The hydrogen atom

Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole moment**, μ, is proportional to its spin angular momentum, **S.**

$$\mu = \gamma \mathbf{S}$$

The proportionality constant, γ , is called the **gyromagnetic ratio.**

The gyromagnetic ratio of an object whose charge and mass are identically distributed is **q/2m**, where **q** is the charge and **m** is the mass.

For reasons that are fully explained only in relativistic quantum theory, the gyromagnetic ratio of the electron is (almost) exactly *twice* the classical value: **γ = –e/m.**

When a magnetic dipole is placed in a magnetic field **B**, it experiences a torque, **μ × B**, which tends to line it up parallel to the field (just like a compass needle).

The hydrogen atom

Electron in a Magnetic Field

The energy associated with this torque is:

$$H = -\boldsymbol{\mu} \cdot \mathbf{B},$$

so the Hamiltonian matrix for a spinning charged particle, at rest in a magnetic field **B**, is:

$$\mathsf{H} = -\gamma \mathbf{B} \cdot \mathsf{S},$$

where S is the appropriate spin matrix:

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The hydrogen atom

Addition of Angular Momenta

Suppose now that we have *two* particles, with spins s_1 and s_2.

$$s_1 \quad \Rightarrow \quad |s_1\, m_1\rangle$$

$$s_2 \quad \Rightarrow \quad |s_2\, m_2\rangle$$

we denote the composite state by: $\quad |s_1\, s_2\, m_1\, m_2\rangle$

$$S^{(1)2} |s_1\, s_2\, m_1\, m_2\rangle = s_1\,(s_1+1)\,\hbar^2\, |s_1\, s_2\, m_1\, m_2\rangle,$$

$$S^{(2)2} |s_1\, s_2\, m_1\, m_2\rangle = s_2\,(s_2+1)\,\hbar^2\, |s_1\, s_2\, m_1\, m_2\rangle,$$

$$S_z^{(1)} |s_1\, s_2\, m_1\, m_2\rangle = m_1\hbar\, |s_1\, s_2\, m_1\, m_2\rangle,$$

$$S_z^{(2)} |s_1\, s_2\, m_1\, m_2\rangle = m_2\hbar\, |s_1\, s_2\, m_1\, m_2\rangle.$$

What is the *total* angular momentum of the system?

$$\mathbf{S} = \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$$

The hydrogen atom

Addition of Angular Momenta

What is the *total* angular momentum of the system? $\mathbf{S} = \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$

What is the net spin, *s*, of the combination, and what is the *z* component, *m*?

The *z* component is easy:

$$S_z \,|s_1\, s_2\, m_1\, m_2\rangle = S_z^{(1)} \,|s_1\, s_2\, m_1\, m_2\rangle + S_z^{(2)} \,|s_1\, s_2\, m_1\, m_2\rangle ,$$
$$= \hbar\,(m_1 + m_2) \,|s_1\, s_2\, m_1\, m_2\rangle = \hbar m \,|s_1\, s_2\, m_1\, m_2\rangle$$

Thus: $m = m_1 + m_2$

The net spin, *s,* is much more subtle. If you combine spin s_1 with spin s_2, what total spins *s* can we get?

The answer is that you get every spin from $(s_1 + s_2)$ down to $(s_1 - s_2)$

or $(s_2 - s_1)$, if $s_2 > s_1$ in integer steps:

$$s = (s_1 + s_2),\; (s_1 + s_2 - 1),\; (s_1 + s_2 - 2),\; \ldots ,\; |s_1 - s_2|.$$

The hydrogen atom

Addition of Angular Momenta

Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another, and the lowest occurs when they are antiparallel.

Example 1: if you package together a particle of spin 3/2 with a particle of spin 2, you could get a total spin of 7/2, 5/2, 3/2, or 1/2, depending on the configuration.

Example 2: If a hydrogen atom is in the state ψ_{nlm}, the net angular momentum of the electron (spin plus orbital) is ℓ +1/2 or ℓ -1/2.

If you now throw in spin of the *proton*, the atom's *total* angular momentum quantum number is ℓ + 1, ℓ, or ℓ - 1 (and ℓ can be achieved in two distinct ways, depending on whether the electron alone is in the ℓ + 1/2 configuration or the ℓ - 1/2 configuration).

The hydrogen atom

Addition of Angular Momenta

The combined state $|sm\rangle$ with total spin s and z-component m will be some linear combination of the composite states $|s_1 s_2 m_1 m_2\rangle$:

$$|s\,m\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} \, |s_1 \, s_2 \, m_1 \, m_2\rangle$$

Because the z components add, the only composite states that contribute are those for which:

$$m_1 + m_2 = m$$

The constants: $C_{m_1 m_2 m}^{s_1 s_2 s}$ are called **Clebsch-Gordan coefficients.**

Example 1: The shaded column of the 2 × 1

$$|3\,0\rangle = \frac{1}{\sqrt{5}}|2\,1\rangle|1-1\rangle + \sqrt{\frac{3}{5}}|2\,0\rangle|1\,0\rangle + \frac{1}{\sqrt{5}}|2-1\rangle|1\,1\rangle$$

If two particles (of spin 2 and spin 1) are at rest in a box, and the *total* spin is 3, and its z component is 0, then a measurement of $S_z^{(1)}$ could return the value $\hbar$ (with probability 1/5), or 0 (with probability 3/5), or $-\hbar$ (with probability 1/5). Notice that the probabilities add up to 1 (the sum of the squares of any column on the Clebsch–Gordan table is 1).

