# Electrons, Spin, and Slater Determinants

Adam Abbott

Goal for the next 2 weeks:

Go from a basic understanding of QM and the Schrodinger equation all the way to full-blown Roothaan-Hall/Pople-Nesbet Hartree Fock Theory, **without skipping any details**

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We won't succeed. There's a lot of details. Instead, we will strive for a really good understanding of HF, and how to program it. Hopefully, many little gaps in understanding will be filled.

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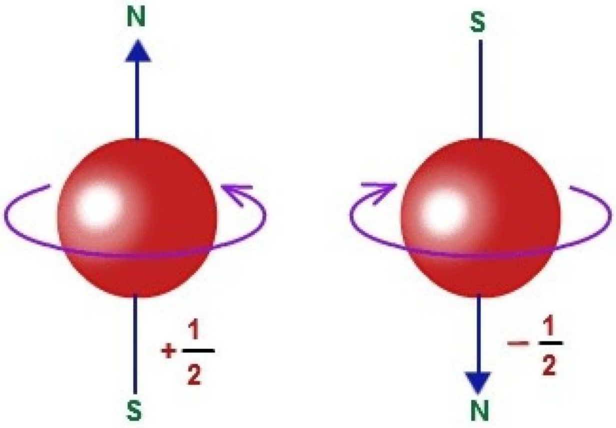
Electron spin explained: imagine a ball that's rotating, except it's not a ball and it's not rotating



# Spin

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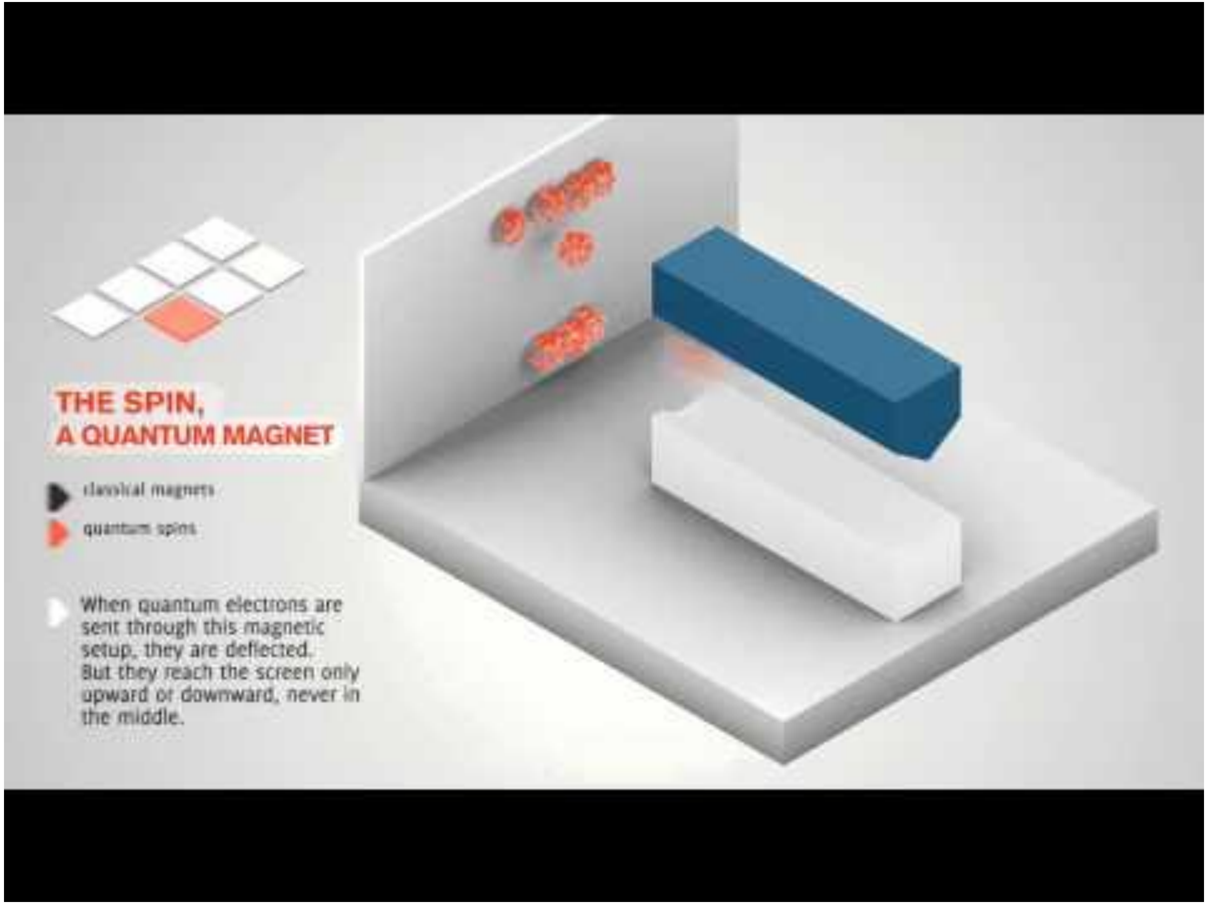
...What is that?

