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Quantum Mechanics

Lecture 13

Identical particles;
Spin-statistics theorem;
Helium atom;
Exchange interaction.

A quick recap

Perturbation theory can be used to estimate energies and eigenstates when the complete Hamiltonian is too complicated to solve explicitly.

Examples:

$H_{SO} \propto \mathbf{S} \cdot \mathbf{L}$	$H_{HF} \propto \mathbf{S} \cdot \mathbf{I}$	$H_{\text{Stark}} \propto e\,\lvert\mathbf{E}\rvert$
Spin-orbit coupling	Hyperfine structure	Stark shift

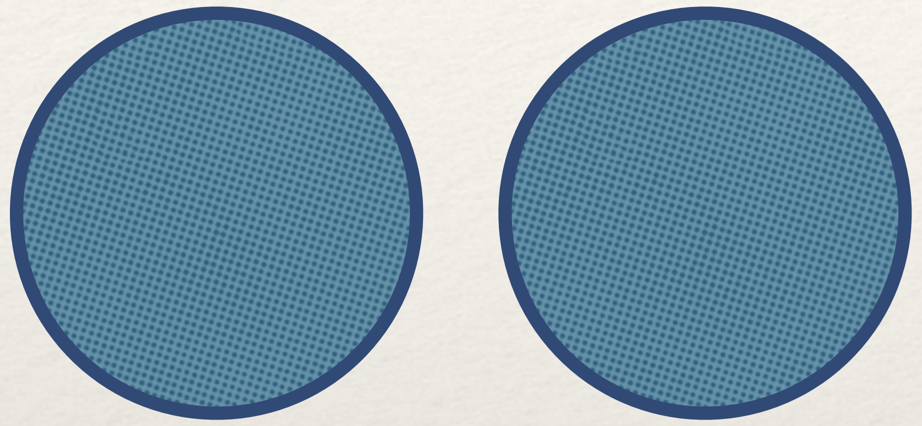
In some cases, the "old" quantum numbers for AM become "bad" and must be replaced by new quantum numbers for total AM. The Clebsch-Gordan coefficients tell us how to express the new eigenstates in terms of the old.

$$|J\,M\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C^{j_1\,j_2\,J}_{m_1\,m_2\,M} |j_1\,m_1\,j_2\,m_2\rangle$$

