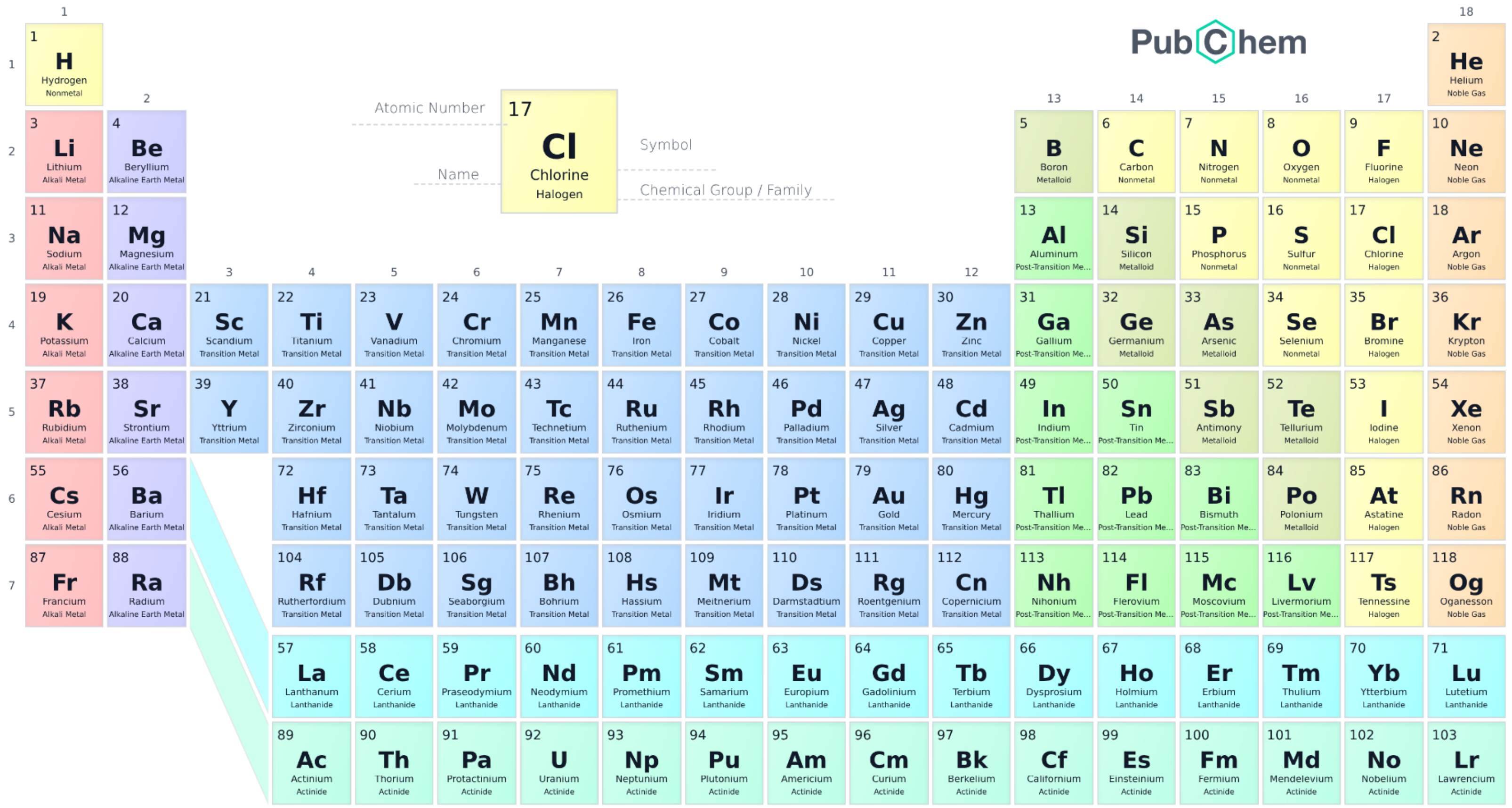
Today in Physics 237: state-vector symmetry, molecules, and atoms

- The exchange operator
- Molecular hydrogen's rotation and two-proton spin states
- H_2's and helium's two-electron states
- Multi-electron atoms
  - L-S coupling
  - The periodic table



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Symmetrization and the exchange operator

