The molecular Hamiltonian

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Nonrelativistic electronic Hamiltonian in an electromagnetic field

- classical mechanics of particles
  - Newtonian mechanics (1687)
  - Lagrangian mechanics (1788)
  - Hamiltonian mechanics (1833)
- electromagnetic fields
  - Maxwell's equations (1864)
  - scalar and vector potentials
  - gauge transformations
- spin-free electron in an electromagnetic field
  - the Lagrangian and the Hamiltonian of a particle in an electromagnetic field
  - the Schrödinger equation (1925)
- spinning electron in an electromagnetic field
  - the Schrödinger–Pauli equation (Pauli, 1927)
  - the Dirac equation (1928)

Classical mechanics

- Matter is described by Newton's equations:

$$\mathbf{F}(\mathbf{r}, \mathbf{v}, t) = m\mathbf{a}$$

  - the force defines the system and is obtained from experiment
  - conservative forces (e.g., gravitational forces) are obtained from potentials:

$$\mathbf{F}(\mathbf{r}) = -\boldsymbol{\nabla} V(\mathbf{r})$$

- Radiation is described by Maxwell's equations:

$$\boldsymbol{\nabla} \cdot \mathbf{E} = \rho/\varepsilon_0 \qquad \leftarrow \text{Coulomb's law}$$

$$\boldsymbol{\nabla} \times \mathbf{B} - \varepsilon_0 \mu_0 \, \partial \mathbf{E}/\partial t = \mu_0 \mathbf{J} \qquad \leftarrow \text{Ampère's law}$$

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0$$

$$\boldsymbol{\nabla} \times \mathbf{E} + \partial \mathbf{B}/\partial t = \mathbf{0} \qquad \leftarrow \text{Faraday's law of induction}$$

- The interaction between matter and radiation is described by the Lorentz force:

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

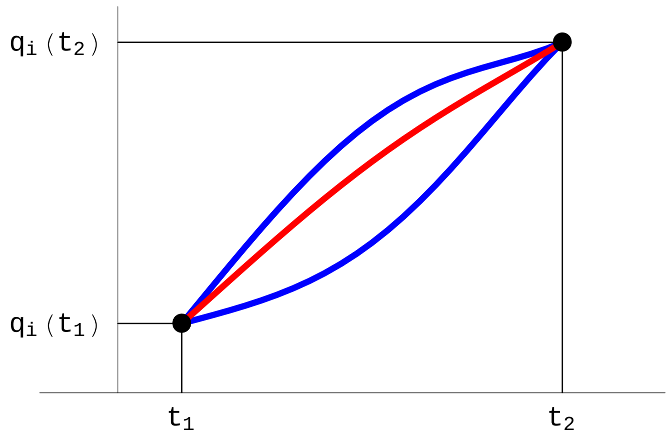
Lagrangian mechanics: the principle of least action

- For a system of n degrees of freedom, there are
  - n generalized coordinates q_i in configuration space
  - n generalized velocities $\dot{q}_i$
- The principle of least action (Hamilton's principle):

  For each system, there exists a Lagrangian $L(q_i, \dot{q}_i, t)$ such that the action integral

$$S = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t)\, \mathrm{d}t$$

  assumes an extremum along the trajectory in configuration space taken by the system.



Lagrange's equations

- From the principle of least action, we obtain

$$\delta S = \delta \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t)\,\mathrm{d}t \;=\; \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q_i}\delta q_i + \frac{\partial L}{\partial \dot{q}_i}\delta \dot{q}_i \right) \mathrm{d}t$$

$$= \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q_i}\delta q_i - \left(\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i \right] \mathrm{d}t = 0$$

- We conclude that the Lagrangian satisfies the following second-order differential equations (one for each degree of freedom):

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}}$$ ← Lagrange's equations of motion

  - the Lagrangian defines the system and is determined so that it reproduces the equations of motion consistent with experiment
  - Lagrange's equations preserve their form in any coordinate system

- A more general formulation than the Newtonian one:
  - unified description of matter and fields (Newton's and Maxwell's equations)
  - springboard for quantum mechanics

Arbitrariness of the Lagrangian and gauge transformations

- The scalar Lagrangian is not uniquely defined.
- Assume that the Lagrangian $L(q, \dot{q}, t)$ satisfies the equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q}.$$

- Consider now the following transformed Lagrangian where the arbitrary gauge function $f\,(q, t)$ is independent of the velocity $\dot{q}$:

$$L'\,(q, \dot{q}, t) = L\,(q, \dot{q}, t) + \frac{\mathrm{d}}{\mathrm{d}t} f\,(q, t).$$

- The new Lagrangian satisfies the same equations of motion as the old one:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L'}{\partial \dot{q}} &= \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} + \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial}{\partial \dot{q}}\left(\frac{\partial f}{\partial q}\dot{q} + \frac{\partial f}{\partial t}\right)\\ &= \frac{\partial L}{\partial q} + \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial f}{\partial q} = \frac{\partial}{\partial q}\left(L + \frac{\mathrm{d}}{\mathrm{d}t} f\right) = \frac{\partial L'}{\partial q}.\end{aligned}$$

- This is an example of a gauge transformation.