**Spin** is an **intrinsic angular momentum** which all particles carry

Intrinsic “rotational” *oomph*

We know spin exists from the Stern-Gerlach experiment

Electrons have two distinct levels of spin, (up/down, +/-½)



$$\hat{H} = -\sum_i \frac{1}{2}\nabla^2_{\boldsymbol{r}_i} - \sum_i \sum_A \frac{Z_A}{|\boldsymbol{R}_A - \boldsymbol{r}_i|} + \sum_{i<j} \frac{1}{\boldsymbol{r}_{ij}} + V_{\text{nuc}}$$

$$\hat{H} = \sum_i \hat{h}(i) + \sum_{i<j} \hat{g}(i,j) + V_{\text{nuc}}$$

Where’s the spin?

It’s not there! Our application of the time-independent Schrodinger equation does not include spin (the Dirac equation does!) so we have to build it into our wavefunction somehow.

QM Postulate: The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin must be included in this set of coordinates. The Pauli exclusion principle is a direct result of this antisymmetry principle.

# This is the way.

To build-in antisymmetry with respect to exchange of electrons, we express the wavefunction as a Slater Determinant composed of spin orbitals: $\psi_i^{\mu}(r^{\mu}, s^{\mu}) = \phi_i(r^{\mu})\omega_i(s^{\mu})$

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1^1 & \psi_2^1 & \psi_3^1 & \cdots & \psi_N^1 \\ \psi_1^2 & \psi_2^2 & \psi_3^2 & \cdots & \psi_N^2 \\ \psi_1^3 & \psi_2^3 & \psi_3^3 & \cdots & \psi_N^N \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_1^N & \psi_2^N & \psi_3^N & \cdots & \psi_N^N \end{vmatrix}$$

$$\Phi = \sqrt{N!}\hat{A}(\psi_1^1\psi_2^2\ldots\psi_N^N)$$

$$\hat{A} = \frac{1}{N!}\sum_{P\in S_N}(-1)^{\pi}\hat{P}$$

# Spin Statistics Theorem

- The wave function of a system of **identical integer-spin** particles has the **same value** when the positions of **any two particles are swapped**. Particles with wave functions symmetric under exchange are called **bosons**.

- The wave function of a system of **identical half-integer–spin** particles **changes sign** when **two particles are swapped**. Particles with wave functions antisymmetric under exchange are called **fermions**.

The actual proof of the Spin Statistics Theorem is a bit too physics-y, so we won't cover it. But we can learn a bit more than just blindly accepting it.

Imagine you have an electron, in its own Universe, totally isolated, on its own, not moving, not experiencing any sort of external interaction. How do you write down its **state**?

What are the **base states?**

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$$|\psi\rangle = c_0|0\rangle + c_1|1\rangle \qquad |c_0|^2 + |c_1|^2 = 1$$