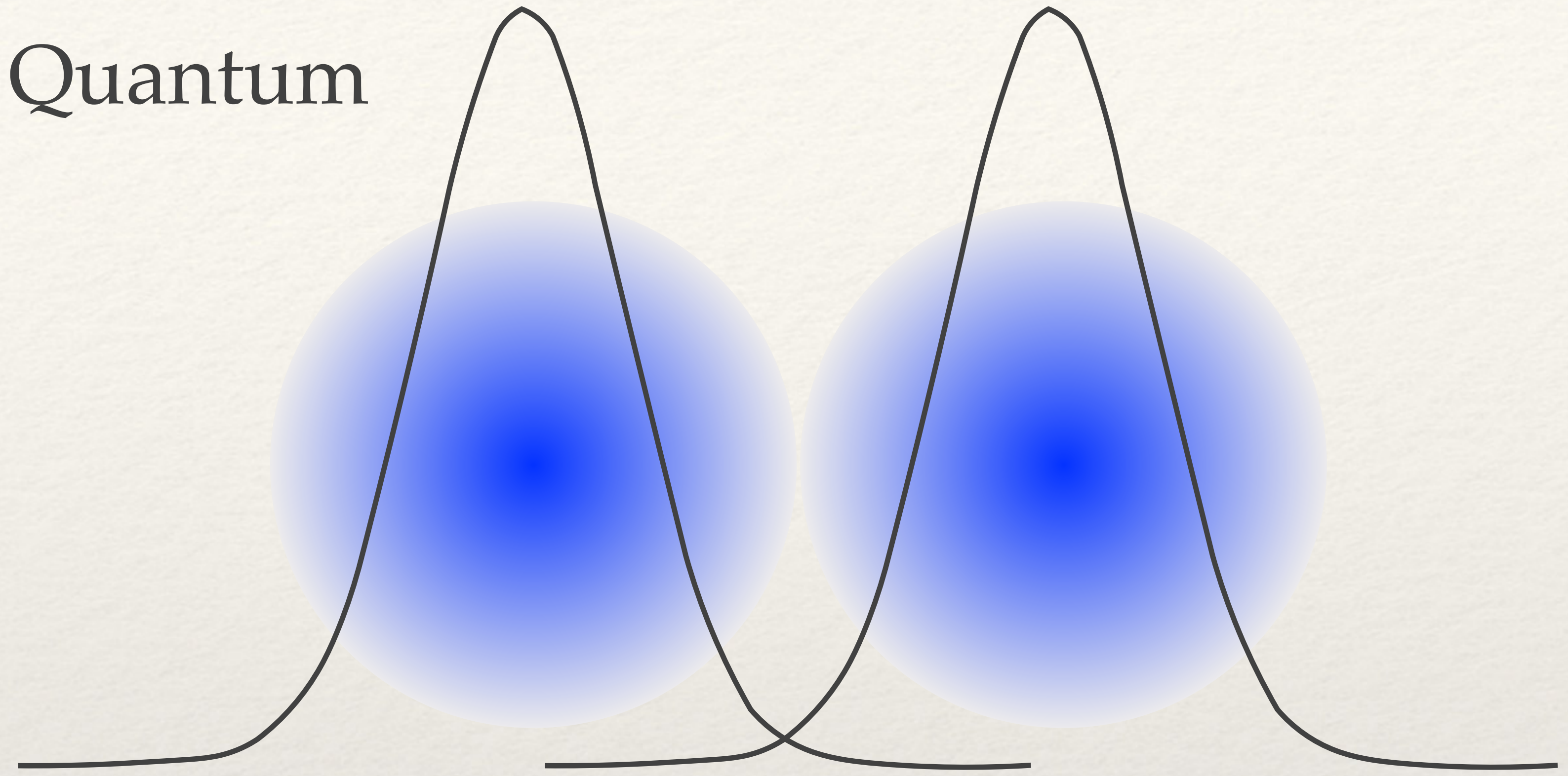
Identical particles

Elementary particles of the same type are all **exactly identical**.

Classical



Quantum



When the wave functions of identical particles overlap, they become **indistinguishable**. Contrast this with classical mechanics, where particles always occupy distinct space and can always (in principle) be distinguished.

This indistinguishability has important physical consequences.

Identical particles

Consider an experiment with two **indistinguishable** particles where we measure position in small regions d**r**. We must have:

$$|\psi(\mathbf{r},\mathbf{r}')|^2 = |\psi(\mathbf{r}',\mathbf{r})|^2 \;\Rightarrow\; \psi(\mathbf{r},\mathbf{r}') = e^{i\phi}\psi(\mathbf{r}',\mathbf{r})$$

Introduce the **exchange operator** (also known as **swap**):

$$P_{1,2}\,\psi(\mathbf{r},\mathbf{r}') = \psi(\mathbf{r}',\mathbf{r}) \qquad\qquad P_{1,2}^2 = 1 \;\Rightarrow\; e^{2i\phi} = 1 \;\Rightarrow\; e^{i\phi} = \pm 1$$

Thus, indistinguishable particles (invariant under exchange) come in two types:

$$\psi(\mathbf{r},\mathbf{r}') = +\,\psi(\mathbf{r}',\mathbf{r}) \qquad \textbf{Bosons}$$

$$\psi(\mathbf{r},\mathbf{r}') = -\,\psi(\mathbf{r}',\mathbf{r}) \qquad \textbf{Fermions}$$

