$$

$$a_p \Phi_{(p_1 \cdots p_N)} = 0 \text{ if } p \notin (p_1 \cdots p_N)$$

$$a_p^\dagger \Phi_{(p_1 \cdots p_N)} = (-)^{k-1} \Phi_{(p_1 \cdots p_{k-1} p p_k \cdots p_N)} \text{ if } p \notin (p_1 \cdots p_N)$$

$$a_p^\dagger \Phi_{(p_1 \cdots p_N)} = 0 \text{ if } p \in (p_1 \cdots p_N)$$

The determinant can be represented by a string of creation operators

- For arbitrary indices:

$$|\Phi_{p_1 \cdots p_N}\rangle = a^\dagger_{p_1} \cdots a^\dagger_{p_N} |0\rangle$$

- Anti-symmetry is built into anticommutation relations
- “Second quantization”

Operators acting on the determinant

$$a_p\Phi_{(p_1\cdots p_N)} = (-)^{k-1}\Phi_{(p_1\cdots \cancel{p_k}\cdots p_N)} \text{ if } p = p_k \in (p_1 \cdots p_N)$$

$$a_p\Phi_{(p_1\cdots p_N)} = 0 \text{ if } p \notin (p_1 \cdots p_N)$$

$$a_q \prod a^\dagger \left|0\right\rangle = \sum_i^N (-1)^{i-1}\delta_{qp_i} \prod{}^{p_i} a^\dagger \left|0\right\rangle$$

All quantum mechanical operators can be constructed from a_p and $a_p^\dagger$

- We have a way to write determinants in terms of creation and annihilation operators
- Now, we need to find a way to write the Hamiltonian in terms of creation and annihilation operators

$$\hat{H} = \hat{O}_1 + \hat{O}_2$$

$$\hat{H} = \sum_i \hat{h}(i) + \frac{1}{2}\sum_{ij} \hat{g}(i,j)$$

Deriving the 1-electron operator

$$\hat{O}_1 \prod a^\dagger |0\rangle = \hat{O}_1 \Phi_{p_1 \cdots p_N} = \hat{O}_1 \sqrt{N!}\hat{A}(\psi_{p_1} \cdots \psi_{p_N})$$

$$= \boxed{\sqrt{N!}\hat{A}\hat{O}_1}(\psi_1 \cdots \psi_N)$$

$$= \sqrt{N!}\hat{A}\sum_i^N \hat{h}(\mathbf{r}_i)(\psi_1 \cdots \psi_N)$$

$$= \sqrt{N!}\hat{A}\sum_i^N \hat{h}(\mathbf{r}_i)\psi_{p_i}(\mathbf{r}_i)(\psi_{p_1} \cdots \cancel{\psi_{p_i}} \cdots \psi_{p_N})$$

Resolution of the identity!

$$= \sqrt{N!}\hat{A}\sum_i^N \sum_p \langle p|\hat{h}|p_i\rangle \, \psi_p(\psi_{p_1} \cdots \cancel{\psi_{p_i}} \cdots \psi_{p_N})$$

$$= \sqrt{N!}\hat{A}\sum_{i}^{N}\sum_{p}\langle p|\hat{h}|p_i\rangle\,\psi_p(\psi_{p_1}\cdots\cancel{\psi_{p_i}}\cdots\psi_{p_N})$$

$$= \sqrt{N!}\hat{A}\sum_{i}^{N}\sum_{p}\langle p|\hat{h}|p_i\rangle\,(\psi_{p_1}\cdots\psi_{p_{i-1}}\boxed{\psi_p}\psi_{p_{i+1}}\cdots\psi_{p_N})$$

$$= \sum_{i}^{N}\sum_{p}\langle p|\hat{h}|p_i\rangle\,\sqrt{N!}\hat{A}(\psi_{p_1}\cdots\psi_{p_{i-1}}\psi_p\psi_{p_{i+1}}\cdots\psi_{p_N})$$

$$= \sum_{i}^{N}\sum_{p}\langle p|\hat{h}|p_i\rangle\,\Phi_{p_1\cdots p_{i-1}pp_{i+1}\cdots p_N}$$