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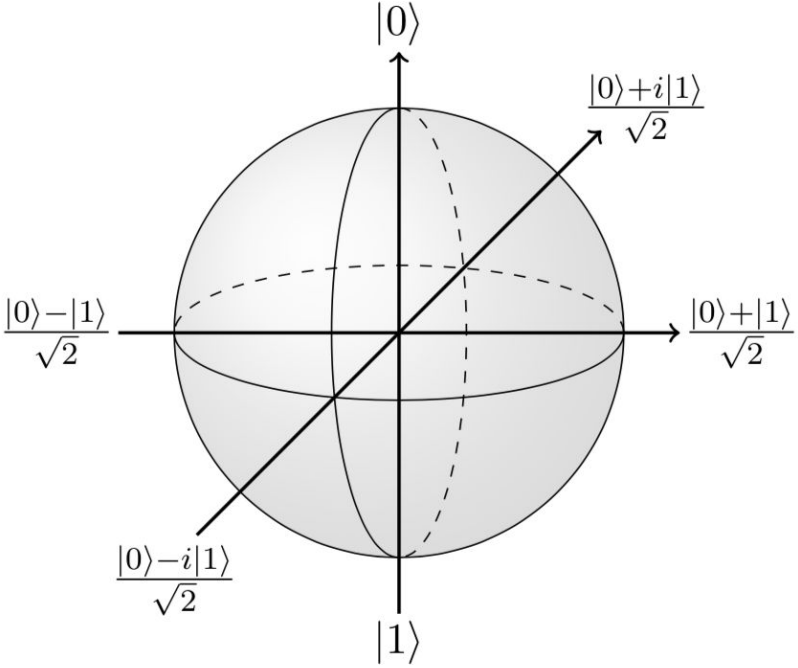
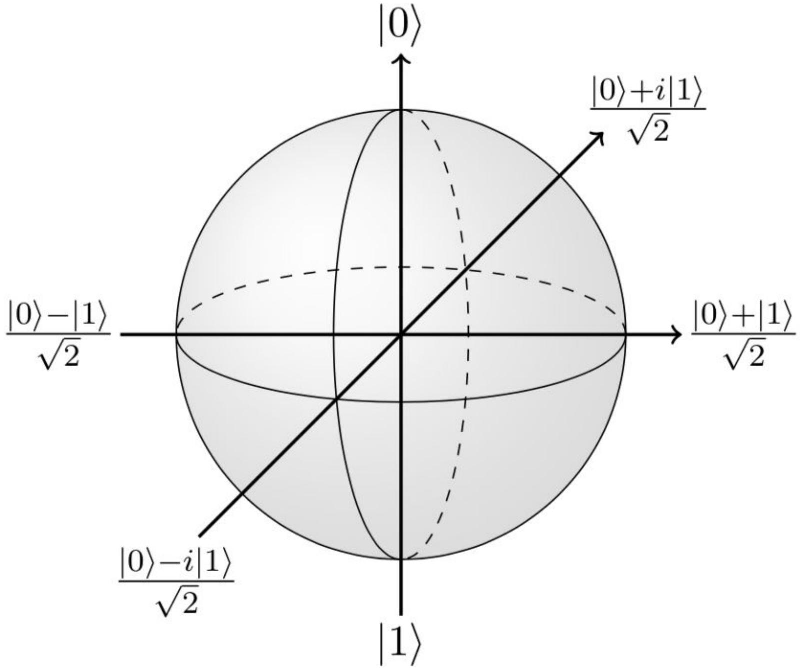
The **Bloch Sphere** depicts all possible normalized spin states



# Rotations on the Bloch Sphere



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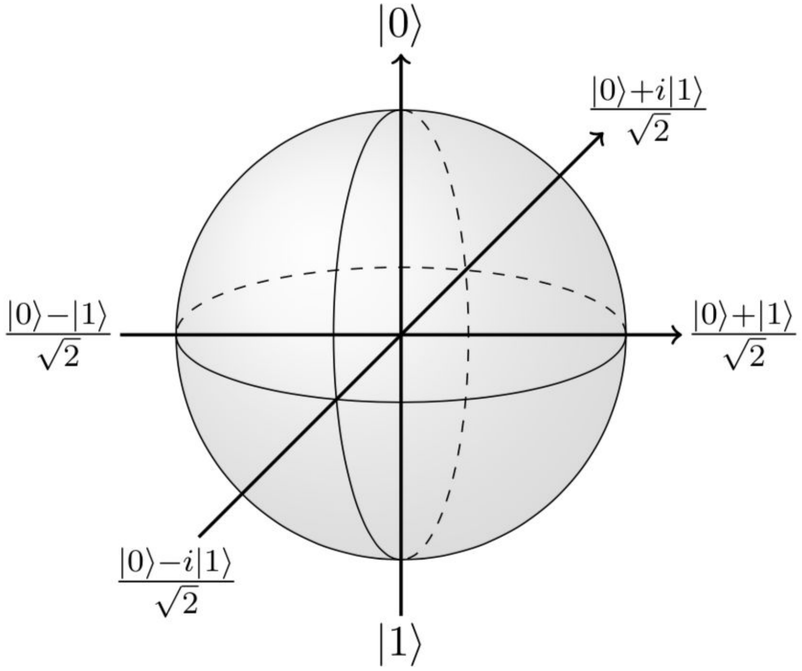