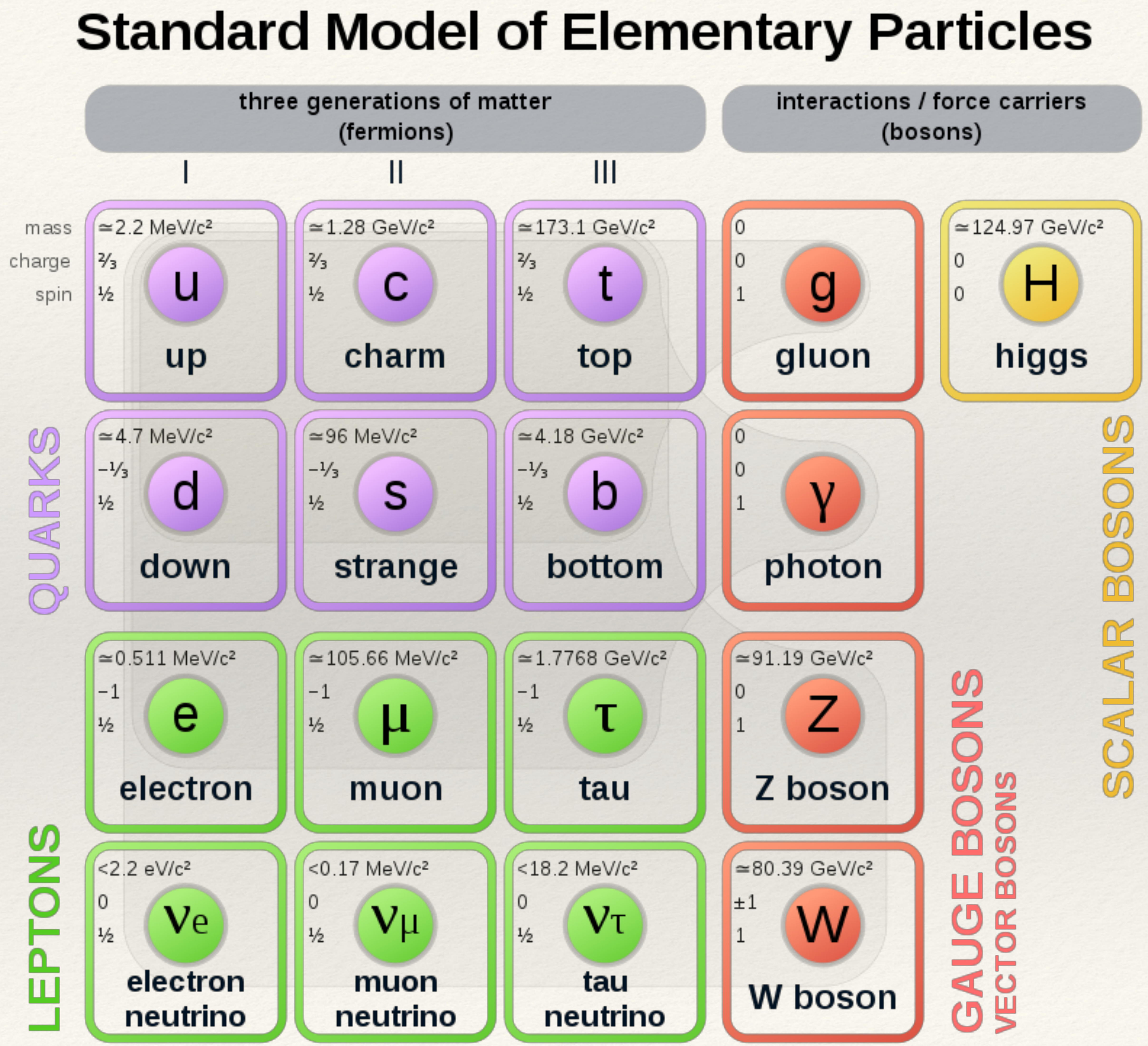
Bosons, Fermions, and the spin-statistics theorem

Bosons have **integer** spin, and **fermions** have **half-integer** spin.