Conservative systems

- The Lagrangian of a particle in a conservative field may be written as

$$L = \underbrace{T(q,\dot{q})}_{\text{kinetic energy}} - \underbrace{V(q)}_{\text{potential energy}}$$

- The Lagrangian is thus easily set up for any conservative system, in any convenient coordinate system.

- Example: Assuming a Cartesian coordinate system

$$L = \frac{1}{2}mv^2 - V(\mathbf{r}),$$

we find that Lagrange's equations immediately reduce to Newton's equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \mathbf{v}} = \frac{\partial L}{\partial \mathbf{r}} \quad \Rightarrow \quad \frac{\mathrm{d}}{\mathrm{d}t}m\mathbf{v} = -\boldsymbol{\nabla}V(\mathbf{r}) \quad \Rightarrow \quad m\mathbf{a} = \mathbf{F}.$$

- For particles in a (nonconservative) electromagnetic field, the Lagrangian can be cast in a similar but slightly different form as discussed later.

The energy function

- In Lagrangian mechanics, the energy function is defined as:

$$h\left(q,\dot{q},t\right)=\frac{\partial L}{\partial \dot{q}}\dot{q}-L\left(q,\dot{q},t\right).$$

- For a conservative Cartesian system with Lagrangian $L=\frac{1}{2}mv^2-V\left(\mathbf{r}\right)$:

$$h=\frac{\partial L}{\partial \mathbf{v}}\mathbf{v}-L=\frac{\partial T}{\partial \mathbf{v}}\mathbf{v}-\left(T-V\right)=2T-T+V=T+V=\text{total energy}$$

  – more generally, h is equal to the total energy if $T\left(\dot{q}\right)$ is quadratic in $\dot{q}$ and if $V\left(q\right)$ is independent of $\dot{q}$

- The energy function h is conserved if L does not depend explicitly on time:

$$\frac{\mathrm{d}h}{\mathrm{d}t}=-\frac{\partial L}{\partial t}$$

  – proof:

$$\begin{aligned}\frac{\mathrm{d}h}{\mathrm{d}t}&=\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}}\dot{q}\right)-\frac{\mathrm{d}L}{\mathrm{d}t}\\&=\left[\left(\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}}\right)\dot{q}+\frac{\partial L}{\partial \dot{q}}\ddot{q}\right]-\left[\frac{\partial L}{\partial q}\dot{q}+\frac{\partial L}{\partial \dot{q}}\ddot{q}+\frac{\partial L}{\partial t}\right]=-\frac{\partial L}{\partial t}\end{aligned}$$

Generalized momentum

- The generalized momentum p_i conjugate to the generalized coordinate q_i is defined as

$$\boxed{p_i = \frac{\partial L}{\partial \dot{q}_i}} \qquad \leftarrow \text{generalized momentum}$$

- For a conservative system in Cartesian coordinates $L = \frac{1}{2}mv^2 - V(\mathbf{r})$, the conjugate momentum corresponds to the linear momentum:

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} = \frac{1}{2}m\frac{\partial v^2}{\partial \mathbf{v}} = m\mathbf{v} \qquad \leftarrow \text{linear momentum}$$

- The momentum conjugate to a coordinate that does not occur in the Lagrangian is conserved:

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} = 0 \qquad \leftarrow \text{if } L \text{ is independent of } q_i$$

  – such coordinates are said to be cyclic

- Compare: h is conserved if L does not depend explicitly on t,
  p_i is conserved if L does not depend explicitly on q_i

Hamiltonian mechanics

- For a system of n degrees of freedom, there are n second-order differential equations (Lagrange's equations):

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

- The motion is completely specified by the initial values of the n coordinates and the n velocities.
- In this sense, we may view q_i and $\dot{q}_i$ as $2n$ independent variables.
- Alternatively, let us treat q_i and p_i as $2n$ independent variables:

$$\{q_i, \dot{q}_i\} \quad \to \quad \{q_i, p_i\}$$

- Possible advantages of such a scheme:
  - first-order equations
  - better suited to cyclic coordinates