The hydrogen atom

Clebsch-Gordan coefficients $C^{s_1 s_2 s}_{m_1 m_2 m}$

Table 4.8: *Clebsch–Gordan coefficients. (A square root sign is understood for every entry; the minus sign, if present, goes outside the radical.)*

1/2 × 1/2

		1
		+1
+1/2 +1/2	1	

	1	0
	0	0
+1/2 −1/2	1/2	1/2	1
−1/2 +1/2	1/2	−1/2	−1
−1/2 −1/2		1

1 × 1/2

		3/2
		+3/2
+1 +1/2	1	

	3/2	1/2
	+1/2	+1/2
+1 −1/2	1/3	2/3
0 +1/2	2/3	−1/3

	3/2	1/2
	−1/2	−1/2
0 −1/2	2/3	1/3
−1 +1/2	1/3	−2/3

	3/2
	−3/2
−1 −1/2	1

2 × 1

		3
		+3
+2 +1	1	

	3	2
	+2	+2
+2 0	1/3	2/3
+1 +1	2/3	−1/3

	3	2	1
	+1	+1	+1
+2 −1	1/15	1/3	3/5
+1 0	8/15	1/6	−3/10
0 +1	6/15	−1/2	1/10

1 × 1

		2
		+2
+1 +1	1	

	2	1
	+1	+1
+1 0	1/2	1/2
0 +1	1/2	−1/2

	2	1	0
	0	0	0
+1 −1	1/6	1/2	1/3
0 0	2/3	0	−1/3
−1 +1	1/6	−1/2	1/3

	3	2	1
	0	0	0
+1 −1	1/5	1/2	3/10
0 0	3/5	0	−2/5
−1 +1	1/5	−1/2	3/10

	3	2	1
	−1	−1	−1
0 −1	6/15	1/2	1/10
−1 0	8/15	−1/6	−3/10
−2 +1	1/15	−1/3	3/5

	2	1
	−1	−1
0 −1	1/2	1/2
−1 0	1/2	−1/2

	2
	−2
−1 −1	1

	3	2
	−2	−2
−1 −1	2/3	1/3
−2 0	1/3	−2/3

	3
	−3
−2 −1	1

3/2 × 1

		5/2
		+5/2
+3/2 +1	1	

	5/2	3/2
	+3/2	+3/2
+3/2 0	2/5	3/5
+1/2 +1	3/5	−2/5

	5/2	3/2	1/2
	+1/2	+1/2	+1/2
+3/2 −1	1/10	2/5	1/2
+1/2 0	3/5	1/15	−1/3
−1/2 +1	3/10	−8/15	1/6

	5/2	3/2	1/2
	−1/2	−1/2	−1/2
+1/2 −1	3/10	8/15	1/6
−1/2 0	3/5	−1/15	−1/3
−3/2 +1	1/10	−2/5	1/2

	5/2	3/2
	−3/2	−3/2
−1/2 −1	3/5	2/5
−3/2 0	2/5	−3/5

	5/2
	−5/2
−3/2 −1	1

2 × 1/2

		5/2
		+5/2
+2 1/2	1	

	5/2	3/2
	3/2	+3/2
+2 −1/2	1/5	4/5
+1 +1/2	4/5	−1/5

	5/2	3/2
	+1/2	+1/2
+1 −1/2	2/5	3/5
0 +1/2	3/5	−2/5

	5/2	3/2
	−1/2	−1/2
0 −1/2	3/5	2/5
−1 +1/2	2/5	−3/5

	5/2	3/2
	−3/2	−3/2
−1 −1/2	4/5	1/5
−2 +1/2	1/5	−4/5

	5/2
	−5/2
−2 −1/2	1

3/2 × 1/2

		2
		+2
+3/2 +1/2	1	

	2	1
	+1	+1
+3/2 −1/2	1/4	3/4
+1/2 +1/2	3/4	−1/4

	2	1
	0	0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

	2	1
	−1	−1
−1/2 −1/2	3/4	1/4
−3/2 +1/2	1/4	−3/4

	2
	−2
−3/2 −1/2	1

ELECTROMAGNETIC INTERACTIONS

Minimal Coupling

In classical electrodynamics the force on a particle of charge q moving with velocity **v** through electric and magnetic fields **E** and **B** is given by the **Lorentz force law**:

$$\mathbf{F} = q\,(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

This force cannot be expressed as the gradient of a scalar potential energy function, and therefore the Schrödinger equation in its original form cannot accommodate it. But in the more sophisticated form there is no problem:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

The classical Hamiltonian for a particle of charge q and momentum **p**, in the presence of electromagnetic fields is

$$H = \frac{1}{2m}\,(\mathbf{p} - q\mathbf{A})^2 + q\varphi,$$

where **A** is the vector potential and φ is the scalar potential:

$$\mathbf{E} = -\nabla\varphi - \partial\mathbf{A}/\partial t, \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

ELECTROMAGNETIC INTERACTIONS

Minimal Coupling

Making the standard substitution $\mathbf{p} \rightarrow -i\hbar\nabla$, we obtain the Hamiltonian operator

$$\hat{H} = \frac{1}{2m}\left(-i\hbar\nabla - q\mathbf{A}\right)^2 + q\varphi,$$

and the Schrödinger equation becomes:

$$i\hbar\frac{\partial\Psi}{\partial t} = \left[\frac{1}{2m}\left(-i\hbar\nabla - q\mathbf{A}\right)^2 + q\varphi\right]\Psi.$$

This is the quantum implementation of the Lorentz force law; it is sometimes called the **minimal coupling rule.**

IDENTICAL PARTICLES

Two-particle systems:

For a *single* particle, $\Psi(\mathbf{r},t)$ is a function of the spatial coordinates, $\mathbf{r}$, and the time, t (we'll ignore spin, for the moment).

The state of a *two*-particle system is a function of the coordinates of particle one ($\mathbf{r}_1$), the coordinates of particle two ($\mathbf{r}_2$), and the time:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t).$$

Its time evolution is determined by the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi,$$

where H is the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$$

the subscript on ∇ indicates differentiation with respect to the coordinates of particle 1 or particle 2, as the case may be.

IDENTICAL PARTICLES

Two-particle systems:

The statistical interpretation indicates: the probability of finding particle 1 in the volume $d^3\mathbf{r}_1$ and particle 2 in the volume $d^3\mathbf{r}_2$

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2$$

Ψ must be normalised:

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2 = 1.$$

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)e^{-iEt/\hbar},$$

where the spatial wave function (ψ) satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E\psi,$$

where E is the total energy of the system.