In relativistic quantum mechanics, this is a provable statement known as the **spin-statistics theorem**.

The exchange phases are internally consistent under composition of particles:

B + B = B B + F = F F + F = B



Symmetrizing wave functions

When quantum statistics are important, we need to explicitly enforce the exchange symmetry in our wave functions.

Consider non-interacting fermions in a spin-independent potential:

$$H_i = \frac{\hat{\mathbf{p}}_i^2}{2m} + V(\hat{\mathbf{r}}_i)\,, \quad H = \sum_{i=1}^{N} H_i \qquad \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi_N(\mathbf{r}_N)$$

Single-particle eigenstates of the Schrödinger equation do not have the required symmetry!

We can make this anti-symmetric with the use of the **Slater determinant**:

Ex: $N = 3$

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \psi_1(\mathbf{r}_3) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \psi_2(\mathbf{r}_3) \\ \psi_3(\mathbf{r}_1) & \psi_3(\mathbf{r}_2) & \psi_3(\mathbf{r}_3) \end{vmatrix} = \frac{1}{\sqrt{N!}} \det(\{\psi_i(\mathbf{r}_j)\})$$

For bosons, the determinant gets replaced with the "permanent", the same sum but with all + signs instead of alternating signs.

The **Pauli exclusion principle**: this vanishes whenever $\psi_i = \psi_j$.

Symmetrizing wave functions

If the Hamiltonian is spin-independent and non-interacting, the wave function is a product of spatial and spin degrees of freedom.

Example: 2 particles

$$|\psi_{\text{tot}}(\mathbf{r}, s, \mathbf{r}', s')\rangle = |\phi(\mathbf{r}, \mathbf{r}')\rangle\, |\chi(s, s')\rangle$$

Spatial ↗ ↖ Spin

Symmetrization of spin has different consequences for bosons and fermions.

Example: 2 particles

spin-0 spin states:

$$\{\,|0{,}0\rangle\}$$

Symmetric product state (unique).

spin-1/2 spin states:

$$\{\,|1{,}1\rangle,\ |1{,}0\rangle,\ |1,-1\rangle,\ \ |0{,}0\rangle\} =$$

$$\left\{ |\uparrow\uparrow\rangle, \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), |\downarrow\downarrow\rangle,\ \ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \right\}$$

Triplet - symmetric   Singlet - antisymmetric

Symmetrizing wave functions

The **total** wave function must have appropriate symmetry.

Example: 2 particles

$$|\phi_n(\mathbf{r})\rangle = $$ nth excited spatial state at position $\mathbf{r}$.

