- **Multiple Particles**
  - States + Wave functions
    - We can choose our basis of states to be factorized (in principle). Call this factorized basis.
      + This is like separation of variables in Cartesian coordinates in 3D: wavefunction $\Psi(\vec{x}) = X(x) Y(y) Z(z)$
        or several angular momenta listed individually $|\ell, m\rangle |s, m_s\rangle$ for ea.
      + So we write the state
        $$|\Psi\rangle = |\alpha\rangle_1 |\beta\rangle_2 \quad \text{(ie, particle 1 in state } |\alpha\rangle, \text{ etc)}$$
        or, for the position-basis wavefunction
        $$\langle \vec{x}_1, \vec{x}_2 | \Psi \rangle = \Psi(\vec{x}_1, \vec{x}_2) = \Psi_\alpha(\vec{x}_1) \Psi_\beta(\vec{x}_2)$$
    - **Distinguishable vs indistinguishable particles**
      + Different types of particles (ie, #1 = electron, #2 = proton) are distinguishable. This is always true classically.
      + But particles of the same type (like 2 electrons) are <u>indistinguishable</u> even in principle. In that case, we can't tell if we've measured particle 1 or 2. States must allow each particle to be in each state b/c it's <u>impossible</u> to tell the difference. That is
        $$|\Psi\rangle = a |\alpha\rangle_1 |\beta\rangle_2 + b |\beta\rangle_1 |\alpha\rangle_2 \quad \text{or} \quad \Psi(\vec{x}_1, \vec{x}_2) = a \Psi_\alpha(\vec{x}_1) \Psi_\beta(\vec{x}_2) + b \Psi_\alpha(\vec{x}_2) \Psi_\beta(\vec{x}_1)$$
    - We can define the <u>exchange operator</u> $\mathcal{E}$ (text calls it P) that switches particles
      $$\mathcal{E}(|\alpha\rangle_1 |\beta\rangle_2) = |\beta\rangle_1 |\alpha\rangle_2 \quad \text{or} \quad \mathcal{E} \cdot (\Psi_\alpha(\vec{x}_1) \Psi_\beta(\vec{x}_2)) = \Psi_\alpha(\vec{x}_2) \Psi_\beta(\vec{x}_1)$$
      + Clearly $\mathcal{E}^2 =$ identity. Eigenvalues are ± 1

+ Since the particles are indistinguishable, the Hamiltonian
  must be symmetric in exchange $[E, H] = 0$
  So stationary states can be written in basis as E eigenstates
+ Therefore, it helps to work with states in E eigen basis

| $E = +1$ | $E = -1$ | |
| symmetric states | antisymmetric states | $A =$ normalization constant |

$$|\Psi\rangle = A[|\alpha\rangle_1 |\beta\rangle_2 + |\beta\rangle_1 |\alpha\rangle_2] \qquad |\Psi\rangle = A[|\alpha\rangle_1 |\beta\rangle_2 - |\beta\rangle_1 |\alpha\rangle_2] \quad \text{(work out)}$$

• Spin-Statistics Theorem from relativity + QM (like spin itself)
+Statement:
   Particles with integer spin $(s = 0, 1, ...)$ must have symmetric
      states (including spatial wavefunction, spin, etc).
   Particles with odd-half-integer spin $(s = 1/2, 3/2, ...)$ must have
      antisymmetric states

+ Integer spin particles are <u>bosons</u> (after Satyendra Nath Bose)
Odd Half-Integer spin particles are <u>fermions</u> (after Enrico Fermi)

   + Note: It is the <u>total</u> state that must be symmetric or antisymmetric
   For example,

         (symmetric spatial wavefunction $\Psi(\vec{x}_1, \vec{x}_2)$) × (antisymmetric spin state)
   is allowed for fermions. Most often useful to factorize this way.

   + Pauli Exclusion Principle: No 2 electrons can occupy the same state.
   B/c electrons are fermions, and both in same state $\Rightarrow$ symmetric state

• Exchange "Force"
   Due to symmetry/antisymmetry, symmetric spatial wavefunctions
   bring particles closer, antisymmetric ones bring them apart.