$$= \sum_{i}^{N}\sum_{p}\langle p|\hat{h}|p_i\rangle\,a^\dagger_{p_1}\cdots a^\dagger_{p_{i-1}}a^\dagger_p a^\dagger_{p_{i+1}}\cdots a^\dagger_{p_N}\,|0\rangle$$

$$= \sum_{i}^{N}\sum_{p}\langle p|\hat{h}|p_i\rangle\,a^\dagger_p(-1)^{i-1}a^\dagger_{p_1}\cdots a^\dagger_{p_{i-1}}a^\dagger_{p_{i+1}}\cdots a^\dagger_{p_N}\,|0\rangle$$

$$= \sum_{i}^{N} \sum_{p} \langle p|\hat{h}|p_i\rangle \, a_p^\dagger (-1)^{i-1} a_{p_1}^\dagger \cdots a_{p_{i-1}}^\dagger a_{p_{i+1}}^\dagger \cdots a_{p_N}^\dagger \, |0\rangle$$

$$= \sum_{i}^{N} \sum_{pq} \langle p| \, \hat{h}|q\rangle \, \langle q|p_i\rangle a_p^\dagger (-1)^{i-1} a_{p_1}^\dagger \cdots a_{p_{i-1}}^\dagger a_{p_{i+1}}^\dagger \cdots a_{p_N}^\dagger \, |0\rangle$$

$$= \sum_{i}^{N} \sum_{pq} \langle p|\hat{h}|q\rangle \, \delta_{qp_i} a_p^\dagger (-1)^{i-1} a_{p_1}^\dagger \cdots a_{p_{i-1}}^\dagger a_{p_{i+1}}^\dagger \cdots a_{p_N}^\dagger \, |0\rangle$$

$$= \sum_{pq} \langle p|\hat{h}|q\rangle \, a_p^\dagger \sum_{i}^{N} \delta_{qp_i} (-1)^{i-1} a_{p_1}^\dagger \cdots a_{p_{i-1}}^\dagger a_{p_{i+1}}^\dagger \cdots a_{p_N}^\dagger \, |0\rangle$$

$$\boxed{a_q \prod a^\dagger \left|0\right\rangle = \sum_i^N (-1)^{i-1} \delta_{qp_i} \prod{}^{p_i} a^\dagger \left|0\right\rangle}$$

$$= \sum_{pq} \langle p|\hat{h}|q\rangle \, a_p^\dagger \sum_i^N \delta_{qp_i} (-1)^{i-1} a_{p_1}^\dagger \cdots a_{p_{i-1}}^\dagger a_{p_{i+1}}^\dagger \cdots a_{p_N}^\dagger \left|0\right\rangle$$

$$= \sum_{pq} \langle p|\hat{h}|q\rangle \, a_p^\dagger a_q \prod a^\dagger \left|0\right\rangle$$

$$\hat{O}_1 \prod a^\dagger \left|0\right\rangle = \sum_{pq} \langle p|\hat{h}|q\rangle \, a_p^\dagger a_q \prod a^\dagger \left|0\right\rangle$$

$$\hat{O}_1 = \sum_{pq} \langle p|\hat{h}|q\rangle \, a_p^\dagger a_q$$

Two-electron operator

$$\hat{O}_2 = \frac{1}{2}\sum_{pqrs} \langle pq|\hat{g}|rs\rangle \, a_p^\dagger a_q^\dagger a_s a_r$$

Note order of indices!!

Final Hamiltonian

$$\hat{H} = \sum_{pq} \langle p|\hat{h}|q\rangle \, a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} \langle pq|\hat{g}|rs\rangle \, a_p^\dagger a_q^\dagger a_s a_r$$

- Independent of system size!
- What is the effect of the Hamiltonian on the determinant?

General N-body operator

$$\hat{O}_k = \frac{1}{k!} \sum_{\substack{p_1 \cdots p_k \\ q_1 \cdots q_k}} \langle p_1 \cdots p_k | \hat{o}_k | q_1 \cdots q_k \rangle \, a^\dagger_{p_1} \cdots \; a^\dagger_{p_k} a_{q_k} \cdots a_{q_1}$$

Matrix elements are non-symmetric!