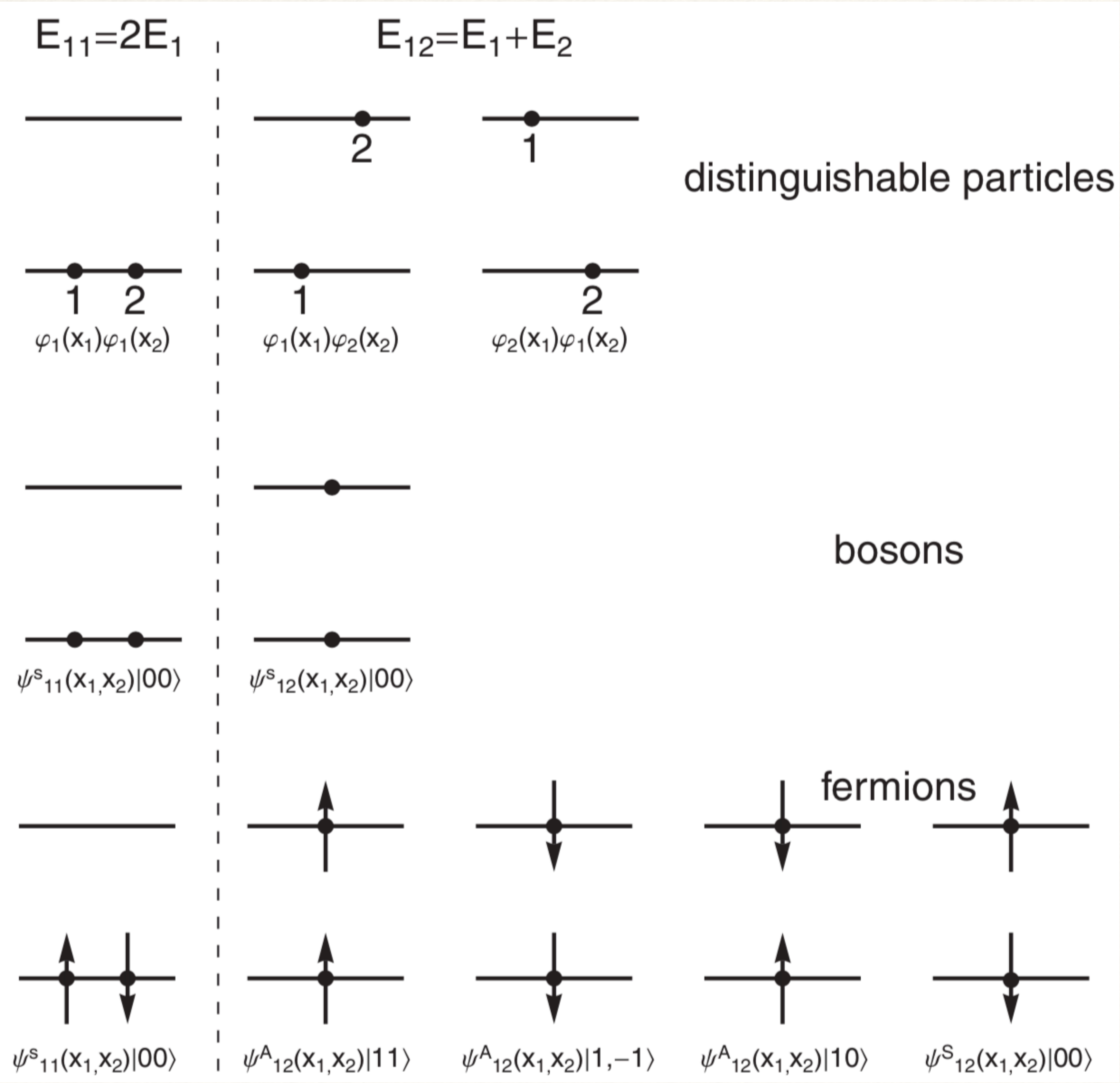
In the non-interacting case, we can symmetrize space and spin separately.