The Hamiltonian

- The differential of the Lagrangian $L\,(q, \dot{q}, t)$ is given by

$$\mathrm{d}L\,(q, \dot{q}, t) = \frac{\partial L}{\partial q}\,\mathrm{d}q + \frac{\partial L}{\partial \dot{q}}\,\mathrm{d}\dot{q} + \frac{\partial L}{\partial t}\,\mathrm{d}t = \dot{p}\,\mathrm{d}q + p\,\mathrm{d}\dot{q} + \frac{\partial L}{\partial t}\,\mathrm{d}t$$

- We now introduce the Hamiltonian, whose differential should be given by:

$$\mathrm{d}H\,(q, p, t) = \frac{\partial H}{\partial q}\,\mathrm{d}q + \frac{\partial H}{\partial p}\,\mathrm{d}p + \frac{\partial H}{\partial t}\,\mathrm{d}t. \tag{1}$$

- The Legendre transformation

$$\boxed{H = p\dot{q} - L} \quad \leftarrow \text{the Hamiltonian function}$$

gives the required differential:

$$\mathrm{d}H = (p\,\mathrm{d}\dot{q} + \dot{q}\,\mathrm{d}p) - (\dot{p}\,\mathrm{d}q + p\,\mathrm{d}\dot{q} + \frac{\partial L}{\partial t}\,\mathrm{d}t) = -\dot{p}\,\mathrm{d}q + \dot{q}\,\mathrm{d}p - \frac{\partial L}{\partial t}\,\mathrm{d}t \tag{2}$$

- A comparison of (1) and (2) yields

$$\boxed{\frac{\partial H}{\partial q} = -\dot{p}, \qquad \frac{\partial H}{\partial p} = \dot{q}} \quad \leftarrow \text{Hamilton's equations of motion}$$

The Hamiltonian as the Legendre transform of the Lagrangian

- The transformation to Hamiltonian mechanics is a Legendre transformation
- The Lagrangian is convex in $\dot{q}$ and may be represented by a conjugate function

$$H(q,p,t) = \max_{\dot{q}} \left[p\dot{q} - L(q,\dot{q},t) \right] \quad \leftarrow \quad \text{Hamiltonian}$$

$$L(q,\dot{q},t) = \max_{p} \left[p\dot{q} - H(q,p,t) \right] \quad \leftarrow \quad \text{Lagrangian}$$

- The two stationary conditions establish the reciprocal relations:

$$p = \frac{\partial L}{\partial \dot{q}} \quad \leftarrow \quad \text{definition of conjugate momentum } p$$

$$\dot{q} = \frac{\partial H}{\partial p} \quad \leftarrow \quad \text{Hamilton's equation of motion for } q$$

- Hamilton's equation for $\dot{p}$ is obtained from Lagrange's equation of motion

$$\dot{p} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q} = -\frac{\partial H}{\partial q} \quad \leftarrow \quad \text{Hamilton's equation of motion for } p$$

where the last relation follows by differentiating the Legendre transformation.

Prescription for setting up the Hamiltonian

1. Choose n generalized coordinates q_i.
2. Set up the Lagrangian $L(q_i, \dot{q}_i, t)$ such that
$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} \tag{1}$$
reproduces the equations of motion.
3. Introduce the conjugate momenta
$$p_i = \frac{\partial L}{\partial \dot{q}_i}. \tag{2}$$
4. Construct the Hamiltonian
$$H = \sum_i p_i \dot{q}_i - L(q_i, \dot{q}_i, t) \tag{3}$$
and invert (2) to express the Hamiltonian $H(q_i, p_i)$ in terms of q_i and p_i.
5. Write down Hamilton's equations of motion:
$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{4}$$

Comparison of Lagrangian and Hamiltonian mechanics

Lagrangian mechanics	Hamiltonian mechanics
n second-order equations: $\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$	$2n$ first-order equations: $\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$
q_i are the primary variables in configuration space, $\dot{q}_i$ secondary variables	q_i and p_i are independent variables in phase space, connected only by the equations of motion
the state of the system is determined when the variables $(q_i, \dot{q}_i)$ are known at a given time t	the state of the system is defined by a point (q_i, p_i) in phase space, moving on a trajectory that satisfies Hamilton's equations of motion

Poisson brackets

- The Poisson bracket of two dynamical variables $A\,(q,p,t)$ and $B\,(q,p,t)$ is

$$\{A,B\} = \sum_i \left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i}\frac{\partial A}{\partial p_i} \right)$$

  – the fundamental Poisson brackets among conjugate coordinates and momenta:

$$\{q_i, q_j\} = 0, \quad \{p_i, p_j\} = 0, \quad \{q_i, p_j\} = \delta_{ij}$$

- The total time derivatives are given by

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial q}\dot{q} + \frac{\partial A}{\partial p}\dot{p} + \frac{\partial A}{\partial t} = \frac{\partial A}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial A}{\partial p}\frac{\partial H}{\partial q} + \frac{\partial A}{\partial t},$$

  and may therefore be expressed compactly as

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \{A,H\} + \frac{\partial A}{\partial t}.$$