- We need to define an operator which can act on a two-quantum state vector and swap the quanta: can move quantum *a* from $\boldsymbol{r}_1$ to $\boldsymbol{r}_2$, and simultaneously quantum *b* from $\boldsymbol{r}_2$ to $\boldsymbol{r}_1$, while treating them as identical quanta.
- I guess we'll call it *P*:

$$\hat{P}\left|1,2\right\rangle = \left|2,1\right\rangle \quad ; \quad \hat{P}^2\left|1,2\right\rangle = \left|1,2\right\rangle \quad .$$

- This operator therefore acts on the two-quantum states we introduced on Lecture 22 page 3, like this:

$$\hat{P}\psi_\pm(\boldsymbol{r}_1,\boldsymbol{r}_2) = \hat{P}A\big(\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \pm \psi_b(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)\big) = A\big(\psi_a(\boldsymbol{r}_2)\psi_b(\boldsymbol{r}_1) \pm \psi_b(\boldsymbol{r}_2)\psi_a(\boldsymbol{r}_1)\big)$$

$$= \pm A\big(\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \pm \psi_b(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)\big) = (\pm 1)\psi_\pm(\boldsymbol{r}_1,\boldsymbol{r}_2) \quad ;$$

$\psi_\pm(\boldsymbol{r}_1,\boldsymbol{r}_2)$ are eigenstates of $\hat{P}$, with eigenvalues ±1 respectively.

Symmetrization and the exchange operator (continued)

- The Hamiltonian (Lecture 21, p. 13), which is $\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$, perforce treats identical quanta at locations 1 and 2 indistinguishably: $m_1 = m_2$, $V(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = V(\boldsymbol{r}_2, \boldsymbol{r}_1, t)$.
- So $\hat{P}$ and $\hat{H}$ are compatible:

$$E|2,1\rangle = E|1,2\rangle = \hat{H}|1,2\rangle = \hat{H}|2,1\rangle = \hat{H}\hat{P}|1,2\rangle$$

$$\Rightarrow \quad [\hat{H},\hat{P}]|\psi\rangle = \hat{H}\hat{P}|\psi\rangle - \hat{P}\hat{H}|\psi\rangle = E|\psi\rangle - E|\psi\rangle \quad = 0 \quad .$$

- According to the generalized Ehrenfest theorem (Lecture 11, p. 5), therefore,

$$\frac{d}{dt}\langle P\rangle = \frac{i}{\hbar}\left\langle [\hat{H},\hat{P}]\right\rangle + \left\langle \frac{\partial}{\partial t}\hat{P}\right\rangle = 0 \quad ;$$

  - That is, if a system starts off in an eigenstate of $\hat{P}$, symmetric or antisymmetric, it stays that way forever.

The hydrogen molecule<u>s</u>

Example: molecular hydrogen and symmetrization.

a. Consider H_2 to be a rigid rotor. Find its time-independent angular momentum eigenstates ψ and eigenvalues $J\hbar$. Then determine the symmetry of these states: that is, evaluate $\hat{P}|\psi\rangle$.

b. Similarly, noting the protons in H_2 to be noninteracting identical fermions, find the properly symmetrized spin eigenstates χ and their eigenvalues $s(s+1)\hbar^2$ and $m\hbar$, and evaluate $\hat{P}|\chi\rangle$.

c. Combine these states into states of angular momentum *and* spin, $|\psi\chi\rangle$. Evaluate $\hat{P}|\psi\chi\rangle$, and show that the joint states violate Fermi statistics unless certain combinations of ψ and χ are ruled out. Specifically: show that states with **even** angular momentum quantum number *J* combine only with **antisymmetric** spin states, and those of **odd** *J* combine only with **symmetric** spin states. And thus show that H_2 could be two separate molecular species, which we call para-H_2 and ortho-H_2, respectively.

This is the simplest practical system for combining two spins with an orbital angular momentum. It's simple because the protons in H_2 do not interact significantly by electromagnetic forces/torques.