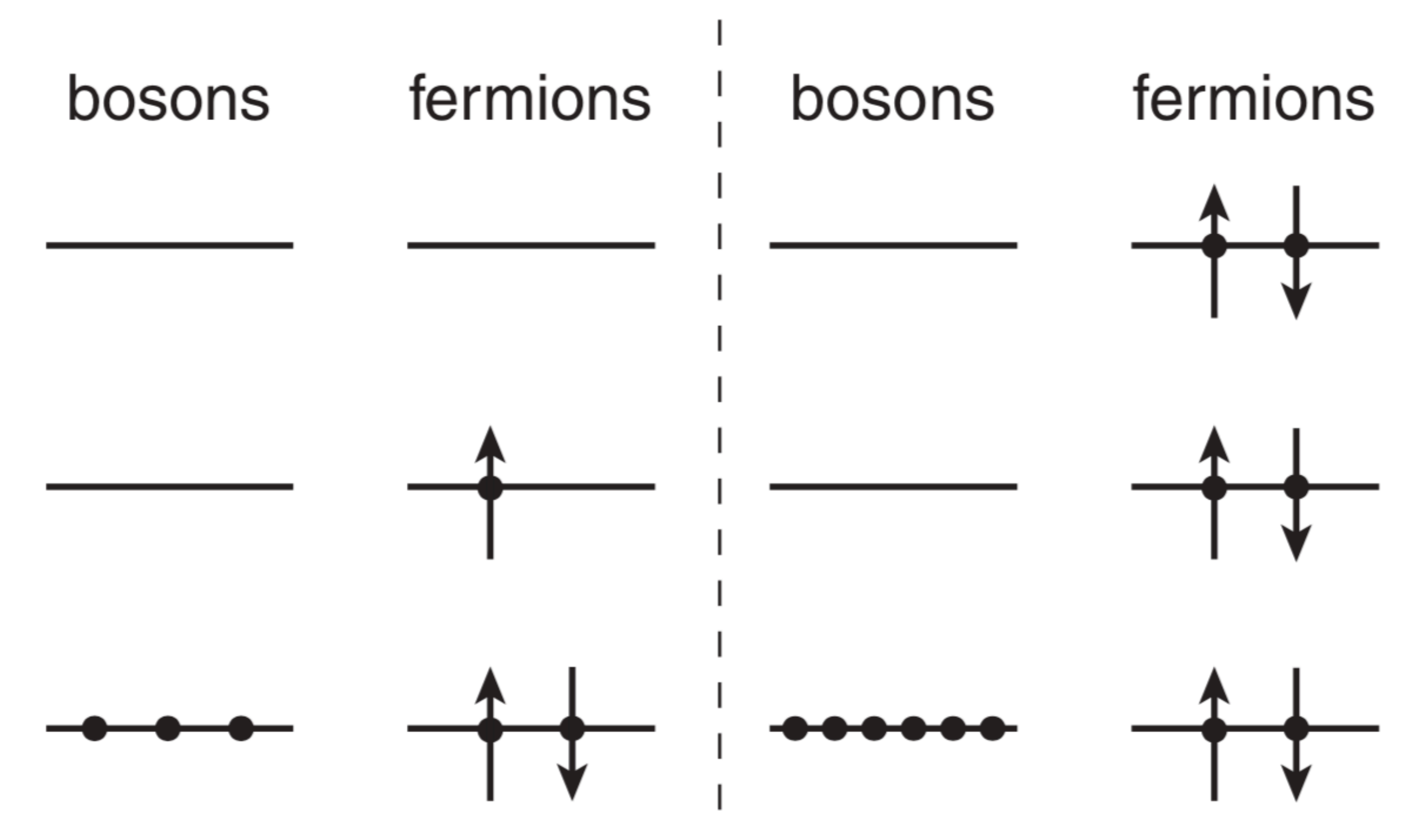
	spin-0 Bosons:	spin-1/2 Fermions:
Ground state:	$\frac{1}{\sqrt{2}}\big(|\phi_1(\mathbf{r})\rangle|\phi_1(\mathbf{r}')\rangle + |\phi_1(\mathbf{r}')\rangle|\phi_1(\mathbf{r})\rangle\big)|0{,}0\rangle$	$\frac{1}{\sqrt{2}}\big(|\phi_1(\mathbf{r})\rangle|\phi_1(\mathbf{r}')\rangle + |\phi_1(\mathbf{r}')\rangle|\phi_1(\mathbf{r})\rangle\big)\underline{|0{,}0\rangle}$ anti-sym.
Excited states:	$\frac{1}{\sqrt{2}}\big(|\phi_1(\mathbf{r})\rangle|\phi_2(\mathbf{r}')\rangle + |\phi_1(\mathbf{r}')\rangle|\phi_2(\mathbf{r})\rangle\big)|0{,}0\rangle$	$\begin{cases}\frac{1}{\sqrt{2}}\big(|\phi_1(\mathbf{r})\rangle|\phi_2(\mathbf{r}')\rangle + |\phi_1(\mathbf{r}')\rangle|\phi_2(\mathbf{r})\rangle\big)\underline{|0{,}0\rangle} \\ \frac{1}{\sqrt{2}}\big(\underline{|\phi_1(\mathbf{r})\rangle|\phi_2(\mathbf{r}')\rangle - |\phi_1(\mathbf{r}')\rangle|\phi_2(\mathbf{r})\rangle}\big)|1{,}m\rangle\end{cases}$

Fermionic excited states are four-fold degenerate, other states are unique.