IDENTICAL PARTICLES

Two-particle systems:

Solving this is difficult, but two special cases can be reduced to one-particle problems:

1. Noninteracting particles: Suppose the particles do not interact with one another, but each is subject to some external force. For example, they might be attached to two different springs. In that case the total potential energy is the *sum* of the two:

$$V(\mathbf{r}_1, \mathbf{r}_2) = V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2),$$

Using separation of variables: $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2).$

we find that $\psi_a(\mathbf{r}_1)$ and $\psi_b(\mathbf{r}_2)$ each satisfy the one-particle Schrödinger equation:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_a(\mathbf{r}_1) + V_1(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = E_a\psi_a(\mathbf{r}_1),$$

$$-\frac{\hbar^2}{2m_2}\nabla_2^2\psi_b(\mathbf{r}_2) + V_2(\mathbf{r}_2)\psi_b(\mathbf{r}_2) = E_b\psi_b(\mathbf{r}_2),$$

and $E = E_a + E_b$.

IDENTICAL PARTICLES

Two-particle systems:

In this case the two-particle wave function is a simple *product* of one-particle wave functions:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)e^{-i(E_a+E_b)t/\hbar}$$

$$= \left(\psi_a(\mathbf{r}_1)e^{-iE_at/\hbar}\right)\left(\psi_b(\mathbf{r}_2)e^{-iE_bt/\hbar}\right) = \Psi_a(\mathbf{r}_1, t)\Psi_b(\mathbf{r}_2, t),$$

It makes sense to say that particle 1 is in state *a*, and particle 2 is in state *b*.

Any linear combination of such solutions will still satisfy the (time-dependent) Schrödinger:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \frac{3}{5}\Psi_a(\mathbf{r}_1, t)\,\Psi_b(\mathbf{r}_2, t) + \frac{4}{5}\Psi_c(\mathbf{r}_1, t)\,\Psi_d(\mathbf{r}_2, t).$$

The state of particle 1 depends on that of particle 2, and vice versa. If we measured the energy of particle 1, we might get E_a (with probability 9/25), then the energy of particle 2 is definitely E_b, or you might get E_c (probability 16/25), in which case the energy of particle 2 is E_d.

We say that the two particles are **entangled** (Schrödinger's lovely term). An entangled state is one that *cannot* be written as a product of single-particle states.

IDENTICAL PARTICLES

Two-particle systems:

2. Central potentials: Suppose the particles interact *only* with one another, via a potential that depends on their separation:

$$V(\mathbf{r}_1, \mathbf{r}_2) \rightarrow V(|\mathbf{r}_1 - \mathbf{r}_2|).$$

The hydrogen atom would be an example, if you include the motion of the proton. In this case the two-body problem reduces to an equivalent one-body problem.

In general, though, the two particles will be subject both to external forces *and* to mutual interactions, and this makes the analysis more complicated.

Example: potential of the two electrons in a helium atom: each feels the Coulomb attraction of the nucleus (charge 2e), and at the same time they repel one another:

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi\epsilon_0} \left(-\frac{2e^2}{|\mathbf{r}_1|} - \frac{2e^2}{|\mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right).$$

IDENTICAL PARTICLES

Bosons and Fermions

Suppose we have two noninteracting particles, number 1 in the (one-particle) state $\psi_a(\mathbf{r})$, and number 2 in the state $\psi_b(\mathbf{r})$. In that case $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is the product:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2).$$

This assumes that we can tell the particles apart—otherwise it wouldn't make any sense to claim that number 1 is in state ψ_a and number 2 is in state ψ_b; all we could say is that *one* of them is in the state ψ_a and the other is in state ψ_b, but we wouldn't know which is which.

All electrons are *utterly identical*, in a way that no two classical objects can ever be. It's not just that *we* don't know which electron is which.

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We simply construct a wave function that is *noncommittal* as to which particle is in which state. There are actually two ways to do it:

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A\left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\right];$$

IDENTICAL PARTICLES

Bosons and Fermions

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A\left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\right];$$

(Symmetrisation requirement)

The theory admits two kinds of identical particles:

– **bosons** (the plus sign), and

– **fermions** (the minus sign).

Boson states are **symmetric** under interchange, $\psi_+(\mathbf{r}_2, \mathbf{r}_1) = \psi_+(\mathbf{r}_1, \mathbf{r}_2)$; fermion states are **antisymmetric** under interchange, $\psi_-(\mathbf{r}_2, \mathbf{r}_1) = -\psi_-(\mathbf{r}_1, \mathbf{r}_2)$. It so happens that:

$$\begin{cases} \text{all particles with } \textit{integer} \text{ spin are bosons, and} \\ \text{all particles with } \textit{half integer} \text{ spin are fermions.} \end{cases}$$

This **connection between spin and statistics** (bosons and fermions have quite different statistical properties) can be *proved* in *relativistic* quantum mechanics.

IDENTICAL PARTICLES

Bosons and Fermions

T*wo identical fermions* (for example, two electrons) *cannot occupy the same state*.

For if $\psi_a = \psi_b$, we are left with no wave function at all:

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = A\left[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\right] = 0,$$

This is the **Pauli exclusion principle,** which is a consequence of the rules for constructing two-particle wave functions, applying to *all* identical fermions.

IDENTICAL PARTICLES

Exchange Forces

Suppose one particle is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalised.

If the two particles are distinguishable, and number 1 is the one in state ψ_a, then the combined wave function is:

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2);$$

Identical bosons:
$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)];$$

Identical fermions:
$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)].$$

The expectation value of the square of the separation distance between the two particles:

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle.$$

Exchange Forces:

Case 1: Distinguishable particles.

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 \, dx_1 \int |\psi_b(x_2)|^2 \, dx_2 = \langle x^2 \rangle_a$$

(the expectation value of x^2 in the one-particle state ψ_a),

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 \, dx_1 \int x_2^2 |\psi_b(x_2)|^2 \, dx_2 = \langle x^2 \rangle_b,$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 \, dx_1 \int x_2 |\psi_b(x_2)|^2 \, dx_2 = \langle x \rangle_a \langle x \rangle_b.$$

In this case, then,

$$\left\langle (x_1 - x_2)^2 \right\rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b.$$

(Incidentally, the answer would—of course—be the same if particle 1 had been in state ψ_b, and particle 2 in state ψ_a.)