- Anti-symmetrized form:

$$\hat{O}_k = \left(\frac{1}{k!}\right)^2 \sum_{\substack{p_1 \cdots p_k \\ q_1 \cdots q_k}} \langle p_1 \cdots p_k | \hat{o}_k | q_1 \cdots q_k \rangle_{\mathscr{A}} \, a^\dagger_{p_1} \cdots \; a^\dagger_{p_k} a_{q_k} \cdots a_{q_1}$$

$$\hat{O}_2 = \left(\frac{1}{2!}\right)^2 \sum_{pqrs} \langle pq | \hat{g} | rs \rangle_{\mathscr{A}} \, a^\dagger_p a^\dagger_q a_s a_r = \frac{1}{4} \sum_{pqrs} (\langle pq | \hat{g} | rs \rangle - \langle pq | \hat{g} | sr \rangle) a^\dagger_p a^\dagger_q a_s a_r$$

Some notation

$$\hat{H} = \sum_{pq} \underbrace{\langle p|\hat{h}|q\rangle}_{h_{pq}} a_p^\dagger a_q + \frac{1}{2}\sum_{pqrs} \underbrace{\langle pq|\hat{g}|rs\rangle}_{\langle pq|rs\rangle} a_p^\dagger a_q^\dagger a_s a_r$$

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle\, a_p^\dagger a_q^\dagger a_s a_r$$

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4}\sum_{pqrs} \underbrace{\langle pq||rs\rangle}_{\langle pq|\hat{g}|rs\rangle - \langle pq|\hat{g}|sr\rangle} a_p^\dagger a_q^\dagger a_s a_r$$

General remarks

- We can now express both the determinant and the Hamiltonian in terms of strings of creation and annihilation operators

$$|\Phi_{p_1 \cdots p_N}\rangle = a^\dagger_{p_1} \cdots a^\dagger_{p_N} |0\rangle$$

$$\hat{H} = \sum_{pq} h_{pq} a^\dagger_p a_q + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle\, a^\dagger_p a^\dagger_q a_s a_r$$

- Major mathematical manipulations boils down to finding the expectation value of creation and annihilation operators in the vacuum

$$E = \sum_{\substack{p_1 < \cdots p_N \\ q_1 < \cdots q_N}} \langle \Phi_{q_1 \cdots q_N} | c^*_q \hat{H} c_p | \Phi_{p_1 \cdots p_N} \rangle = \sum_{\substack{p_1 < \cdots p_N \\ q_1 < \cdots q_N}} c^*_q c_p \langle \Phi_{q_1 \cdots q_N} | \hat{H} | \Phi_{p_1 \cdots p_N} \rangle$$

Example

$$\langle \Phi_t | \hat{O}_1 | \Phi_t \rangle = \langle \Phi_t | \sum_{pq} h_{pq} a_p^\dagger a_q | \Phi_t \rangle$$

$$\langle \Phi_t | \hat{O}_2 | \Phi_t \rangle = \frac{1}{4} \langle \Phi_t | \sum_{pqrs} \langle pq || rs \rangle \, a_p^\dagger a_q^\dagger a_s a_r | \Phi_t \rangle$$

$$\{a_p, a_q\} = 0$$

$$\{a_p^\dagger, a_q^\dagger\} = 0$$

$$\{a_p^\dagger, a_q\} = \delta_{pq}$$

Example

$$\langle \Phi_{rs} | \hat{h} | \Phi_{rs} \rangle = \langle \Phi_{rs} | \sum_{pq} h_{pq} a_p^\dagger a_q | \Phi_{rs} \rangle$$

$$\{a_p, a_q\} = 0$$

$$\{a_p^\dagger, a_q^\dagger\} = 0$$

$$\{a_p^\dagger, a_q\} = \delta_{pq}$$

$$\langle \Phi_{rs} | a_p^\dagger a_q | \Phi_{rs} \rangle$$

$$\langle 0 | a_s a_r a_p^\dagger a_q a_r^\dagger a_s^\dagger | 0 \rangle$$

$$\langle 0 | a_s a_r a_p^\dagger a_q a_r^\dagger a_s^\dagger | 0 \rangle$$

$$\langle 0 | a_s (\delta_{pr} - a_p^\dagger a_r) a_q a_r^\dagger a_s^\dagger | 0 \rangle$$

