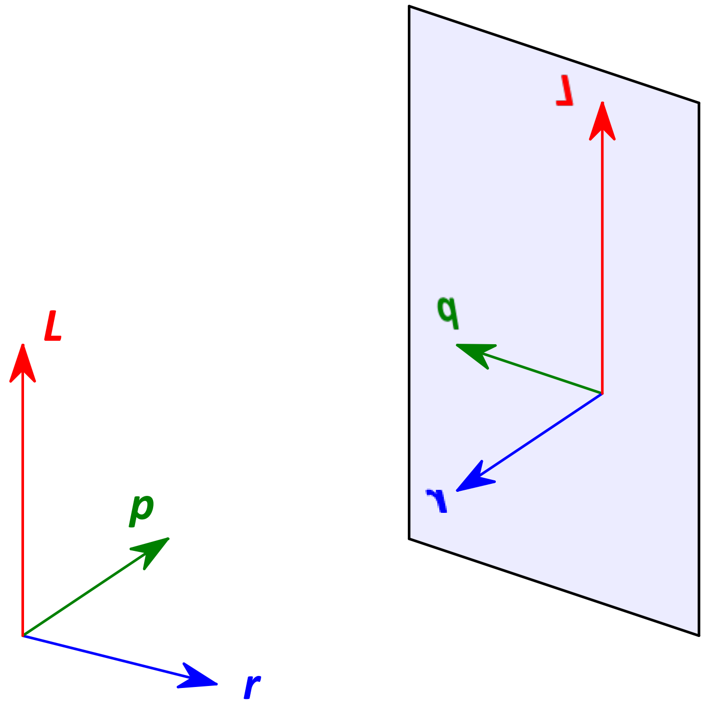
Today in Physics 237: parity

- Conservation laws, more generally
- Inversion symmetry and parity conservation
- Vectors and pseudovectors
- Parity selection rules:
  - Radiative transitions between quantum states
  - Permitted and forbidden transitions



Two things we may mean by Conservation

- Here are two ways to express conservation. We can easily show them to be equivalent:

  1. *Q* is conserved if its expectation value $\langle Q\rangle$ is independent of time.
  2. *Q* is conserved if the probability of observing any particular value of *Q* in a state *f*, say $q\left|f\right\rangle=\hat{Q}\left|f\right\rangle$, is independent of time.

- Let's suppose for simplicity that there is no explicit time dependence: $\partial Q/\partial t=0$.

- In this case, the Ehrenfest theorem (Lecture 11) says that $d\langle Q\rangle/dt=0$ if $\left[\hat{H},\hat{Q}\right]=0$.

- What would $\left[\hat{H},\hat{Q}\right]=0$ imply about the probability of observing any particular value of *Q*?

  - Recall that if $\left[\hat{H},\hat{Q}\right]=0$, then there is a complete set of states which are eigenstates of both $\hat{H}$ and $\hat{Q}$.
  - If $\hat{Q}\left|f_n\right\rangle=q_n\left|f\right\rangle$, then the probability of observing q_n is $P(q_n)=\left|\left\langle f_n\middle|\Psi(t)\right\rangle\right|^2$.

Conservation (continued)

- In terms of the stationary eigenstates of $\hat{H}$, $\left|\psi_n\right\rangle$, and the energy eigenvalues E_n,

$$\left|\Psi(t)\right\rangle = \sum_m e^{-iE_m t/\hbar} c_m \left|\psi_m\right\rangle \quad .$$

- Then assume $\left[\hat{H},\hat{Q}\right]=0$ and choose $\left|f_n\right\rangle = \left|\psi_n\right\rangle$:

$$P\left(q_n\right) = \left|\left\langle\psi_n\middle|\Psi(t)\right\rangle\right|^2 = \left|\sum_m e^{-iE_m t/\hbar} c_m \left\langle\psi_n\middle|\psi_m\right\rangle\right|^2 = \left|c_n\right|^2 \neq f(t),\ \text{q.e.d.}$$