Exchange Forces:

Case 2: Identical particles.

$$\langle x_1^2 \rangle = \frac{1}{2} \left[\int x_1^2 |\psi_a(x_1)|^2 \, dx_1 \int |\psi_b(x_2)|^2 \, dx_2 \right.$$

$$+ \int x_1^2 |\psi_b(x_1)|^2 \, dx_1 \int |\psi_a(x_2)|^2 \, dx_2$$

$$\pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) \, dx_1 \int \psi_b(x_2)^* \psi_a(x_2) \, dx_2$$

$$\left. \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) \, dx_1 \int \psi_a(x_2)^* \psi_b(x_2) \, dx_2 \right]$$

$$= \frac{1}{2} \left[\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0 \right] = \frac{1}{2} \left(\langle x^2 \rangle_a + \langle x^2 \rangle_b \right).$$

Similarly,

$$\langle x_2^2 \rangle = \frac{1}{2} \left(\langle x^2 \rangle_b + \langle x^2 \rangle_a \right).$$

(Naturally, $\langle x_2^2 \rangle = \langle x_1^2 \rangle$, since you can't tell them apart.) But

Exchange Forces:

Case 2: Identical particles.

$$\langle x_1 x_2 \rangle = \frac{1}{2} \left[\int x_1 |\psi_a(x_1)|^2 \, dx_1 \int x_2 |\psi_b(x_2)|^2 \, dx_2 \right.$$

$$+ \int x_1 |\psi_b(x_1)|^2 \, dx_1 \int x_2 |\psi_a(x_2)|^2 \, dx_2$$

$$\pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) \, dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) \, dx_2$$

$$\left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) \, dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) \, dx_2 \right]$$

$$= \frac{1}{2} \left(\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab} \right)$$

$$= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2,$$

where

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) \, dx.$$

Thus

$$\left\langle (x_1 - x_2)^2 \right\rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2.$$

IDENTICAL PARTICLES

Exchange Forces:

Case 2: Identical particles.

Distinguishable particles:
$$\left\langle (x_1 - x_2)^2 \right\rangle_d = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2 \left\langle x \right\rangle_a \left\langle x \right\rangle_b.$$

Identical particles.:
$$\left\langle (x_1 - x_2)^2 \right\rangle_\pm = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2\left\langle x \right\rangle_a \left\langle x \right\rangle_b \mp 2|\left\langle x \right\rangle_{ab}|^2.$$

Difference:
$$\left\langle (\Delta x)^2 \right\rangle_\pm = \left\langle (\Delta x)^2 \right\rangle_d \mp 2\left| \left\langle x \right\rangle_{ab} \right|^2;$$

Identical bosons (the upper signs) tend to be somewhat closer together, and **identical fermions** (the lower signs) somewhat farther apart, than distinguishable particles in the same two states.

$\left\langle x \right\rangle_{ab}$ *vanishes* unless the two wave functions actually *overlap.*

IDENTICAL PARTICLES

Exchange Forces:

Case 2: Identical particles.

The *interesting* case is when the overlap integral is *not* zero.

The system behaves as though there were:

a **"force of attraction"** between identical bosons, **pulling them closer together**, and

a **"force of repulsion"** between identical fermions, **pushing them apart**.

We call it an **exchange force**, although it's not really a force at all—no physical agency is pushing on the particles. **What is it then?**

It is a purely *geometrical* consequence of the symmetrisation requirement. It is also a strictly quantum mechanical phenomenon, with no classical counterpart.

IDENTICAL PARTICLES

Spin:

The *complete* state of an electron (say) includes not only its position wave function, but also a **spinor**, describing the orientation of its **spin**:

$$\psi(\mathbf{r})\chi.$$

In the absence of coupling between spin and position, we are free to assume that the state is *separable* in its spin and spatial coordinates.

The probability of getting spin up is independent of the *location* of the particle.

In the presence of coupling, the general state would take the form of a linear combination:

$$\psi_+(\mathbf{r})\,\chi_+ + \psi_-(\mathbf{r})\,\chi_-.$$

The two-particle state is:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1, 2)$$

Where $\chi(1,2)$ stand for the combined spin state. in Dirac notation it is some linear combination of the states $|s_1 s_2 m_1 m_2\rangle$. We assume that the state is again a simple product of a position state and a spin state.

IDENTICAL PARTICLES

Spin:

The two-particle state is:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1, 2)$$

And it has to be antisymmetric with respect to exchange:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1, 2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)\chi(2, 1).$$

Thus, the Pauli principle actually allows *two* electrons in a given position state, as long as their spins are in the singlet configuration (but they could not be in the same position state *and* in the same spin state—say, both spin up).

$$\left\{ |0\,0\rangle \quad = \quad \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \right\} \quad s = 0 \text{ (singlet)}$$

$$\left\{ \begin{array}{lcl} |1\,1\rangle & = & |\uparrow\uparrow\rangle \\ |1\,0\rangle & = & \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1-1\rangle & = & |\downarrow\downarrow\rangle \end{array} \right\} \quad s = 1 \text{ (triplet)}$$

IDENTICAL PARTICLES

Generalised Symmetrisation Principle

For the sake of simplicity, we have assumed that:

- the particles are noninteracting,

- the spin and position are decoupled (with the combined state a product of position and spin factors), and

- the potential is time-independent.

But the fundamental symmetrisation/antisymmetrisation requirement for identical bosons/fermions is much more general.

Let us define the **exchange operator**, $\hat{P}$, which interchanges the two particles:

$$\hat{P}\,|(1, 2)\rangle = |(2, 1)\rangle$$

$\hat{P}$ switches the particles (1 $\leftrightarrow$ 2), exchanging their positions, their spins, and any other properties they might possess.

Here, $\hat{P}^2 = 1$, and the eigenvalues of $\hat{P}$ are ±1. If the two particles are identical, the Hamiltonian must treat them the same:

$$m_1 = m_2 \text{ and } V(\mathbf{r}_1, \mathbf{r}_2, t) = V(\mathbf{r}_2, \mathbf{r}_1, t).$$

Generalised Symmetrisation Principle

It follows that $\hat{P}$ and $\hat{H}$ are compatible observables, $\left[\hat{P}, \hat{H}\right] = 0,$

and hence: $$\frac{d\left\langle \hat{P} \right\rangle}{dt} = 0.$$

If the system starts out in an eigenstate of $\hat{P}$, **symmetric** $\langle \hat{P} \rangle = 1$ or **antisymmetric** $\langle \hat{P} \rangle = -1$, it will stay that way forever.