  – important special cases:

$$\dot{q} = \{q,H\}\,, \quad \dot{p} = \{p,H\}\,, \quad \frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial t}$$

Quantization of a particle in conservative force field

- The Hamiltonian formulation is more general than the Newtonian formulation:
  - it is invariant to coordinate transformations
  - it provides a uniform description of matter and radiation
  - it constitutes the springboard to quantum mechanics
- The Hamiltonian function (the total energy) of a particle in a conservative force field:

$$H(q,p) = \frac{p^2}{2m} + V(q)$$

- Standard rule for quantization (in Cartesian coordinates):
  - perform the substitutions

$$\mathbf{p} \rightarrow -\mathrm{i}\hbar\boldsymbol{\nabla}, \quad H \rightarrow \mathrm{i}\hbar\frac{\partial}{\partial t}$$

  - multiply the resulting expression by the wave function $\Psi(q)$ from the right:

$$\mathrm{i}\hbar\frac{\partial\Psi(q)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(q)\right]\Psi(q)$$

- This approach is sufficient for a treatment of electrons in an electrostatic field.
- It is insufficient for nonconservative systems—that is, for systems in a general electromagnetic field.

Review: Hamiltonian mechanics

- In classical Hamiltonian mechanics, a system of particles is described in terms their positions q_i and conjugate momenta p_i.
- For each such system, there exists a scalar Hamiltonian function $H(q_i, p_i)$ such that the classical equations of motion are given by:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \text{(Hamilton's equations of motion)}$$

- Example: a single particle of mass m in a conservative force field $F(q)$
  - the Hamiltonian function is constructed from a scalar potential:

$$H(q,p) = \frac{p^2}{2m} + V(q), \quad F(q) = -\frac{\partial V(q)}{\partial q}$$

  - Hamilton's equations are equivalent to Newton's equations:

$$\left.\begin{array}{l} \dot{q} = \frac{\partial H(q,p)}{\partial p} = \frac{p}{m} \\ \dot{p} = -\frac{\partial H(q,p)}{\partial q} = -\frac{\partial V(q)}{\partial q} \end{array}\right\} \Rightarrow m\ddot{q} = F(q) \quad \text{(Newton's equations of motion)}$$

- Whereas Newton's equations of motion are second-order differential equations, Hamilton's equations are first-order.
- We must now generalize this approach to particles in an electromagnetic field!

The Lorentz force and Maxwell's equations

- In the presence of an electric field $\mathbf{E}$ and a magnetic field (magnetic induction) $\mathbf{B}$, a classical particle of charge z experiences the Lorentz force:

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

  - since this force depends on the velocity $\mathbf{v}$ of the particle, it is not conservative

- The electric and magnetic fields $\mathbf{E}$ and $\mathbf{B}$ satisfy Maxwell's equations (1861–1868):

$$\begin{aligned}
\boldsymbol{\nabla} \cdot \mathbf{E} &= \rho/\varepsilon_0 && \leftarrow \text{Coulomb's law} \\
\boldsymbol{\nabla} \times \mathbf{B} - \varepsilon_0\mu_0\, \partial\mathbf{E}/\partial t &= \mu_0 \mathbf{J} && \leftarrow \text{Ampère's law with Maxwell's correction} \\
\boldsymbol{\nabla} \cdot \mathbf{B} &= 0 && \\
\boldsymbol{\nabla} \times \mathbf{E} + \partial\mathbf{B}/\partial t &= \mathbf{0} && \leftarrow \text{Faraday's law of induction}
\end{aligned}$$

  - when the charge and current densities $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$ are known, Maxwell's equations can be solved for $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$
  - on the other hand, since the charges (particles) are driven by the Lorentz force, $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$ are functions of $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$

- In the following, we shall consider the motion of particles in a given (fixed) electromagnetic field.

Scalar and vector potentials

- The second, homogeneous pair of Maxwell's equations involve only **E** and **B**:

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0 \tag{1}$$

$$\boldsymbol{\nabla} \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} \tag{2}$$

1. Equation (1) is satisfied by introducing the vector potential **A**:

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0 \quad \Rightarrow \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} \qquad \leftarrow \text{vector potential} \tag{3}$$

2. Inserting Eq. (3) in Eq. (2) and introducing a scalar potential ϕ, we obtain

$$\boldsymbol{\nabla} \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = \mathbf{0} \quad \Rightarrow \quad \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\boldsymbol{\nabla}\phi \qquad \leftarrow \text{scalar potential}$$

- The second pair of Maxwell's equations are thus automatically satisfied by writing

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}$$
$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

- The potentials $(\phi, \mathbf{A})$ contain four rather than six components as in $(\mathbf{E}, \mathbf{B})$.
- They are obtained by solving the first, inhomogeneous pair of Maxwell's equations, which contains ρ and **J**.