Particle statistics

Particle symmetry leads to different degeneracies, and eventually to different notions of particle statistics.





These differences eventually lead to **Bose-Einstein statistics** for bosons and to **Fermi-Dirac statistics** for fermions.

Helium atom

The Hamiltonian for Helium, ignoring spin-orbit coupling and other spin-dependent effects is:

$$H_i = \frac{\hat{\mathbf{p}}_i^2}{2m} - \frac{Ze^2}{|\hat{\mathbf{r}}_i|}, \quad V = \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}, \quad H = H_1 + H_2 + V, \quad (Z = 2).$$

It is natural to try perturbation theory starting with $H_1 + H_2$ eigenstates.

Ground state:

$$|\psi_1^{(0)}\rangle = |1,0,0\rangle|1,0,0\rangle|0,0\rangle \longrightarrow \langle \mathbf{r}, \mathbf{r}'|\psi_1^{(0)}\rangle = \frac{1}{\sqrt{2}}\big(\psi_{1,0,0}(\mathbf{r})\psi_{1,0,0}(\mathbf{r}') + \psi_{1,0,0}(\mathbf{r}')\psi_{1,0,0}(\mathbf{r})\big)|0,0\rangle$$

First order energy correction:

$$\langle\psi_1^{(0)}|V|\psi_1^{(0)}\rangle = \text{(some nasty integral)} = +34 \text{ eV}$$

Total 1st order energy:

$(Z = 2)^3$ x (-13.6 eV) + 34 eV = - 74.8 eV

From experiment: -79.0 eV

Helium atom

There are several excited states with the requisite symmetry:

$$|\psi_2^{(0)}\rangle = \begin{cases} \frac{1}{\sqrt{2}}\left(|\psi_{1,0,0}(\mathbf{r})\rangle|\psi_{2,l,m}(\mathbf{r}')\rangle + |\psi_{1,0,0}(\mathbf{r}')\rangle|\psi_{2,l,m}(\mathbf{r})\rangle\right)|0,0\rangle \\ \frac{1}{\sqrt{2}}\left(|\psi_{1,0,0}(\mathbf{r})\rangle|\psi_{2,l,m}(\mathbf{r}')\rangle - |\psi_{1,0,0}(\mathbf{r}')\rangle|\psi_{2,l,m}(\mathbf{r})\rangle\right)|1,m_s\rangle \end{cases}$$

The explicit energy integrals in position space only depend on the spatial part:

$$E^{(1)} = \iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'|\langle 1,0,0|\mathbf{r}\rangle|^2|\langle 2,l,m|\mathbf{r}'\rangle|^2\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$$

$$\pm\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\langle 1,0,0|\mathbf{r}\rangle\langle 2,l,m|\mathbf{r}'\rangle\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\langle 2,l,m|\mathbf{r}\rangle\langle 1,0,0|\mathbf{r}'\rangle \quad =: J \pm K$$

In fact, K > 0.

Energy shift in He

The energy shift depends on l and the symmetry of the spatial wave function

$E^{(1)}(l = 0) = 11.4\text{eV} \pm 1.2\text{eV}$ $E^{(1)}(l = 1) = 13.2\text{eV} \pm 0.9\text{eV}$

Spin-dependent energy shifts have appeared from spin-free Hamiltonian interactions!

This effect is called the **exchange interaction**.

Antisymmetric wave functions tend to avoid overlapping in space, so they are farther apart and have less Coulomb repulsion.

Symmetric wave functions clump together and therefore have larger Coulomb repulsion.