The **symmetrisation axiom** says that for identical particles the state is not merely *allowed*, but *required* to satisfy:

$$|(1, 2)\rangle = \pm|(2, 1)\rangle,$$

with the plus sign for bosons, and the minus sign for fermions.

IDENTICAL PARTICLES

Generalised Symmetrisation Principle

If you have **n** identical particles, of course, the state must be symmetric or antisymmetric under the interchange of *any two*:

$$|(1, 2, \ldots, i, \ldots, j, \ldots, n))\rangle = \pm|(1, 2, \ldots, j, \ldots, i, \ldots, n))\rangle,$$

This is the **generalised symmetrisation principle**, of which the following equation is a special case.

$$\psi_\pm(\mathbf{r}_1, \mathbf{r}_2) = A\left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\right]$$

It is perfectly possible to imagine a system of two **distinguishable particles** (say, an electron and a positron) for which the Hamiltonian is symmetric, and yet there is no requirement that the state be symmetric (or antisymmetric).

Identical particles have to occupy symmetric or antisymmetric states, and this is a *new fundamental law*—on a par, logically, with Schrödinger's equation and the statistical interpretation.

Quantum mechanics allows for the *possibility* of identical particles.

IDENTICAL PARTICLES

Atoms:

A neutral atom, of atomic number Z, consists of a heavy (assumed stationary) nucleus, with electric charge Ze, surrounded by Z electrons (mass m and charge $-e$).

The Hamiltonian for this system is:

$$\hat{H} = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^{Z} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}$$

The term in curly brackets represents the kinetic plus potential energy of the jth electron, in the electric field of the nucleus.

The second sum (which runs over all values of j and k except $j = k$) is the potential energy associated with the mutual repulsion of the electrons (the factor of 1/2 in front corrects for the fact that the summation counts each pair twice).

The problem is to solve Schrödinger's equation for the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_z)$:

$$\hat{H}\psi = E\psi,$$

This cannot be solved exactly, except for the very simplest case, $Z = 1$ (hydrogen). We must resort to elaborate approximation methods (you will study them in QM II).

IDENTICAL PARTICLES

Helium:

After hydrogen, the simplest atom is helium (Z = 2).

The Hamiltonian consists of two hydrogenic Hamiltonians (with nuclear charge 2e), one for electron 1 and one for electron 2, together with a final term describing the repulsion of the two electrons.

$$\hat{H} = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

It is this last term that causes all the trouble.

If we simply *ignore* it, the Schrödinger equation separates, and the solutions can be written as products of *hydrogen* wave functions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n\ell m}(\mathbf{r}_1)\psi_{n'\ell'm'}(\mathbf{r}_2),$$

only with half the Bohr radius and four times the Bohr energies.

The total energy would be:

$$E = 4\left(E_n + E_{n'}\right),$$

where: $E_n = -13.6/n^2$ eV.

Helium:

The ground state would be:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a},$$

and its energy would be:

$$E_0 = 8\,(-13.6\,\text{eV}) = -109\,\text{eV}.$$

Because ψ_0 is a symmetric function, the spin state has to be *antisymmetric*, so the ground state of helium should be a *singlet* configuration, with the spins "oppositely aligned."

The *actual* ground state of helium is indeed a singlet, but the experimentally determined energy is –78.975 eV, so the agreement is not very good as we ignored electron–electron repulsion, which is certainly *not* a small contribution.

The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited state:

$$\psi_{n\ell m}\psi_{100}$$

IDENTICAL PARTICLES

Helium:

If we try to put *both* electrons in excited states, one immediately drops to the ground state, releasing enough energy to knock the other one into the continuum ($E > 0$), leaving you with a helium *ion* (He+) and a free electron.

We can construct both symmetric and antisymmetric combinations. The former go with the *antisymmetric* spin configuration (the singlet)—they are called **parahelium**—while the latter require a *symmetric* spin configuration (the triplet)—they are known as **orthohelium**.

The ground state is necessarily parahelium; the excited states come in both forms.