The hydrogen molecule<u>s</u> (continued)

a. You got started on this example in G&S problem 4.27 on assignment 9. Recap: you considered a diatomic molecule to be a rigid rotor: two masses separated by a fixed distance *r* and having moment of inertia *I* about their center of mass. You took the classical expression of energy of a rigid rotor with angular momentum of magnitude *J*,

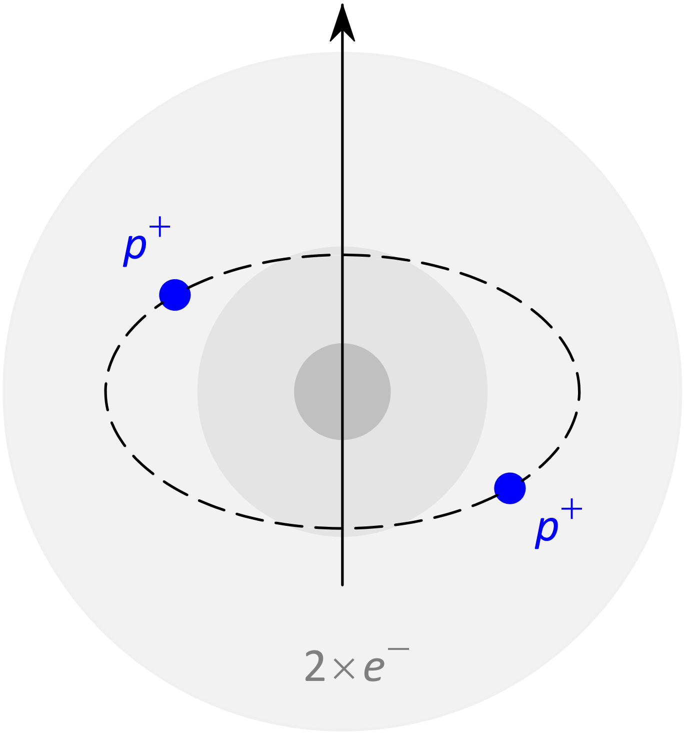
$$H = \frac{1}{2} I\omega^2 = \frac{1}{2I}(I\omega)^2 = \frac{J^2}{2I} \quad ,$$

to correspond to the Hamiltonian, and found thereby that

$$\hat{H}\psi = \frac{1}{2I}\hat{J}^2 = E\psi = \frac{\hbar^2}{2I} J(J+1)\psi$$

$$\Rightarrow \boxed{\psi_{JM} = Y_J^M , \quad J = 0,1,2,\ldots \quad \text{and} \quad M = -J, -J+1, \ldots J} \ .$$

See also Lecture 14.



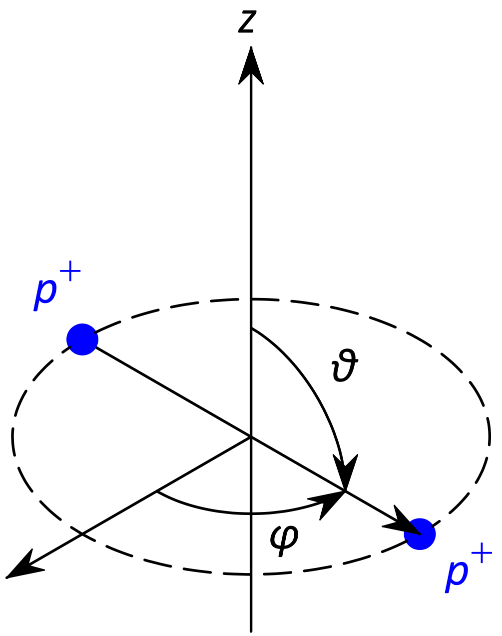
- And thus the component $\hat{J}_z$ has eigenvalues $\boxed{J\hbar.}$
- For H_2, $I = m_H (r/2)^2$, with $r = 0.074$ nm.

The hydrogen molecules (continued)

- The angular momentum eigenfunctions are the spherical harmonics (Lecture 14, pp. 8-12):

$$Y_J^M(\vartheta,\varphi)=\sqrt{\frac{2J+1}{4\pi}\frac{(J-M)!}{(J+M)!}}e^{iM\varphi}P_J^M(\cos\vartheta)\quad,\quad\text{where}$$

$$P_J^M(x)=\frac{(-1)^M\left(1-x^2\right)^{M/2}}{2^J J!}\left(\frac{d}{dx}\right)^M\left(\frac{d}{dx}\right)^J\left(x^2-1\right)^J\quad.$$



- In spherical coordinates: if one proton lies at $\boldsymbol{r}_1=\left[r/2\quad\vartheta\quad\varphi\right]$, the other lies at $\boldsymbol{r}_2=\left[r/2\quad\pi-\vartheta\quad\varphi+\pi\right]$.

