·SECOND·QUANTIZATION·

1-particle Hilbert space:

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$\mathcal{H}$

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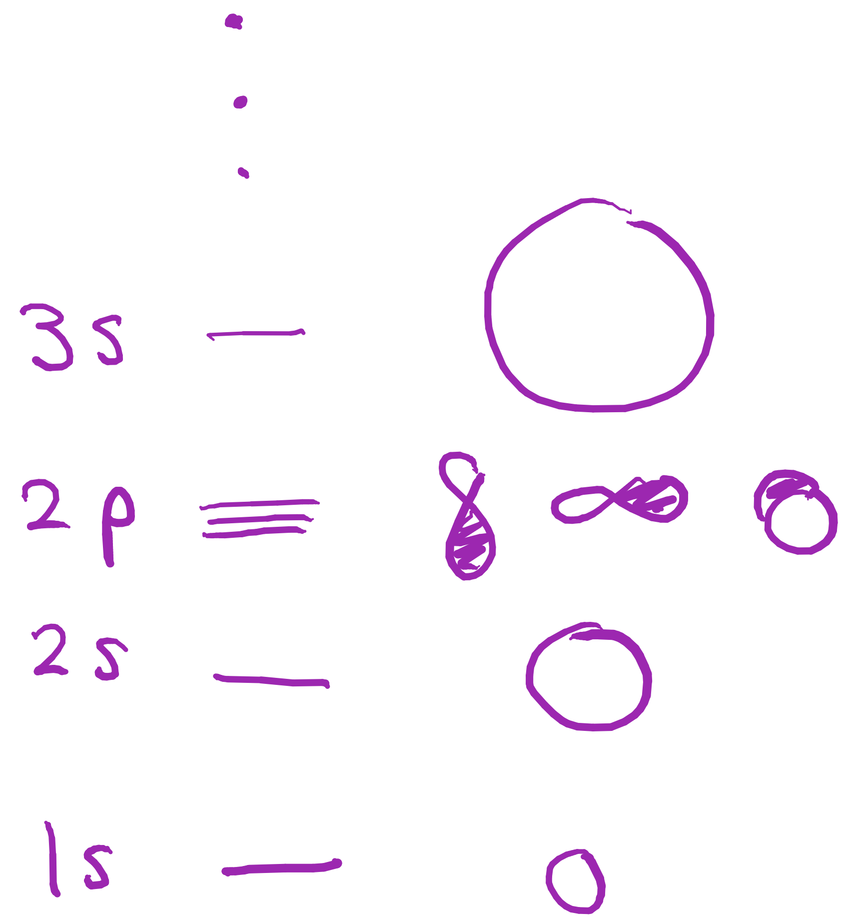

n-particle Hilbert space:

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"Hartree products"

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upshot: Hilbert space is <u>too</u> <u>big</u>!

use $\mathcal{F}_n(\mathcal{H}) = \text{span}\{ \Phi_{(p_1 \cdots p_n)} \}$

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space of physically realistic (a.s.)
n-particle wavefunctions

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$$\Psi(1, \ldots, n) = \frac{1}{\sqrt{n}} \sum_{p=1}^{\infty} \psi_p(1)\, (\hat{a}_p \Psi)(2, \ldots, n)$$

$$\langle \Psi | \hat{H}_e \Psi' \rangle$$

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$$= \sum_{i=1}^{n} \langle \Psi | \hat{h}(i) \Psi' \rangle + \sum_{i<j}^{n} \langle \Psi | \hat{g}(i,j) \Psi' \rangle$$

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same for all $\mathcal{F}_n$!

Fock space:

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Fock space Hamiltonian:

$$H_e = \sum_{pq} h_{pq}\, a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq \| rs \rangle\, a_p^\dagger a_q^\dagger a_s a_r$$

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$$c_p \Phi_{(p_1 \cdots p_n)} = \begin{cases} \Phi_{(p\, p_1 \cdots p_n)} & \text{if } p \notin (p_1 \cdots p_n) \\ 0 & \text{otw.} \end{cases}$$

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$$|\Phi_{(p_1 \cdots p_n)}\rangle = a_{p_1}^\dagger \cdots a_{p_n}^\dagger |\Phi_{()}\rangle$$

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$$|\Phi_{(p_1 \cdots p_n)}\rangle = a_{p_1}^\dagger \cdots a_{p_n}^\dagger |vac\rangle$$

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$$[a_p, a_p^\dagger]_+ = 1$$

let's work through some examples:

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1. $\langle vac | a_p a_q^\dagger | vac \rangle$

2. $\langle vac | a_p a_q a_s^\dagger a_r^\dagger | vac \rangle$

strategy: move the daggers to the left

brief interlude: occupation number formalism

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$$|\text{vac}\rangle = |0, \dots, 0, 0, \dots\rangle$$

$$|\Phi\rangle = |1, \dots, 1, 0, \dots\rangle$$

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$|\text{vac}\rangle$

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$$\begin{array}{ccc} |vac\rangle & & |\Phi\rangle \\ \downarrow & & \downarrow \\ |\Phi\rangle & & |vac\rangle \end{array} \qquad a_i \quad a_i^\dagger$$

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|\mathrm{vac}\rangle & |\Phi\rangle & a_i & a_i^\dagger & a_a & a_a^\dagger \\
\downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\
|\widetilde{\Phi}\rangle & |\widetilde{\mathrm{vac}}\rangle & b_i^\dagger & b_i & b_a & b_a^\dagger
\end{array}$$

$$\sum_{pq} h_{pq} \, a_p^{\dagger} a_q$$

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$$= \sum_{ab} h_{ab}\, a_a^\dagger a_b + \sum_{ai} h_{ai}\, a_a^\dagger a_i$$

$$+ \sum_{ia} h_{ia}\, a_i^\dagger a_a + \sum_{ij} h_{ij}\, a_i^\dagger a_j$$

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examples to work through:

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examples to work through:

1. $\langle \Phi | H_{core} | \Phi \rangle$
2. $\langle \Phi | H_{core} | \Phi_i^a \rangle$
3. $\langle \Phi | H_{core} | \Phi_{ij}^{ab} \rangle$

if there's time:

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expand $\frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r$

& work out matrix elements

the end.