Particle in an electromagnetic field

- For a particle in an electromagnetic field, we must set up a Lagrangian such that

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

reduces to Newton's equations with the Lorentz force

$$\mathbf{F} = z\,(\mathbf{E} + \mathbf{v} \times \mathbf{B})\,, \quad \mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

- This is not a conservative system, for which

$$L = T - V, \quad F_i = -\frac{\partial V}{\partial q_i}$$

- Rather, it belongs to a broader class of systems, for which

$$L = T - U, \quad F_i = -\frac{\partial U}{\partial q_i} + \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial U}{\partial \dot{q}_i}\right)$$

- For a particle subject to the Lorentz force, the generalized potential is given by

$$U = z\,(\phi - \mathbf{v} \cdot \mathbf{A}) \quad \leftarrow \text{velocity-dependent potential}$$

and the Lagrangian becomes

$$\boxed{L = T - z\,(\phi - \mathbf{v} \cdot \mathbf{A})} \quad \leftarrow \text{particle in an electromagnetic field}$$

Conjugate momentum in an electromagnetic field

- We recall that, for a conservative system described by Lagrangian of the form

$$L(q,\dot{q}) = T(\dot{q}) - V(q),$$

the conjugate momentum in Cartesian coordinates

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} = m\mathbf{v} \equiv \boldsymbol{\pi}$$

is equal to the linear (kinetic) momentum $\boldsymbol{\pi}$:

$$\boxed{\mathbf{p} = \boldsymbol{\pi}} \quad \leftarrow \text{particle in a conservative field}$$

- By contrast, for a nonconservative system described by Lagrangian

$$L(q,\dot{q}) = T(\dot{q}) - U(q,\dot{q}),$$

the conjugate and kinetic momenta are no longer the same.

- In particular, for a particle in an electromagnetic field

$$L = T - z(\phi - \mathbf{v}\cdot\mathbf{A})$$

we obtain

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} + z\mathbf{A} \quad \Rightarrow \quad \boxed{\mathbf{p} = \boldsymbol{\pi} + z\mathbf{A}} \quad \leftarrow \text{particle in an electromagnetic field}$$

The Hamiltonian in an electromagnetic field

- We recall that, for a conservative system with Lagrangian

$$L = T(\dot{q}) - V(q),$$

where $T(\dot{q})$ is quadratic in $\dot{q}$, the Hamiltonian is given by

$$H = T(\dot{q}) + V(q).$$

- Let us now consider the nonconservative system consisting of a particle in a field

$$L = T(\dot{q}) - U(q,\dot{q}) = \frac{1}{2}mv^2 - z(\phi - \mathbf{v}\cdot\mathbf{A}).$$

- From the conjugate momentum

$$\mathbf{p} = m\mathbf{v} + z\mathbf{A},$$

we obtain the Hamiltonian

$$H = \mathbf{p}\cdot\mathbf{v} - L = \left(mv^2 + z\mathbf{v}\cdot\mathbf{A}\right) - \left(\frac{1}{2}mv^2 - z\phi + z\mathbf{v}\cdot\mathbf{A}\right) = \frac{1}{2}mv^2 + z\phi = T + z\phi.$$

- Expressed in canonical coordinates, the Hamiltonian now becomes:

$$\boxed{H = T + z\phi = \frac{(\mathbf{p}-z\mathbf{A})\cdot(\mathbf{p}-z\mathbf{A})}{2m} + z\phi}$$

  – note: $H = T + U + z\mathbf{v}\cdot\mathbf{A} \neq T + U$

Gauge transformations

- The scalar and vector potentials ϕ and $\mathbf{A}$ are not unique.
- Consider the following transformation of the potentials:

$$\left.\begin{array}{l}\phi' = \phi - \frac{\partial f}{\partial t} \\ \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} f\end{array}\right\} \; f = f(q,t) \quad \leftarrow \text{gauge function of position and time}$$

- This gauge transformation of the potentials does not affect the physical fields:

$$\mathbf{E}' = -\boldsymbol{\nabla}\phi' - \frac{\partial \mathbf{A}'}{\partial t} = -\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}\frac{\partial f}{\partial t} - \frac{\partial \mathbf{A}}{\partial t} - \frac{\partial \boldsymbol{\nabla} f}{\partial t} = \mathbf{E}$$

$$\mathbf{B}' = \boldsymbol{\nabla} \times (\mathbf{A} + \boldsymbol{\nabla} f) = \mathbf{B} + \boldsymbol{\nabla} \times \boldsymbol{\nabla} f = \mathbf{B}$$

- We are free to choose $f(q,t)$ so as to make ϕ and $\mathbf{A}$ satisfy additional conditions.
- In the Coulomb gauge, the gauge function is chosen such that the vector potential becomes divergenceless:

$$\boldsymbol{\nabla} \cdot \mathbf{A} = 0 \qquad \leftarrow \text{Coulomb gauge}$$

- Note: Gauge transformations induce the following transformations:

$$L' = L + z\frac{\mathrm{d}f}{\mathrm{d}t}, \quad \mathbf{p}' = \mathbf{p} + z\boldsymbol{\nabla} f, \quad H' = H - z\frac{\partial f}{\partial t}, \quad T' = T$$

  – however, the equations of motion are unaffected!