- With $x=\cos\vartheta$: if one proton lies at x, the other lies at

$$\cos(\pi-\vartheta)=\cos\pi\cos\vartheta-\sin\pi\sin\vartheta=-\cos\vartheta=-x\quad\Rightarrow\quad\hat{P}\left|x,\varphi\right\rangle=\left|-x,\varphi+\pi\right\rangle\quad.$$

- And if $x\rightarrow-x$, then $\frac{d}{dx}\rightarrow\frac{d(-x)}{dx}\frac{d}{d(-x)}=-\frac{d}{d(-x)}\quad.$

The hydrogen molecules (continued)

- This gives us

$$\hat{P}Y_J^M(x,\varphi)=Y_J^M(-x,\varphi+\pi)=\sqrt{\frac{2J+1}{4\pi}\frac{(J-M)!}{(J+M)!}}e^{iM\varphi}\left[e^{iM\pi}\right]\frac{(-1)^M\left(1-[-x]^2\right)^{M/2}}{2^J J!}\left[\frac{d}{d(-x)}\right]^M\left[\frac{d}{d(-x)}\right]^J\left([-x]^2-1\right)^J$$

$$=\sqrt{\frac{2J+1}{4\pi}\frac{(J-M)!}{(J+M)!}}e^{iM\varphi}\left[(-1)^M\right]\frac{(-1)^M\left(1-[x]^2\right)^{M/2}}{2^J J!}\left[(-1)\frac{d}{dx}\right]^M\left[(-1)\frac{d}{dx}\right]^J\left([x]^2-1\right)^J$$

$$=[-1]^M[-1]^M[-1]^J\sqrt{\frac{2J+1}{4\pi}\frac{(J-M)!}{(J+M)!}}e^{iM\varphi}\frac{(-1)^M\left(1-x^2\right)^{M/2}}{2^J J!}\left(\frac{d}{dx}\right)^M\left(\frac{d}{dx}\right)^J\left(x^2-1\right)^J=\boxed{(-1)^J Y_J^M(x,\varphi)}\ .$$

The hydrogen molecule<u>s</u> (continued)

b. Each proton has spin ½, and (in good approximation) the spins don't exert forces or torques on each other, so the spin eigenstates are singlet and triplets, just like the pair of electrons considered in Lecture 20, p. 4, so

$$
\begin{aligned}
|sm\rangle &= |11\rangle = |\uparrow\uparrow\rangle \\
&= |10\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \\
&= |1-1\rangle = |\downarrow\downarrow\rangle
\end{aligned}
\quad \text{and} \quad |sm\rangle = |00\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \quad ,
$$

$$
\hat{P}|1m\rangle = |1m\rangle = (-1)^{s+1}|1m\rangle \qquad \hat{P}|00\rangle = -|00\rangle = (-1)^{s+1}|00\rangle \quad .
$$

- for which

$$
\hat{J}^2|sm\rangle = 2\hbar^2|sm\rangle \text{ (triplet states)} \quad , \quad = 0 \text{ (singlet state)} \quad ;
$$

$$
\hat{J}_z|sm\rangle = \hbar m|sm\rangle \text{ (triplet states)} \quad , \quad = 0 \text{ (singlet state)} \quad .
$$

Here s = 1 and m = 1, 0, -1, for the triplet states.

The hydrogen molecules (continued)

c. So, for the complete state vector $\left|JMsm\right\rangle$,

$$\hat{P}\left|JMsm\right\rangle = (-1)^J(-1)^{s+1}\left|JMsm\right\rangle \quad , \quad \text{and}$$

$$= (-1)\left|JMsm\right\rangle \quad \text{because the nuclei being exchanged are identical fermions.}$$

- So for

  and for

$$\left.\begin{array}{l} \boxed{\begin{array}{l} s=0 \quad , \quad (-1)^J = 1 \quad \Rightarrow \quad J = 2J' \\ \\ s=1 \quad , \quad (-1)^J = -1 \quad \Rightarrow \quad J = 2J'+1 \end{array}} \; . \end{array}\right\} \quad J' = 0,1,2,\ldots$$

Even-*J* states have to be spin singlets (para-H_2) and odd-*J* states have to be spin triplets (ortho-H_2): two different subspecies of H_2.