Parity in 1-D

- In 1-D, and in the same language as used for translation $\hat{T}$, parity works like this: $\hat{\Pi}\psi(x) = \psi'(x) = \psi(-x)$.
- Because $\hat{\Pi}\psi(-x) = \psi'(-x) = \psi(x)$, $\hat{\Pi}\hat{\Pi}\psi(x) = \psi(x)$, so $\hat{\Pi}^{-1} = \hat{\Pi}$.
- In G&S problem 6.8, on this week's assignment, you will show that the parity operator is Hermitian too: $\hat{\Pi} = \hat{\Pi}^{\dagger}$.
- And it can transform operators as well as states: $\hat{Q}' = \hat{\Pi}^{\dagger}\hat{Q}\hat{\Pi}$.
  - This, of course, is very similar to how the translation operator works.
- In G&S problem 6.10, also on this week's assignment, you will show that the position and momentum operators have **odd parity**, meaning that their sign changes when $\hat{\Pi}$ is applied:

$$\hat{x}' = \hat{\Pi}^{\dagger}\hat{x}\hat{\Pi} = -\hat{x} \quad , \quad \hat{p}' = \hat{\Pi}^{\dagger}\hat{p}\hat{\Pi} = -\hat{p} \quad .$$

- So, similar to translation (Lecture 25, p. 7; see also Lecture 2, p. 12), we know how $\hat{\Pi}$ transforms any operator $\hat{Q}$:

$$\boxed{\hat{Q}'(\hat{x},\hat{p}) = \hat{\Pi}^{\dagger}\hat{Q}(\hat{x},\hat{p})\hat{\Pi} = \hat{Q}(\hat{x}',\hat{p}') = \hat{Q}(-\hat{x},-\hat{p}) \quad .}$$

Parity in 1-D (continued)

- A system is said to be **inversion-symmetric** if the Hamiltonian does not change under parity transformation, meaning that $\hat{H}$ and $\hat{\Pi}$ commute:

$$\hat{H}' = \hat{\Pi}^\dagger \hat{H} \hat{\Pi} = \hat{H} \quad \Rightarrow \quad \left(\hat{\Pi}\hat{\Pi}^\dagger\right)\hat{H}\hat{\Pi} = \hat{\Pi}\hat{H} \quad \Rightarrow \quad \left[\hat{H},\hat{\Pi}\right] = 0 \quad .$$

- If this Hamiltonian includes a 1-D potential energy *V*(*x*), then *V*(*x*) is inversion symmetric too, meaning that it is an **even** function of *x:* $V(x) = V(-x) \quad .$

- And since in the case of inversion symmetry $\left[\hat{H},\hat{\Pi}\right] = 0$, there is a complete set of states which are simultaneously eigenstates of $\hat{H}$ and $\hat{\Pi}$. Call those states ψ_n :

$$\hat{\Pi}\psi_n(x) = \psi_n(-x) = \pm\psi_n(x) \quad ,$$

since the eigenvalues of $\hat{\Pi}$ are ± 1, as you will also show in G&S problem 6.8.

- Finally, parity is conserved, by either of our definitions, e.g. by the Ehrenfest theorem, $\frac{d}{dt}\langle \Pi \rangle = \frac{i}{\hbar}\left[\hat{H},\hat{\Pi}\right] = 0 \quad .$

Parity in 3-D

- Much the same as 1-D, $\hat{\Pi}\psi(\boldsymbol{r}) = \psi'(\boldsymbol{r}) = \psi(-\boldsymbol{r})$.
- And if we proceed one by one through the Cartesian coordinates, we find that position and momentum still have odd parity:

$$\hat{\boldsymbol{r}}' = \hat{\Pi}^\dagger \hat{\boldsymbol{r}} \hat{\Pi} = -\hat{\boldsymbol{r}} \quad , \quad \hat{\boldsymbol{p}}' = \hat{\Pi}^\dagger \hat{\boldsymbol{p}} \hat{\Pi} = -\hat{\boldsymbol{p}} \quad .$$