Quantization of a particle in an electromagnetic field

- We have now constructed a Hamiltonian function such that Hamilton's equations are equivalent to Newton's equation with the Lorentz force:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \& \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \qquad \Leftrightarrow \qquad m\mathbf{a} = z\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

- To this end, we introduced scalar and vector potentials ϕ and $\mathbf{A}$ such that

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

- In terms of these potentials, the classical Hamiltonian function takes the form

$$H = \frac{\pi^2}{2m} + z\phi, \quad \boldsymbol{\pi} = \mathbf{p} - z\mathbf{A} \quad \leftarrow \text{kinetic momentum}$$

- Quantization is now accomplished in the usual manner, by the substitutions

$$\mathbf{p} \to -\mathrm{i}\hbar\boldsymbol{\nabla}, \quad H \to \mathrm{i}\hbar\frac{\partial}{\partial t}$$

- This results in the following time-dependent Schrödinger equation for a particle in an electromagnetic field:

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} = \frac{1}{2m}\left(-\mathrm{i}\hbar\boldsymbol{\nabla} - z\mathbf{A}\right) \cdot \left(-\mathrm{i}\hbar\boldsymbol{\nabla} - z\mathbf{A}\right)\Psi + z\phi\,\Psi$$

Electron spin

- According to our previous discussion, the nonrelativistic Hamiltonian for an electron in an electromagnetic field is given by:

$$H = \frac{\pi^2}{2m} - e\phi, \quad \boldsymbol{\pi} = -\mathrm{i}\hbar\boldsymbol{\nabla} + e\mathbf{A}$$

- However, this description ignores a fundamental property of the electron: spin.
- Spin was introduced by Pauli in 1927, to fit experimental observations:

$$H = \frac{(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m}\mathbf{B}\cdot\boldsymbol{\sigma} - e\phi$$

where $\boldsymbol{\sigma}$ contains three operators, represented by the two-by-two Pauli spin matrices

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

- The Schrödinger equation now becomes a two-component equation

$$\begin{pmatrix} \frac{\pi^2}{2m} - e\phi + \frac{e\hbar}{2m}B_z & \frac{e\hbar}{2m}(B_x - \mathrm{i}B_y) \\ \frac{e\hbar}{2m}(B_x + \mathrm{i}B_y) & \frac{\pi^2}{2m} - e\phi - \frac{e\hbar}{2m}B_z \end{pmatrix} \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix} = E \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix}$$

  – the two components are only coupled in the presence of an external magnetic field

Spin and relativity

- The introduction of spin by Pauli in 1927 may appear somewhat ad hoc.
- By contrast, spin arises naturally from Dirac's relativistic treatment in 1928.
  - is spin a relativistic effect?
- However, reduction of Dirac's equation to nonrelativistic form yields the Hamiltonian

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m}\mathbf{B} \cdot \boldsymbol{\sigma} - e\phi \neq \frac{\pi^2}{2m} - e\phi$$

  - spin is therefore not a relativistic property of the electron
- Indeed, it is possible to take the factorized form

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi$$

  as the starting point for a nonrelativistic treatment, with unspecified operators $\boldsymbol{\sigma}$.
- All algebraic properties of $\boldsymbol{\sigma}$ then follow from the requirement $(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = p^2$:

$$[\sigma_i, \sigma_j]_+ = 2\delta_{ij}, \quad [\sigma_i, \sigma_j] = 2\textstyle\sum_k \epsilon_{ijk}\sigma_k$$

  - these operators are represented by the two-by-two Pauli spin matrices
- We interpret $\boldsymbol{\sigma}$ by associating an intrinsic angular momentum (spin) with the electron:

$$\mathbf{s} = \hbar\boldsymbol{\sigma}/2$$

Molecular Hamiltonian

- The nonrelativistic Hamiltonian for an electron in an electromagnetic field

$$H = \frac{\pi^2}{2m} + \frac{e}{m}\mathbf{B}\cdot\mathbf{s} - e\phi, \quad \boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}, \quad \mathbf{p} = -i\hbar\boldsymbol{\nabla}$$