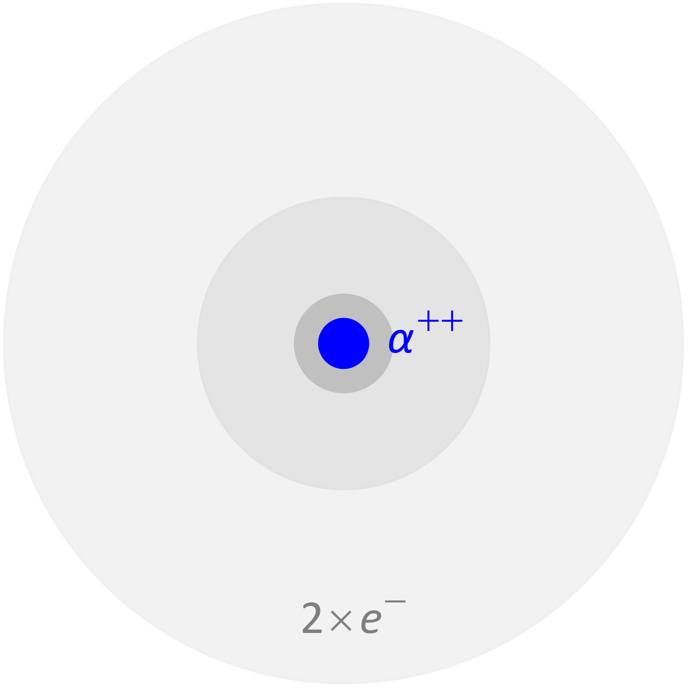
- It turns out that, because of the symmetry of the molecule, it is impossible for para-H_2 and ortho-H_2 to convert to one another, either by photon emission or by collisions at low or moderate speeds (Lecture). It takes chemical reactions to change one to the other. Thus in low temperature or low density environments (e.g. interstellar space), para-H_2 and ortho-H_2 really do behave like separate, independent species.

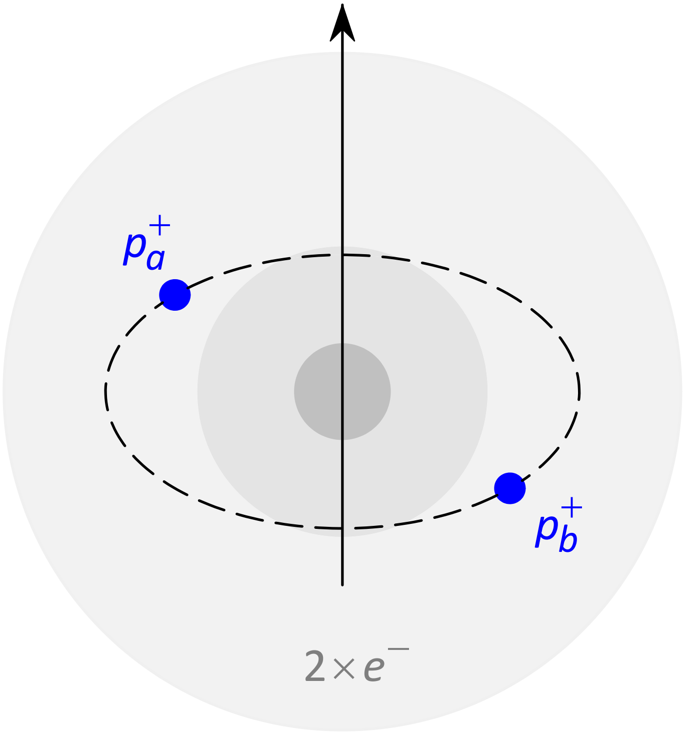
Spin symmetry of electrons in helium and molecular hydrogen

- The simplest systems in which to consider the state-vector symmetry of pairs of electrons are He and H_2.
- Neither can be solved analytically. For fixed proton or nuclear position, in cgs units,

$$\hat{H}_{H_2} = \left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 \right] + \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} - e^2\left(\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_a|} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_b|} + \frac{1}{|\boldsymbol{r}_2 - \boldsymbol{r}_a|} + \frac{1}{|\boldsymbol{r}_2 - \boldsymbol{r}_b|} \right) ,$$

$$\hat{H}_{He} = \left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 \right] - e^2\left(\frac{2}{r_1} + \frac{2}{r_2} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) .$$