Because the symmetric spatial state brings the electrons closer together, we expect a higher interaction energy in parahelium, and indeed, it is experimentally confirmed that the parahelium states have somewhat higher energy than their orthohelium counterparts.
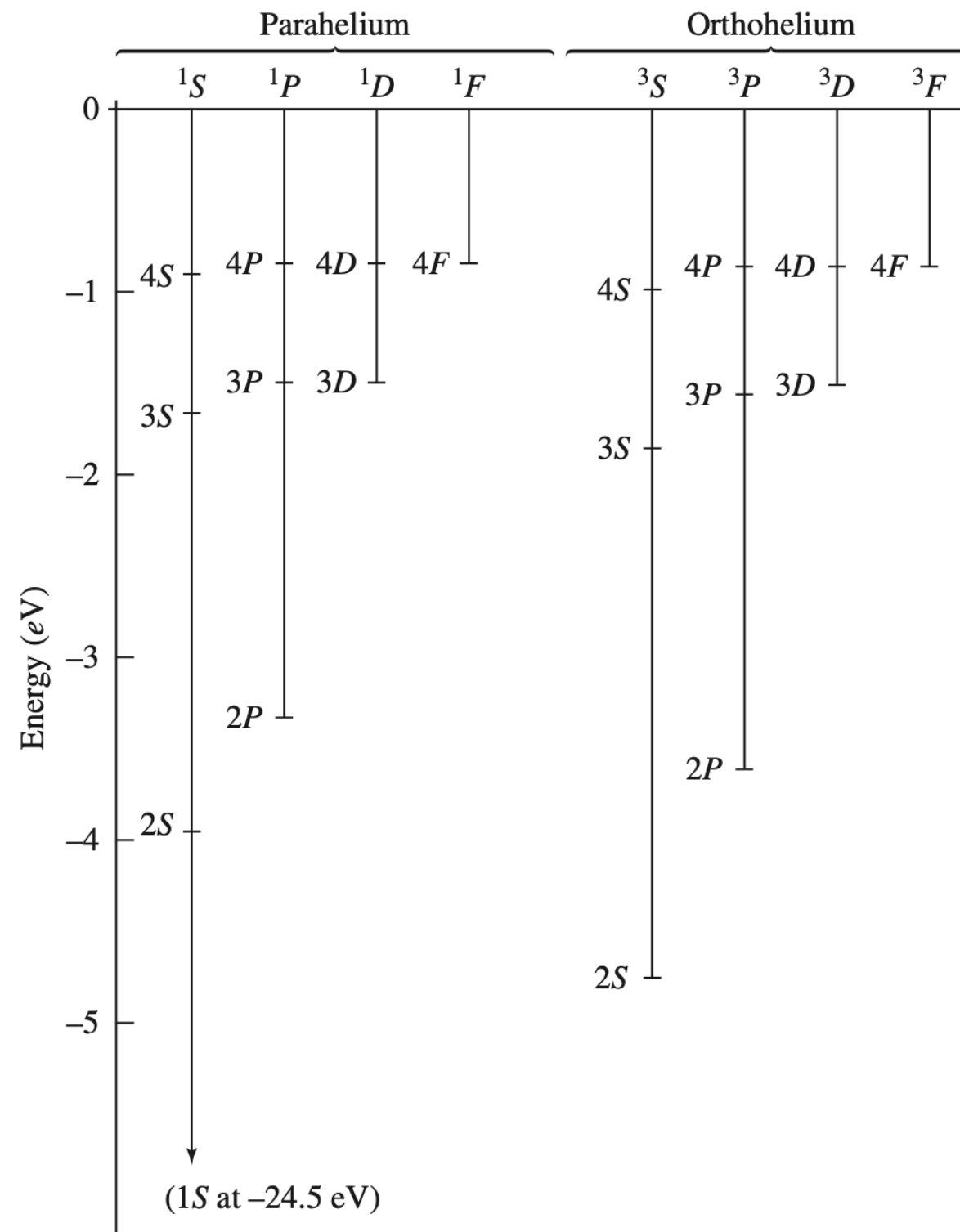
IDENTICAL PARTICLES

Helium:

Figure 5.1: Energy level diagram for helium (the notation is explained in Section 5.2.2). Note that parahelium energies are uniformly higher than their orthohelium counterparts. The numerical values on the vertical scale are relative to the ground state of ionized helium (He$^+$): $4 \times (-13.6)$ eV $= -54.4$ eV; to get the *total* energy of the state, subtract 54.4 eV.

IDENTICAL PARTICLES

The Periodic Table:

The ground state electron configurations for heavier atoms can be pieced together in much the same way.

To first approximation (ignoring their mutual repulsion altogether) the individual electrons occupy one-particle hydrogenic states (n, l, m), called **orbitals**, in the Coulomb potential of a nucleus with charge Ze.

If electrons were bosons (or distinguishable particles) they would all shake down to the ground state $(1, 0, 0)$, but electrons are in fact identical fermions, subject to the Pauli exclusion principle, so only *two* can occupy any given orbital (one with spin up, and one with spin down—or, more precisely, in the singlet configuration).

There are n^2 hydrogenic wave functions (all with the same energy E_n) for a given value of n, so the $n = 1$ **shell** has room for two electrons, the $n = 2$ shell holds eight, $n = 3$ takes 18, and in general the nth shell can accommodate $2n^2$ electrons.

IDENTICAL PARTICLES

The Periodic Table:

Qualitatively, the horizontal rows on the **Periodic Table** correspond to filling out each shell (if this were the whole story, they would have lengths 2, 8, 18, 32, 50, etc., instead of 2, 8, 8, 18, 18, etc.; we'll see in a moment how the electron–electron repulsion throws the counting off).

Group → Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

IDENTICAL PARTICLES

The Periodic Table:

With helium, the $n = 1$ shell is filled, so the next atom, lithium ($Z = 3$), has to put one electron into the $n = 2$ shell. Now, for $n = 2$ we can have $\ell = 0$ or $\ell = 1$; which of these will the third electron choose?

In the absence of electron–electron interactions, they have the same energy (the Bohr energies depend on n, remember, but not on ℓ). But the effect of electron repulsion is to favor the lowest value of ℓ, for the following reason.

Angular momentum tends to throw the electron outward, and the farther out it gets, the more effectively the inner electrons **screen** the nucleus (roughly speaking, the innermost electron "sees" the full nuclear charge Ze, but the outermost electron sees an effective charge hardly greater than e).

Within a given shell, therefore, the state with lowest energy (which is to say, the most tightly bound electron) is $\ell = 0$, and the energy increases with increasing ℓ. Thus the third electron in lithium occupies the orbital (2,0,0). The next atom (beryllium, with $Z = 4$) also fits into this state (only with "opposite spin"), but boron ($Z = 5$) has to make use of $\ell = 1$.

IDENTICAL PARTICLES

The Periodic Table:

For reasons known best to nineteenth-century spectroscopists:

$\ell = 0$ is called s (for "sharp")

$\ell = 1$ is p (for "principal"),

$\ell = 2$ is d ("diffuse"),

$\ell = 3$ is f ("fundamental").

It continues alphabetically (g, h, i, skip j, k, l, etc.)

The state of a particular electron is represented by the pair $n\ell$, with n (the number) giving the shell, and ℓ (the letter) specifying the orbital angular momentum.

The magnetic quantum number m is not listed, but an exponent is used to indicate the number of electrons that occupy the state in question. Thus the configuration:

$$(1s)^2 \, (2s)^2 \, (2p)^2$$

There are two electrons in the orbital (1,0,0), two in the orbital (2,0,0), and two in some combination of the orbitals (2,1,1), (2,1,0), and (2,1,-1). This happens to be the ground state of carbon.

IDENTICAL PARTICLES

The Periodic Table:

The carbon configuration: $(1s)^2 (2s)^2 (2p)^2$

There are two electrons in the orbital (1,0,0), two in the orbital (2,0,0), and two in some combination of the orbitals (2,1,1), (2,1,0), and (2,1,-1). This happens to be the ground state of carbon.