$$\delta_{pr} \langle 0 | a_s \underline{a_q a_r^\dagger} a_s^\dagger | 0 \rangle - \langle 0 | \underline{a_s a_p^\dagger} a_r a_q a_r^\dagger a_s^\dagger | 0 \rangle$$

$$\delta_{pr} \langle 0 | a_s (\delta_{qr} - a_r^\dagger a_q) a_s^\dagger | 0 \rangle - \langle 0 | (\delta_{sp} - a_p^\dagger a_s) a_r a_q a_r^\dagger a_s^\dagger | 0 \rangle$$

$$\delta_{pr}\delta_{qr} \langle 0 | \underbrace{a_s a_s^\dagger}_{(\delta_{ss} - a_s^\dagger a_s)} | 0 \rangle - \delta_{pr} \langle 0 | \underbrace{a_s a_r^\dagger}_{(\delta_{sr} - a_r^\dagger a_s)} a_q a_s^\dagger | 0 \rangle - \delta_{ps} \langle 0 | a_r \underbrace{a_q a_r^\dagger}_{(\delta_{qr} - a_r^\dagger a_q)} a_s^\dagger | 0 \rangle + \cancelto{0}{\langle 0 | a_p^\dagger a_s a_r a_q a_r^\dagger a_s^\dagger | 0 \rangle}$$

$$\delta_{pr}\delta_{qr}\delta_{ss} - \cancelto{0}{\langle 0 | a_s^\dagger a_s | 0 \rangle} - \delta_{pr}\delta_{sr} \langle 0 | \underbrace{a_q a_s^\dagger}_{(\delta_{qs} - a_s^\dagger a_q)} | 0 \rangle + \delta_{pr} \cancelto{0}{\langle 0 | a_r^\dagger a_s a_q a_s^\dagger | 0 \rangle} - \delta_{ps}\delta_{qr} \langle 0 | \underbrace{a_r a_s^\dagger}_{(\delta_{rs} - a_s^\dagger a_r)} | 0 \rangle + \delta_{ps} \langle 0 | \underbrace{a_r a_r^\dagger}_{(\delta_{rr} - a_r^\dagger a_r)} a_q a_s^\dagger | 0 \rangle$$

$$-\delta_{pr}\delta_{sr}\delta_{qs} + \delta_{pr}\delta_{sr} \cancelto{0}{\langle 0 | a_s^\dagger a_q | 0 \rangle} - \delta_{ps}\delta_{qr}\delta_{rs} + \delta_{ps}\delta_{qr} \cancelto{0}{\langle 0 | a_s^\dagger a_r | 0 \rangle} + \delta_{ps}\delta_{rr} \langle 0 | \underbrace{a_q a_s^\dagger}_{(\delta_{qs} - a_s^\dagger a_q)} | 0 \rangle - \delta_{ps} \cancelto{0}{\langle 0 | a_r^\dagger a_r a_q a_s | 0 \rangle}$$

$$\delta_{ps}\delta_{rr}\delta_{qs} - \delta_{ps}\delta_{rr} \cancelto{0}{\langle 0 | a_s^\dagger a_q | 0 \rangle}$$

$$\sum_{pq} h_{pq} \langle \Phi_{rs} | a_p^\dagger a_q | \Phi_{rs} \rangle = \sum_{pq} h_{pq} \left(\delta_{pr}\delta_{qr}\delta_{ss} - \delta_{pr}\delta_{sr}\delta_{qs} - \delta_{ps}\delta_{qr}\delta_{rs} + \delta_{ps}\delta_{rr}\delta_{qs} \right)$$

$$= h_{rr}\delta_{ss} - \cancelto{0}{h_{rs}\delta_{sr}} - \cancelto{0}{h_{sr}\delta_{sr}} + h_{ss}\delta_{rr}$$

$$= \sum_i h_{ii} \quad \text{where } i \text{ in this case } = r + s$$

- Applying anticommuntation relations to evaluate matrix elements does not seem to simplify the problem
- We need a more efficient way of solving for matrix elements!

Looking ahead

- Wick’s theorem
  - Normal ordering
  - Contractions
  - Normal ordering with contractions