$$\hat{R}_\mu(\theta) = e^{i\frac{\theta}{2}\sigma_\mu} = \cos(\tfrac{\theta}{2})I - i\sin(\tfrac{\theta}{2})\sigma_\mu$$

$$\mu = x, y, \mathrm{or} z$$

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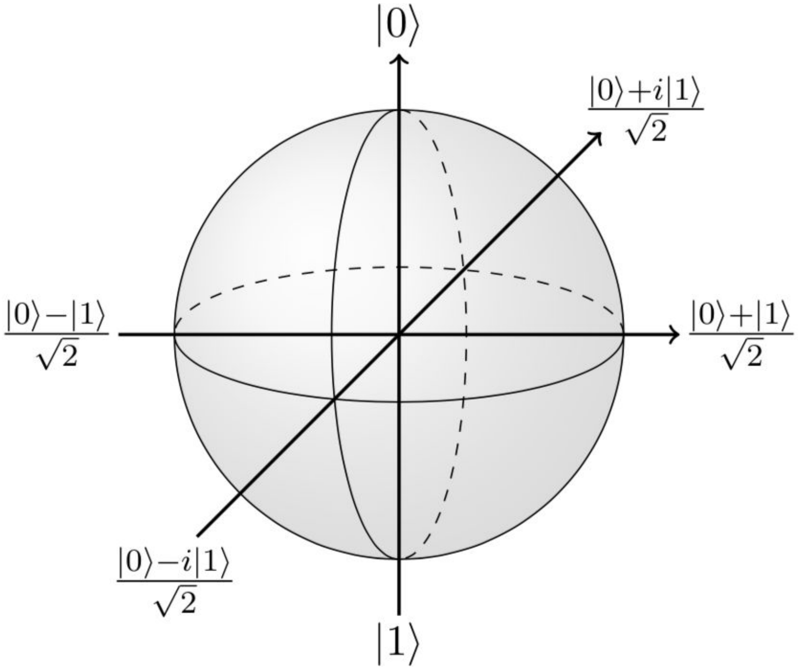


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$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Pauli Matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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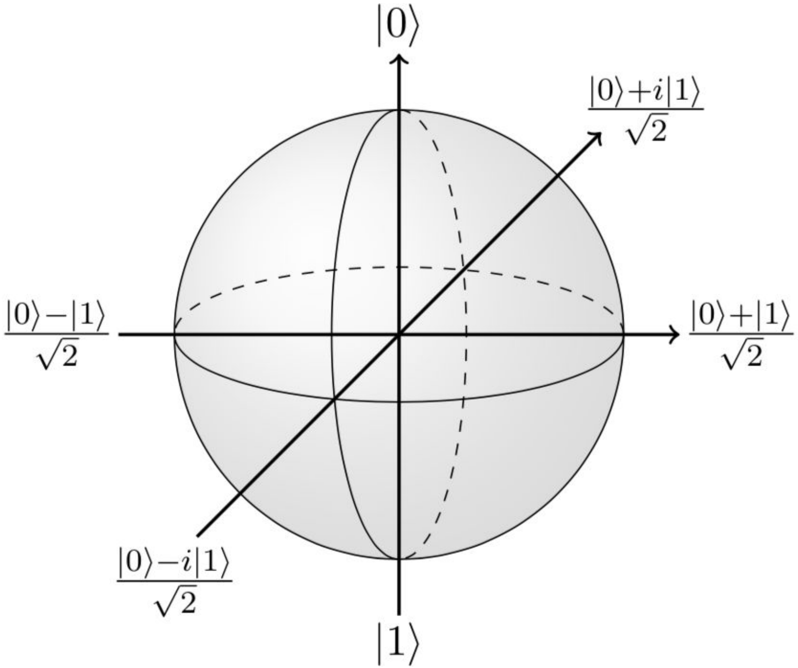