There exist rituals, known as **Hund's Rules** for figuring out what *total* orbital angular momentum quantum number, L, the *total* spin quantum number S, *and* the *grand* total (orbital plus spin), J, will be, for a particular atom.

The result is recorded as the following:

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

The ground state of carbon happens to be $^3P_0$: the total spin is 1 (hence the 3), the total orbital angular momentum is 1 (hence the P), and the *grand* total angular momentum is zero (hence the 0).

ELECTROMAGNETIC INTERACTIONS

The Aharonov–Bohm Effect

In classical electrodynamics the potentials **A** and φ are not uniquely determined; the *physical* quantities are the *fields*, **E** and **B**. Specifically, the potentials

$$\varphi' \equiv \varphi - \frac{\partial \Lambda}{\partial t}, \quad \mathbf{A}' \equiv \mathbf{A} + \nabla \Lambda$$

yield the same fields as φ and **A.** Here, Λ is an arbitrary real function of position and time) This equation is called a **gauge transformation**, and the theory **gauge invariant.**

In quantum mechanics the potentials play a more direct role as they appear in:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{1}{2m} (-i\hbar \nabla - q\mathbf{A})^2 + q\varphi \right] \Psi.$$

They only by a *phase factor*, so they represent the same physical state, and in this sense the theory *is* gauge invariant.

$$\Psi' \equiv e^{iq\Lambda/\hbar} \Psi$$

ELECTROMAGNETIC INTERACTIONS

The Aharonov–Bohm Effect

It was believed that there could be no electromagnetic influences in regions where **E** and **B** are zero.

In 1959 **Aharonov and Bohm** showed that the vector potential *can* affect the quantum behaviour of a charged particle, **even when the particle is confined to a region where the field itself is zero.**

Suppose a particle is moving through a region where **B** is zero (so $\nabla \times \mathbf{A} = \mathbf{0}$), but **A** itself is *not.* Below, $\mathcal{O}$ is some (arbitrarily chosen) reference point.

$$\left[\frac{1}{2m}(-i\hbar\nabla - q\mathbf{A})^2\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t}, \qquad \Psi = e^{ig}\Psi', \qquad \text{where} \qquad g(\mathbf{r}) \equiv \frac{q}{\hbar}\int_{\mathcal{O}}^{\mathbf{r}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}',$$

$$\nabla \times \mathbf{A} = \mathbf{0}$$

The gradient of Ψ is:

$$\nabla\Psi = e^{ig}(i\nabla g)\Psi' + e^{ig}(\nabla\Psi'); \qquad \nabla g = (q/\hbar)\mathbf{A},$$

ELECTROMAGNETIC INTERACTIONS
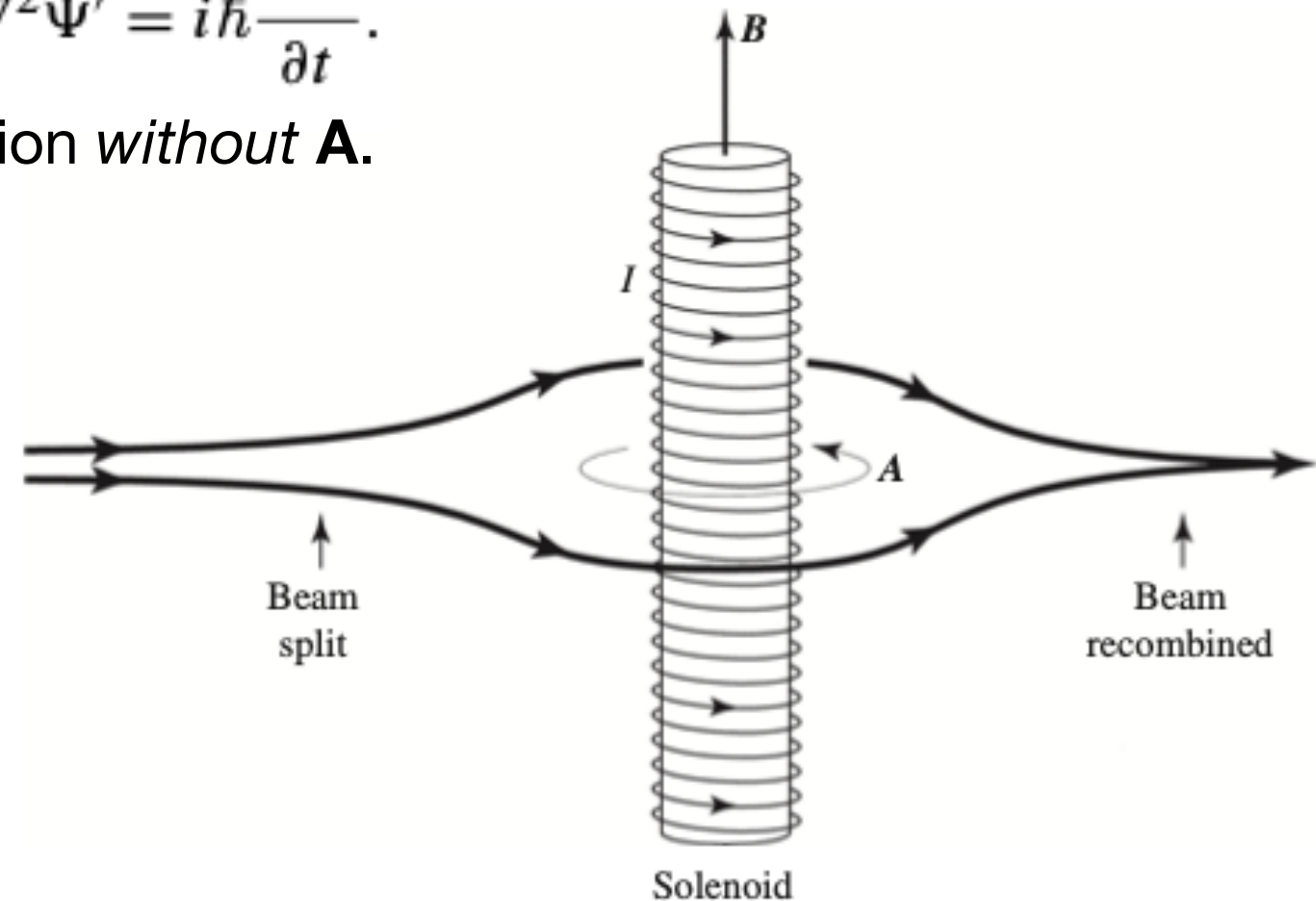
The Aharonov–Bohm Effect