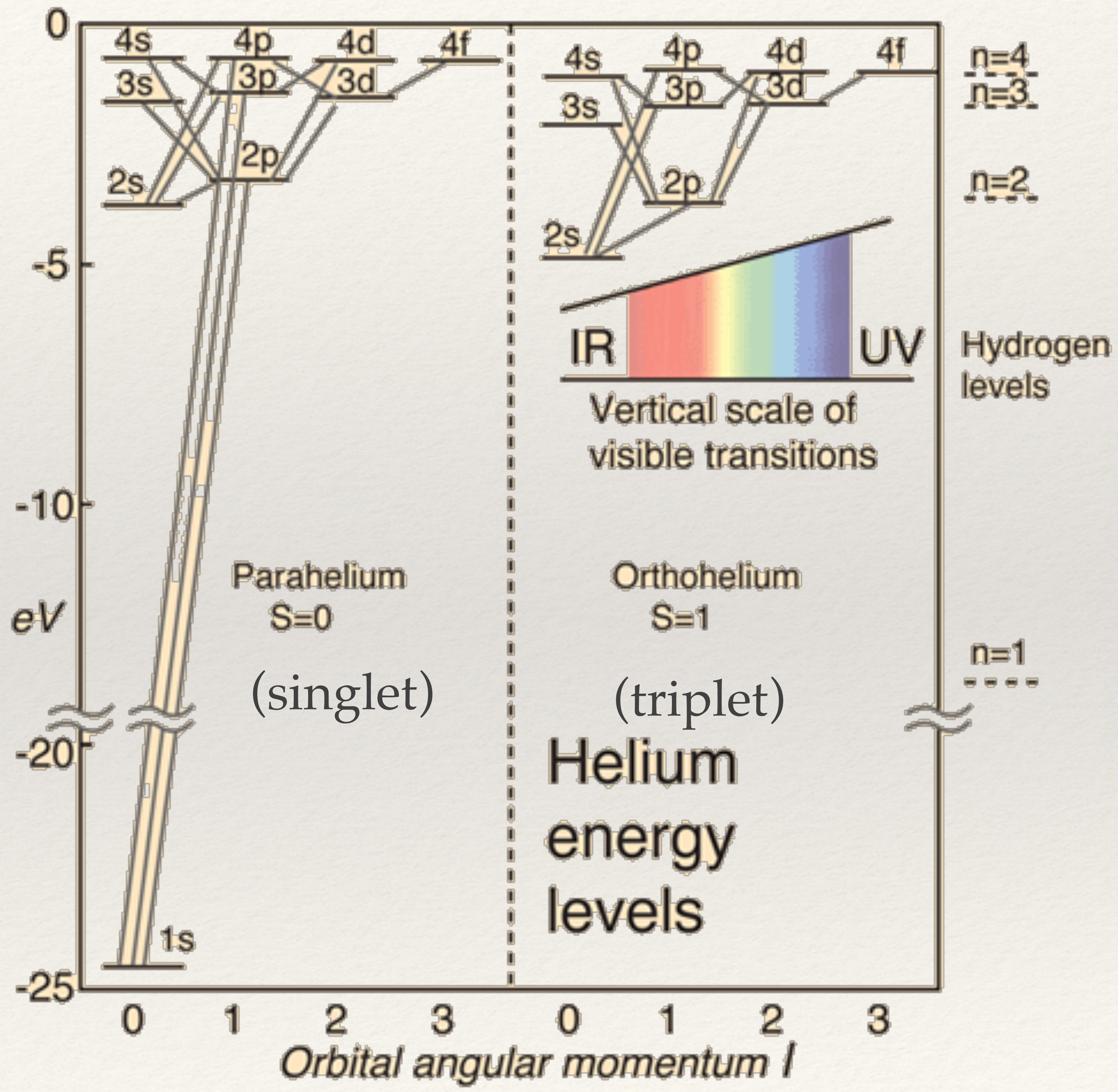


Image: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/helium.html