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$$\begin{aligned} \hat{R}_x(2\pi)|\psi\rangle &= (\cos(\pi)I - i\sin(\pi)\sigma_x)|\psi\rangle \\ &= -I|\psi\rangle \\ &= -|\psi\rangle \end{aligned}$$

# Summary

- 360 degree rotations give a minus sign to the spin state of an isolated electron
- 720 degree rotations give back the original spin state
- Since the exchange of two electrons in a many-electron system is mathematically equivalent to a rotation of each particle by 180 degrees (or, the frame of one particle is rotated by 360), this property must extend to all many-electron wavefunctions

This is strange, isn’t it?

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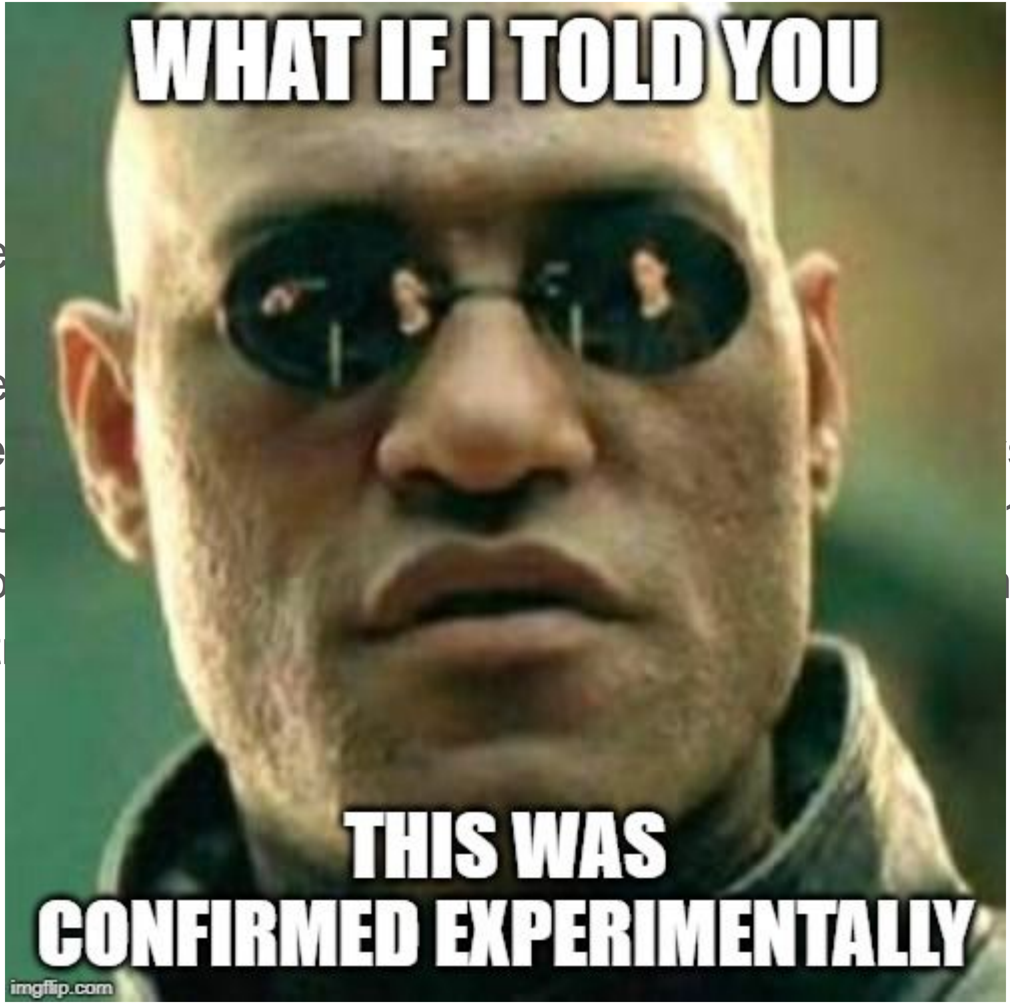
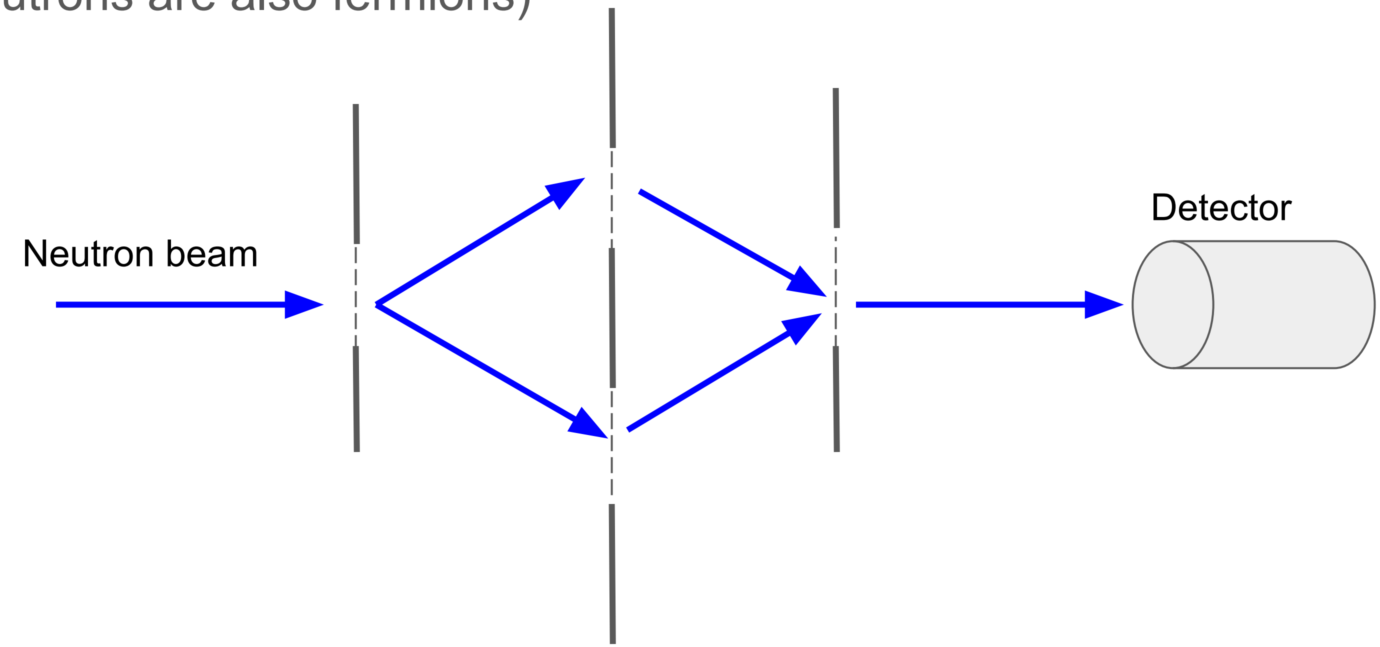