The gradient of Ψ is:

$$\nabla\Psi = e^{ig}\left(i\nabla g\right)\Psi' + e^{ig}\left(\nabla\Psi'\right); \qquad \nabla g = (q/\hbar)\,\mathbf{A},$$

$$(-i\hbar\nabla - q\mathbf{A})\,\Psi = -i\hbar e^{ig}\nabla\Psi',$$

$$(-i\hbar\nabla - q\mathbf{A})^2\,\Psi = -\hbar^2 e^{ig}\nabla^2\Psi'$$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi' = i\hbar\frac{\partial\Psi'}{\partial t}.$$

Evidently Ψ' satisfies the Schrödinger equation *without* **A**.

The Aharonov–Bohm Effect

Aharonov and Bohm proposed an experiment in which a beam of electrons is split in two, and they pass either side of a long solenoid before recombining.

The beams are kept well away from the solenoid itself, so they encounter only regions where **B** = 0. But **A** is *not* zero, and the two beams arrive with *different phases*:
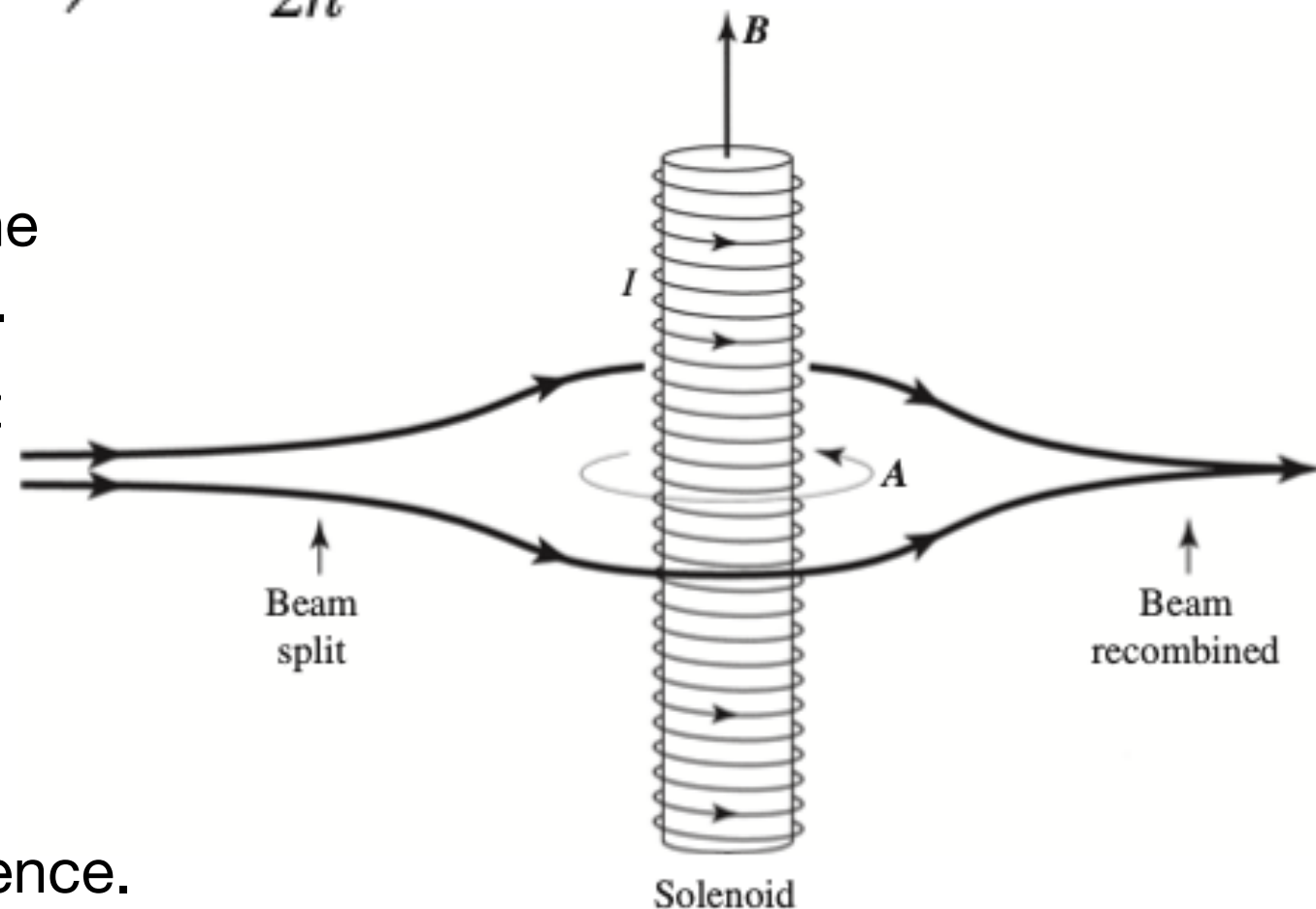
$$g = \frac{q}{\hbar} \int \mathbf{A} \cdot d\mathbf{r} = \frac{q\Phi}{2\pi\hbar} \int \left(\frac{1}{r}\hat{\phi}\right) \cdot \left(r\hat{\phi}\,d\phi\right) = \pm\frac{q\Phi}{2\hbar}.$$

The plus sign applies to the electrons traveling in the same direction as **A**, i.e., in the same direction as the current in the solenoid.

The beams arrive out of phase by an amount proportional to the magnetic flux their paths encircle:

$$\text{phase difference} = \frac{q\Phi}{\hbar}.$$

This phase shift leads to measurable interference.

There *can* be electromagnetic effects in regions where the fields are zero.