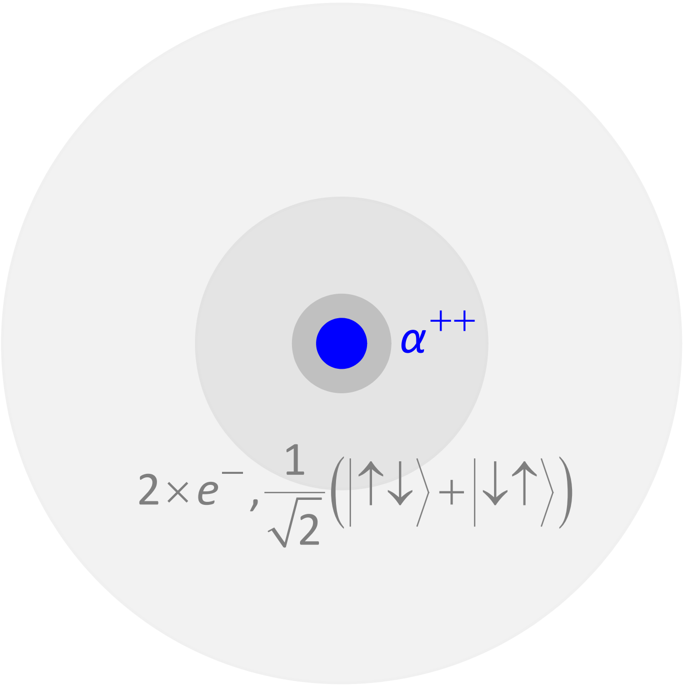


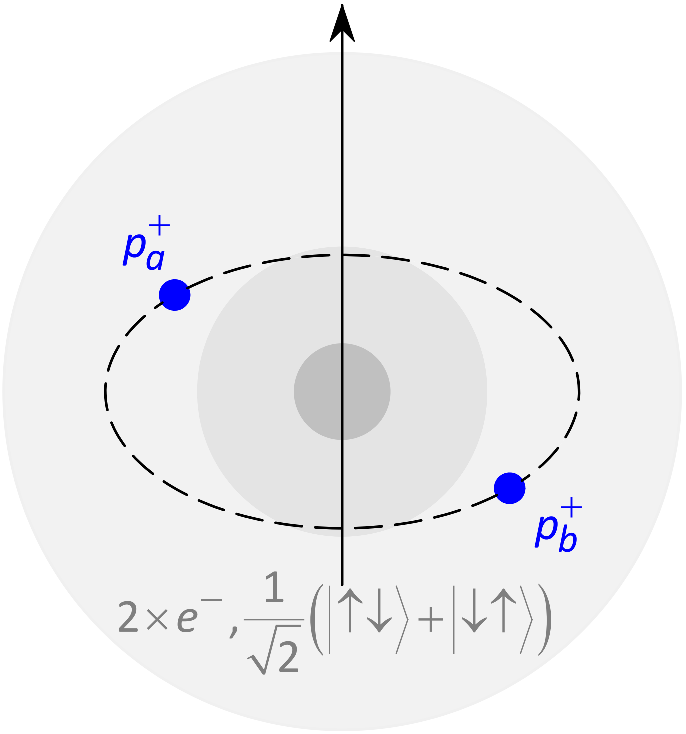
Spin symmetry of electrons in helium and molecular hydrogen (continued)

- But in the ground state, to good approximation, we can take the electrons to be **co-located** in both cases:
  - Mostly lying between the protons in H_2, binding the protons together electrostatically.
  - For He, the first approximation would be a product of hydrogenic ground states, like $\psi \simeq \psi_{n\ell m}\psi_{n'\ell' m'} = \psi_{100}^2$.
  - Both have $\psi \sim \left(Y_0^0\right)^2$ in the ground state, so, as was the case for the proton part of the wavefunction in H_2, the electron wavefunction apart from spin is **symmetric**: $\hat{P}|\psi\rangle = +1|\psi\rangle$.
  - But electrons are fermions, so the complete wavefunction is antisymmetric:

$$\hat{P}|\psi\chi\rangle = -|\psi\chi\rangle \quad \Rightarrow \quad \hat{P}|\chi\rangle = -|\chi\rangle \quad .$$

  Electron spin singlets, in both cases.