# Neutron Interferometry

(Neutrons are also fermions)



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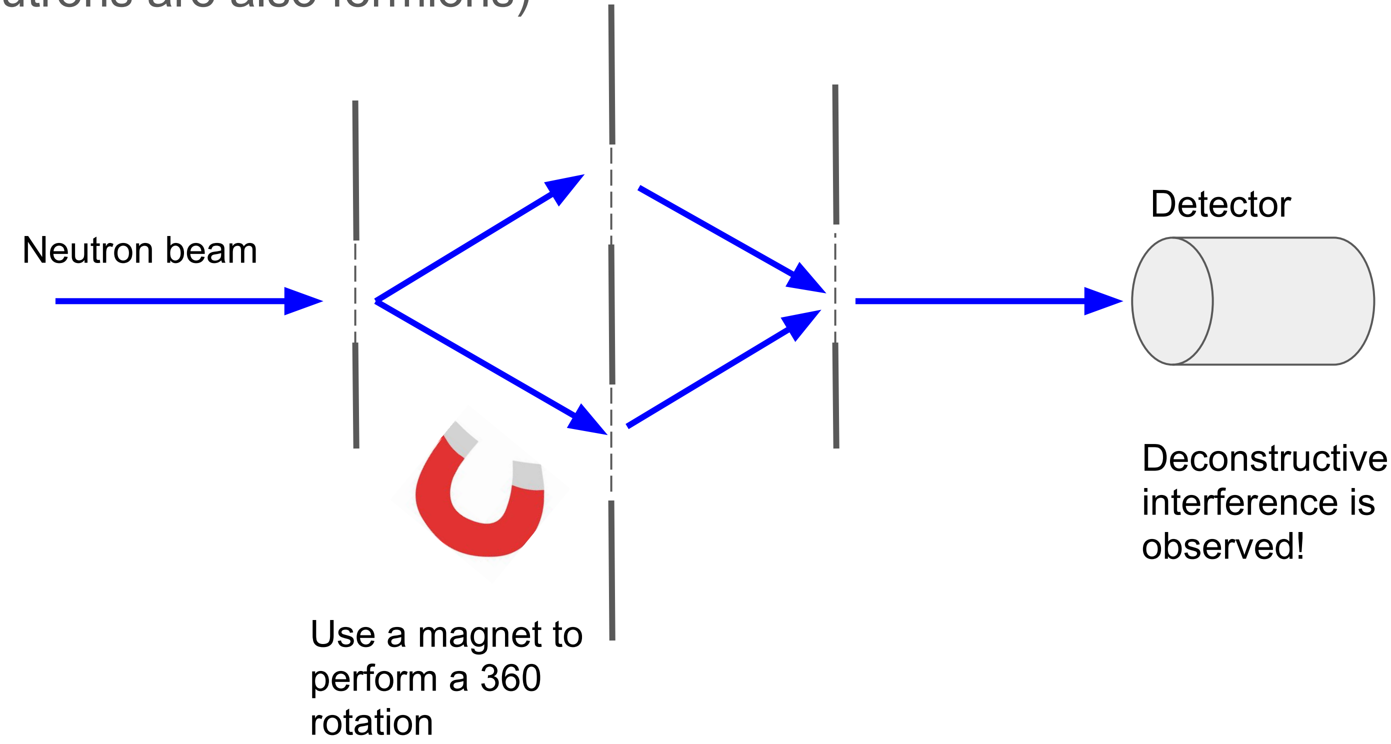
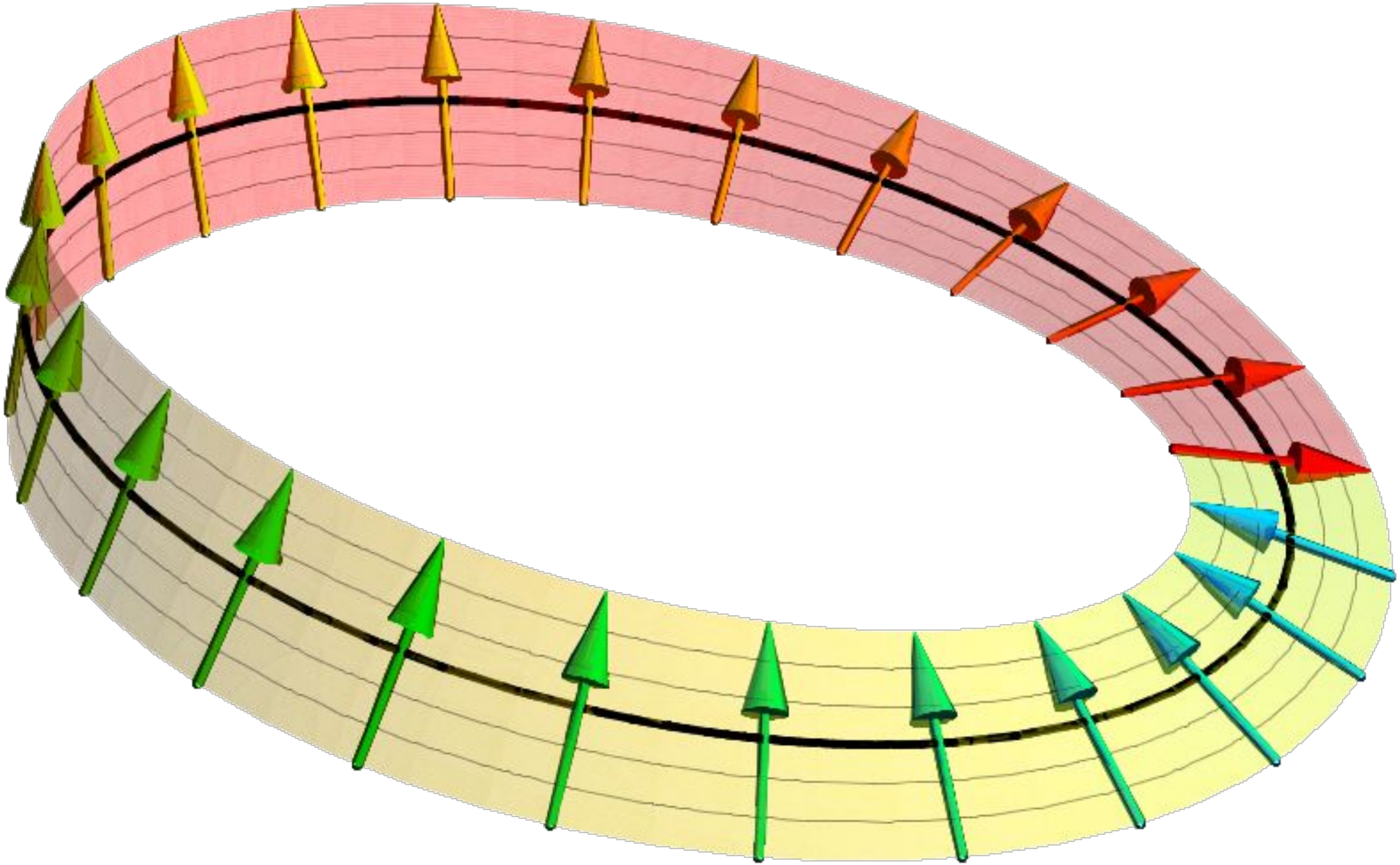
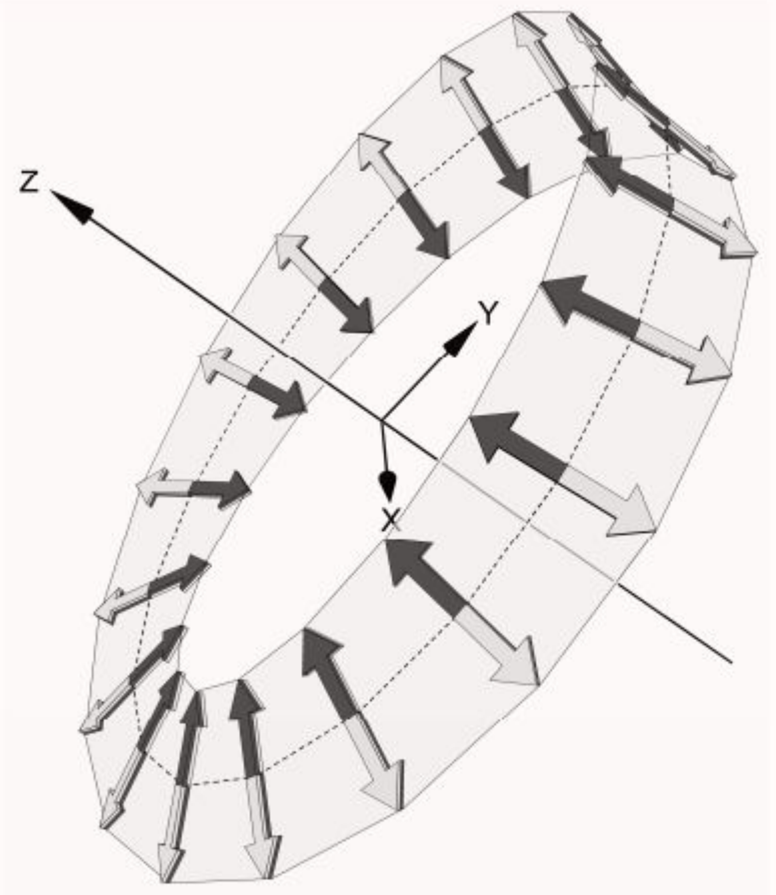


# This is very weird.

Most everyday objects return to themselves after 360 degree rotation;

nothing changes… right?





Z
Y
X

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**Pompous chemist #3:** “*Actually,* it is because fermions are *spinors*. They have the fundamental property that 360 degrees of rotation of the state gives a minus sign, with 720 degree periodicity. Exchange of identical fermions is equivalent to a 360 degree rotation, and must result in a sign flip of the total N-electron wavefunction.”

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