+ To illustrate, consider expectation of $(x_1 - x_2)^2$ in 1D system.
For distinguishable particles in factorizable state $|\alpha\rangle_1 |\beta\rangle_2$

$$\langle (x_1 - x_2)^2 \rangle = \langle \alpha | x_1^2 | \alpha \rangle_1 \langle \beta | \beta \rangle_2 + \langle \alpha | \alpha \rangle_1 \langle \beta | x_2^2 | \beta \rangle_2 - 2 \langle \alpha | x_1 | \alpha \rangle_1 \langle \beta | x_2 | \beta \rangle_2$$

$$= \langle x^2 \rangle_\alpha + \langle x^2 \rangle_\beta - 2 \langle x \rangle_\alpha \langle x \rangle_\beta$$

+ Consider symmetric/antisymmetric states $|\psi_\pm\rangle = \frac{1}{\sqrt{2}} (|\alpha\rangle_1 |\beta\rangle_2 \pm |\beta\rangle_1 |\alpha\rangle_2)$
(Working out the same steps,

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_\alpha + \langle x^2 \rangle_\beta - 2 \langle x \rangle_\alpha \langle x \rangle_\beta \mp (\langle \alpha | x_1 | \beta \rangle_1 \langle \beta | x_2 | \alpha \rangle_2 + \langle \beta | x_1 | \alpha \rangle_1 \langle \alpha | x_2 | \beta \rangle_2)$$

$$= \langle x^2 \rangle_\alpha + \langle x^2 \rangle_\beta - 2 \langle x \rangle_\alpha \langle x \rangle_\beta \mp 2 |x_{\alpha\beta}|^2 \quad \longleftarrow \text{general matrix element}$$

+ Symmetric spatial states have shorter separations & vice versa.

+ Fermions can have symmetric spatial wavefunctions (with antisymmetric spin states). So they can pull closer (as in covalent bonds $\oplus (e^-) \oplus$) or repulse.

+. The matrix element $x_{\alpha\beta} = \int dx \, \psi_\alpha^*(x) \, x \, \psi_\beta(x) \longrightarrow 0$ unless ψ_α and ψ_β are both nonzero in the same place. In other words, well-separated identical particles act distinguishable & don't interfere. This is sometimes called <u>Cluster decomposition</u>.

— Atoms (of the multi-electron variety)

• Hamiltonian for nucleus with Z protons (+ therefore Z e^- in atom)

$$H = \sum_{j=1}^{Z} \left[\frac{\vec{P}_j^2}{2m} - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Z e^2}{|\vec{r}_j|} \right] + \frac{1}{2} \sum_{i \neq j} \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

+ Looks like each electron sees a hydrogen Hamiltonian w/ Z charges in nucleus (1st terms) plus Coulomb repulsion from each other electron.

+ No one has solved this exactly. (we may try approximations later). To get a feel, we will treat electron repulsion heuristically.

⊕ Helium

+ The ground state puts both electrons in the "hydrogen-like" n=1, l=0 state. Spins anti-align in singlet (s=0) state.

+ Excited states: only 1 electron excited

1) If both are excited, it decays + ionizes quickly

2) Parahelium: s=0 antisymmetric spin, symmetric spatial state
   e⁻ are closer together, so Coulomb repulsion increases energy

3) Orthohelium s=1 symmetric spin, antisymmetric spatial state
   e⁻ are farther apart, Coulomb repulsion is less, so lower E

• Other atoms: Key point is that larger $\langle r \rangle$ means other electrons "screen" the charge of the nucleus.

+ Notation: label l by a letter (l=0)=s, (l=1)=p, (l=2)=d, (l=3)=f, (l=4)=g, ─ (skip j).
  So indicate electron states by occupancy of hydrogen-like shells

+ Then

He =(1s)², Li =(1s)⁴(2s)¹, etc across periodic table but the nd shell is farther out + more screened than (n+1)s shell. Similarly for nf and (n+2)s. So that's why the "indented" parts come a row or 2 late.

+ Other notation for the total angular momentum.
  Let L = total orbital angular momentum (meaning, addition of l_1, l_2, etc) quantum number
  S = total spin quantum number,
  J = total angular momentum quantum number (from adding L+S states)
  Then represent electron configuration by

$$2S+1 \underset{\text{written}}{\overset{}{L_J}}$$

total # of spin states   "S", "p", etc.

See examples.