Spin and symmetry in multielectronic atomic wavefunctions

- Considering electron symmetry in **atoms** with more than two electrons, one can proceed as follows, to at least decent approximation, to consider why atoms fill the period table the way they do.

  - As with He, consider the radial and angular part of the wavefunction, ψ, to be a product of hydrogenic wavefunctions $\psi_{n\ell m}$, one factor for each electron, and adjusting for the number of protons in the nucleus.

  - Consider the spin part of the wavefunction χ to factor out of the complete wavefunction. This is to ignore $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ terms (**fine structure**) in the Hamiltonian, usually to good approximation.

  - Apply the symmetrization principle, used so far only for two quanta, to the whole list of electrons in the atom. That is, for the complete electron wavefunction

$$\hat{P}\left|\psi,\chi,j,i\right\rangle = -\hat{P}\left|\psi,\chi,i,j\right\rangle \quad ; \quad \left|0,1,\ldots i,\ldots j,\ldots N\right\rangle = -\left|0,1,\ldots j,\ldots i,\ldots N\right\rangle \quad .$$

    - You can regard this as an axiom for now, but, because it is equivalent to the Pauli principle, it is an experimental fact.

    - Remember that the angular parts of $\psi_{n\ell m}$ are either symmetric or asymmetric, as on pp. 6-7. So if a lone electron is in a symmetric ψ it has to be in an antisymmetric χ, and vice versa.

Spin and symmetry in multielectronic atomic wavefunctions (continued)

- Add some nomenclature: individual-electron parts of wavefunctions are referred by their values of n and ℓ, but the latter is encoded:

$$\ell = 0,1,2,3,4,... \quad \Leftrightarrow \quad s,p,d,f,g,\ldots$$

- And the same for the sums of the atom's orbital, spin, and **total** angular momenta: they are referred to by their integer factors of $\hbar$, but by the capital letters *L*, *S*, and *J*.
  - Adding the orbital angular momenta and spin angular momenta separately, and then adding the results to produce the total, is called ***LS****,* or **Russell-Saunders**, coupling. It works pretty accurately for elements and ions of the first three rows of the periodic table.

- Reminiscent of the individual electrons, *L* = 0, 1, 2, 3, … is encoded as *S, P, D, F, …*

- So electron **configurations** are given, for the example of carbon (element *N* = 6), as $1s^2 2s^2 2p^2$, and as we will see, the angular-momentum-and-symmetry **term** name is encoded in a hieroglyph:

$${}^{2S+1}L_J.$$

Spin and symmetry in multielectronic atomic wavefunctions (continued)