- Which once again means we know everything about every operator in 3-D, since

$$\boxed{\hat{Q}'(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}}) = \hat{\Pi}^\dagger \hat{Q}(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}}) \hat{\Pi} = \hat{Q}(\hat{\boldsymbol{r}}',\hat{\boldsymbol{p}}') = \hat{Q}(-\hat{\boldsymbol{r}},-\hat{\boldsymbol{p}}) \quad .}$$

- For example (G&S example 6.2), consider the angular momentum ***L***: how does it transform under parity?

$$\hat{\boldsymbol{L}}' = \hat{\Pi}^\dagger \hat{\boldsymbol{L}} \hat{\Pi} = \hat{\Pi}^\dagger (\hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}) \hat{\Pi} = \hat{\boldsymbol{r}}' \times \hat{\boldsymbol{p}}' = (-\hat{\boldsymbol{r}}) \times (-\hat{\boldsymbol{p}}) = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = \hat{\boldsymbol{L}} \quad .$$

  - So in contrast to the archetypal vectors ***r*** and ***p***, ***L*** has even parity. We call such an object a **pseudovector**, which transforms under rotation like a vector, but has even parity. Cross products of vectors are pseudovectors.

Parity in 3-D (continued)

- Similarly, scalars like $r^2 = \boldsymbol{r}\cdot\boldsymbol{r}$ have even parity: $\left(r^2\right)' = \hat{\Pi}^\dagger r^2 \hat{\Pi} = \hat{\boldsymbol{r}}'\cdot\hat{\boldsymbol{r}}' = (-\hat{\boldsymbol{r}})\cdot(-\hat{\boldsymbol{r}}) = r^2$. But the inner product of a vector and a pseudovector has odd parity, e.g.

  $$(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{L}})' = \hat{\Pi}^\dagger \hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{L}}\hat{\Pi} = \hat{\Pi}^\dagger \hat{\boldsymbol{r}}\cdot(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})\hat{\Pi} = \hat{\boldsymbol{r}}'\cdot(\hat{\boldsymbol{r}}'\times\hat{\boldsymbol{p}}') = (-\hat{\boldsymbol{r}})\cdot\left[(-\hat{\boldsymbol{r}})\times(-\hat{\boldsymbol{p}})\right] = -\hat{\boldsymbol{r}}\cdot(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}) = -\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{L}} \quad .$$

  Naturally we call such objects **pseudoscalars**.

- Central potentials, like the electrostatic potential energy which is part of the Hamiltonian for the hydrogen atom, are scalars, and have even parity in 3-D as they do in 1-D: $V(\boldsymbol{r}) = V(-\boldsymbol{r}) \quad .$

- Thus such Hamiltonians are inversion symmetric, just as they are in 1-D, meaning that $\left[\hat{H},\hat{\Pi}\right] = 0$, meaning furthermore that parity is still conserved in 3-D as in 1-D, and that we can still choose $\hat{H}$ and $\hat{\Pi}$ to have a common set of eigenstates.

- Central potentials in 3-D lead to wavefunctions of the form $\psi_{n\ell m}(\boldsymbol{r}) = R_{n\ell}(r)Y_\ell^m(\vartheta,\varphi)$. We showed in Lecture 23, in the context of the exchange operator $\hat{P}$, that $\hat{\Pi}Y_\ell^m(\vartheta,\varphi) = Y_\ell^m(\pi-\vartheta,\varphi+\pi) = (-1)^\ell Y_\ell^m(\vartheta,\varphi)$, so for the common eigenstate basis of $\hat{H}$ and $\hat{\Pi}$,

  $$\boxed{\hat{\Pi}\psi_{n\ell m}(\boldsymbol{r}) = (-1)^\ell \psi_{n\ell m}(\boldsymbol{r}).}$$

The electric dipole moment, parity, and selection rules

- Toward the end of PHYS 246 you will master time-dependent perturbation theory, with which you can work out the transition rate – probability per unit time – for a system to change from one state to another by emission or absorption of light, in photon form.

- But today you can derive the **selection rules** for those transitions, as this mostly depends on parity.