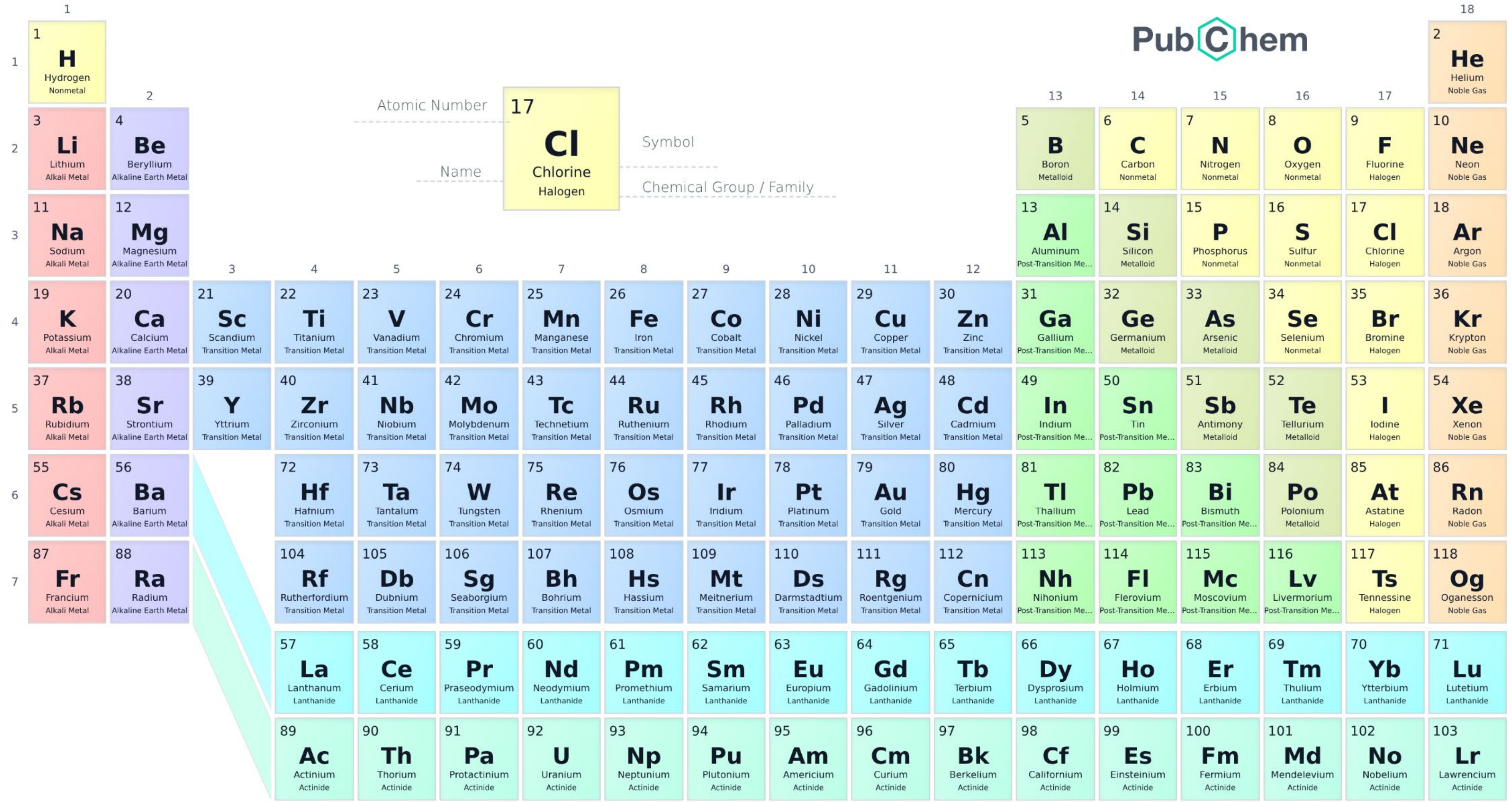
- The ancient, prehistoric, empirical rules for how the configurations and terms go are called **Hund's Rules**, which go like this:

1. Consistent with the Pauli principle, the state with larges total spin S has the lowest energy.

2. For a given S, the state with the largest total orbital angular momentum L, consistent with overall antisymmetrization, has the lowest energy.

3. If a subshell $n\ell$ is no more than half filled, then the lowest energy corresponds to $J = |L - S|$; if more than half filled, the lowest energy corresponds to $J = L + S$.

The period table



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The elements' ground states

- N = 3, lithium. The first two electrons go into the ground state as a spin singlet, same as He. The Pauli principle allows no state lower than n = 2. So the configuration is $1s^2 2s^1$ and the term is $^2S_{1/2}$.
- N = 4, beryllium. The extra electron can go into 2s, as a spin singlet with the other one: $1s^2 2s^2$, $^1S_0$.
- N = 5, boron. No room for another s, so it has ℓ = 1, i.e. is a p: $1s^2 2s^2 2p^1$. Of the two Js, ½ gives lower energy: $^2P_{1/2}$.
- N = 6, carbon. The sixth electron needs to be a p as well: $1s^2 2s^2 2p^2$. It can have m different from the first p electron, in which case their spins should be in a triplet. This makes S = 1 and J can be 0, 1, or 2. The lowest energy turns out to be J = 0: $^3P_0$.
- N = 7, nitrogen, $1s^2 2s^2 2p^3$. Now all the values of m are used, making L = 0, so all the spins need to be up: $^4S_{3/2}$.
- N = 8, oxygen, $1s^2 2s^2 2p^4$. The next p electron joins with one of the others in ℓ and m, but their spins therefore have to be in a singlet. Turns out this time that the J = 2 is lower energy: $^3P_2$.
- N = 9, fluorine. Only one unpaired p electron left, and again the larger J is the lower energy: $1s^2 2s^2 2p^5$, $^2P_{3/2}$.

  And so on.