- The **strongest** transitions – largest probability per unit time, and often called **permitted** transitions – have rates proportional to the matrix element of the electric dipole moment operator, $\hat{\boldsymbol{p}}_e = q\hat{\boldsymbol{r}}$, where q is the electric charge of the quantum involved in the transition, usually an electron ($q = -e$).

- Call the rate $\boldsymbol{R}$, never mind the other physical constants and projection effects which enter, and consider hydrogenic states:

$$\boldsymbol{R} = \langle n'\ell'm'|\hat{\boldsymbol{p}}_e|n\ell m\rangle \quad .$$

- Like $\hat{\boldsymbol{r}}$, $\hat{\boldsymbol{p}}_e$ has odd parity: $\hat{\Pi}^\dagger \hat{\boldsymbol{p}}_e \hat{\Pi} = -\hat{\boldsymbol{p}}_e$.

- Thus $\boldsymbol{R} = \langle n'\ell'm'|\hat{\boldsymbol{p}}_e|n\ell m\rangle = -\langle n'\ell'm'|\hat{\Pi}^\dagger \hat{\boldsymbol{p}}_e \hat{\Pi}|n\ell m\rangle = -\langle n'\ell'm'|(-1)^{\ell'}\, \hat{\boldsymbol{p}}_e\, (-1)^{\ell}|n\ell m\rangle = (-1)^{\ell'+\ell+1}\langle n'\ell'm'|\hat{\boldsymbol{p}}_e|n\ell m\rangle \quad .$

The electric dipole moment, parity, and selection rules (continued)

- If $\ell' + \ell$ is an even number – that is, if the two states have the same parity – then

  $$\langle n'\ell'm' | \hat{\boldsymbol{p}}_e | n\ell m \rangle = -\langle n'\ell'm' | \hat{\boldsymbol{p}}_e | n\ell m \rangle = 0 \quad ,$$

  the transition has $\boldsymbol{R} = 0$.

- So transitions of this sort – **electric dipole transitions** – are **forbidden** between states of like parity. This is called **Laporte's rule** by spectroscopists, and is an example of a selection rule.

- The same would be true for any vector operator on which the rate might depend.

- This also means that for transitions to happen at a nonzero rate, the initial and final states must have different parity: odd and even, or vice versa.
  - This does not mean that parity is not conserved; it means that the emitted or absorbed photon needs to be accounted for in the system's total parity.

The electric dipole moment, parity, and selection rules (continued)

Example (G&S problem 6.11):

Consider the matrix elements of $\hat{\boldsymbol{L}}$ between two definite-parity states: $\langle n'\ell'm'|\hat{\boldsymbol{L}}|n\ell m\rangle$. Under what conditions is this matrix element guaranteed to vanish? Note that the same selection rule would apply to any pseudovector operator, or any (true) scalar operator.

- Easy: proceed the same way as with the dipole moment, using $\hat{\Pi}^{\dagger}\hat{\boldsymbol{L}}\hat{\Pi}=\hat{\boldsymbol{L}}$:

$$\langle n'\ell'm'|\hat{\boldsymbol{L}}|n\ell m\rangle=\langle n'\ell'm'|\hat{\Pi}^{\dagger}\hat{\boldsymbol{L}}\hat{\Pi}|n\ell m\rangle=(-1)^{\ell'+\ell}\langle n'\ell'm'|\hat{\boldsymbol{L}}|n\ell m\rangle=-\langle n'\ell'm'|\hat{\boldsymbol{L}}|n\ell m\rangle=\boxed{0\text{ if }\ell'+\ell\text{ is odd.}}$$

- Most atomic and molecular transitions involve matrix elements of electromagnetic multipoles, in different orders of approximation of time-dependent perturbation theory.
    - You will learn about scary-sounding things like magnetic dipole transitions, electric quadrupole transitions, and so forth, which can be nonzero when the electric dipole matrix elements are zero.
    - Thus forbidden transitions can happen, though at much slower rates than the permitted, electric-dipole types.