  – expanding π^2 and assuming the Coulomb gauge $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$, we obtain

$$\begin{aligned}\pi^2\Psi &= (\mathbf{p} + e\mathbf{A})\cdot(\mathbf{p} + e\mathbf{A})\,\Psi = p^2\Psi + e\mathbf{p}\cdot\mathbf{A}\Psi + e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi \\ &= p^2\Psi + e(\mathbf{p}\cdot\mathbf{A})\Psi + 2e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi = \left(p^2 + 2e\mathbf{A}\cdot\mathbf{p} + e^2A^2\right)\Psi\end{aligned}$$

  – in a molecule, the dominant electromagnetic contribution is from the nuclear charges:

$$\phi = \tfrac{1}{4\pi\epsilon_0}\textstyle\sum_K \frac{Z_K e}{r_K} + \phi_{\mathrm{ext}}$$

- Summing over all electrons and adding pairwise Coulomb interactions, we obtain

$$\begin{aligned}H = &\sum_i \frac{1}{2m}p_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{Ki}\frac{Z_K}{r_{iK}} + \frac{e^2}{4\pi\epsilon_0}\sum_{i>j} r_{ij}^{-1} && \leftarrow \text{zero-order Hamiltonian} \\ &+ \frac{e}{m}\sum_i \mathbf{A}_i\cdot\mathbf{p}_i + \frac{e}{m}\sum_i \mathbf{B}_i\cdot\mathbf{s}_i - e\sum_i \phi_i && \leftarrow \text{first-order Hamiltonian} \\ &+ \frac{e^2}{2m}\sum_i A_i^2 && \leftarrow \text{second-order Hamiltonian}\end{aligned}$$

Detour I: Classical relativistic Hamiltonian

- Hamiltonian for an electron in an electromagnetic field

$$H = \sqrt{m^2c^4 + c^2(\mathbf{p} + e\mathbf{A})^2} - e\phi$$

- Hamilton's equations give us

$$\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}} \quad \Rightarrow \quad \mathbf{p} = \boldsymbol{\pi} - e\mathbf{A} \quad \leftarrow \text{conjugate momentum}$$

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}} \quad \Rightarrow \quad \dot{\boldsymbol{\pi}} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad \leftarrow \text{Lorentz force}$$

where the relativistic kinetic momentum is given by

$$\boldsymbol{\pi} = \frac{m\mathbf{v}}{\sqrt{1 - v^2/c^2}} \quad \leftarrow \text{Lorentz factor} \times \text{nonrelativistic momentum}$$

- Relationship to nonrelativistic mechanics

$$\sqrt{m^2c^4 + c^2\pi^2} = mc^2 + \frac{\pi^2}{2m} + \mathcal{O}\left[(v/c)^2\right]$$

$$\boldsymbol{\pi} = m\mathbf{v} + \mathcal{O}\left[(v/c)^2\right]$$

  - the nonrelativistic limit is obtained as $(v/c)^2 \rightarrow 0$

Detour II: Linearization of Hamiltonian

- The Hamiltonian is given by

$$H = c\sqrt{\pi^2 + m^2c^2} - e\phi$$

but we would like time and space coordinates to appear symmetrically in the equation

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

- Following Dirac, we write

$$\pi^2 + m^2c^2 = (\alpha_x\pi_x + \alpha_y\pi_y + \alpha_z\pi_z + \alpha_0 mc)^2$$

- To determine the α_i, we note that

$$(\alpha_x\pi_x + \alpha_y\pi_y + \cdots)^2 = \alpha_x^2\pi_x^2 + \alpha_y^2\pi_y^2 + (\alpha_x\alpha_y + \alpha_y\alpha_x)\,\pi_x\pi_y + \cdots = \pi_x^2 + \pi_y^2 + \cdots$$

if the α_i operators anticommute

$$\left.\begin{array}{l}\alpha_x^2 = \alpha_y^2 = 1\\ \alpha_x\alpha_y + \alpha_y\alpha_x = 0\end{array}\right\} \Rightarrow [\alpha_i, \alpha_j]_+ = 2\delta_{ij}$$

- The Hamiltonian may now be written as

$$H_{\mathrm{D}} = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi} + \beta mc^2 - e\phi, \quad \boldsymbol{\alpha} = [\alpha_x, \alpha_y, \alpha_z], \quad \beta = \alpha_0$$

Detour III: The Dirac equation

- In matrix representation, the anticommuting operators α_i are represented by four 4×4 matrices

$$\alpha_i = \begin{pmatrix} \mathbf{0} & \sigma_i \\ \sigma_i & \mathbf{0} \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix},$$

where $\mathbf{I}$ is the 2×2 unit matrix and the σ_i are the usual Pauli spin matrices:

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

- In this representation, the Dirac equation

$$\mathrm{i}\hbar \frac{\partial \Psi}{\partial t} = \left(c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta mc^2 - e\phi \right) \Psi$$

therefore has a four-component solution:

$$\mathrm{i}\hbar \begin{pmatrix} \frac{\partial \Psi_1}{\partial t} \\ \frac{\partial \Psi_2}{\partial t} \\ \frac{\partial \Psi_3}{\partial t} \\ \frac{\partial \Psi_4}{\partial t} \end{pmatrix} = \begin{pmatrix} mc^2 - e\phi & 0 & c\pi_z & c(\pi_x - \mathrm{i}\pi_y) \\ 0 & mc^2 - e\phi & c(\pi_x + \mathrm{i}\pi_y) & -c\pi_z \\ c\pi_z & c(\pi_x - \mathrm{i}\pi_y) & -mc^2 - e\phi & 0 \\ c(\pi_x + \mathrm{i}\pi_y) & -c\pi_z & 0 & -mc^2 - e\phi \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}$$

- Positive solutions are associated with electrons (α and β spin), negative with positrons.

Detour IV: The Lévy-Leblond equation

- The time-independent Dirac equation may be written in the form:

$$\begin{pmatrix} -e\phi & c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2mc^2 - e\phi \end{pmatrix} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = (E - mc^2) \begin{pmatrix} \varphi \\ \chi \end{pmatrix}.$$

- Introducing the scaled energy and scaled wave-function component

$$E' = E - mc^2, \quad \chi' = c\chi,$$

  and rearranging, we obtain an equation where c occurs only as c^{-2}:

$$\begin{pmatrix} -e\phi & \boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ \boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2m - c^{-2}e\phi \end{pmatrix} \begin{pmatrix} \varphi \\ \chi' \end{pmatrix} = E' \begin{pmatrix} \varphi \\ c^{-2}\chi' \end{pmatrix}.$$

- Letting $c \to \infty$, we obtain the Lévy-Leblond equation:

$$\begin{pmatrix} -e\phi & \boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ \boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2m \end{pmatrix} \begin{pmatrix} \varphi \\ \chi' \end{pmatrix} = E' \begin{pmatrix} \varphi \\ 0 \end{pmatrix}.$$

- This is the nonrelativistic limit of the Dirac equation—a useful zero-order equation for relativistic perturbation theory.

Detour V: The Schrödinger equation

- The Lévy-Leblond equation is given by (dropping primes):

$$\begin{pmatrix} -e\phi & \boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ \boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2m \end{pmatrix}\begin{pmatrix} \varphi \\ \chi \end{pmatrix} = E\begin{pmatrix} \varphi \\ 0 \end{pmatrix}.$$

- Solving the second equation for χ

$$\chi = \frac{1}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\varphi$$

and substituting the result into the first equation, we obtain

$$\left[\frac{1}{2m}\left(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\right)\left(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\right) - e\phi\right]\varphi = E\varphi$$

- Finally, invoking the identity

$$\left(\boldsymbol{\sigma}\cdot\mathbf{u}\right)\left(\boldsymbol{\sigma}\cdot\mathbf{v}\right) = \mathbf{u}\cdot\mathbf{v} + \mathrm{i}\boldsymbol{\sigma}\cdot\mathbf{u}\times\mathbf{v}$$

we arrive at the two-component Schrödinger equation:

$$\left[\frac{1}{2m}\pi^2 + \frac{1}{2m}\mathrm{i}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\times\boldsymbol{\pi} - e\phi\right]\varphi = E\varphi$$

- In the absence of a vector potential, the second term vanishes:

$$\mathbf{A} = \mathbf{0} \quad \Rightarrow \quad \boldsymbol{\pi}\times\boldsymbol{\pi} = \mathbf{p}\times\mathbf{p} = \mathbf{0}$$

Detour VI: Expansion of the kinetic momentum

- Assuming the Coulomb gauge $\boldsymbol{\nabla}\cdot\mathbf{A}=\mathbf{0}$, we obtain

$$\begin{aligned}\pi^2\Psi &= (\mathbf{p}+e\mathbf{A})\cdot(\mathbf{p}+e\mathbf{A})\,\Psi\\ &= p^2\Psi + e\mathbf{p}\cdot\mathbf{A}\Psi + e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi\\ &= p^2\Psi + e(\mathbf{p}\cdot\mathbf{A})\Psi + 2e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi\\ &= \left(p^2 + 2e\mathbf{A}\cdot\mathbf{p} + e^2A^2\right)\Psi\end{aligned}$$

- Recalling the relation $\boldsymbol{\nabla}\times\mathbf{A}=\mathbf{B}$, we obtain

$$\begin{aligned}(\boldsymbol{\pi}\times\boldsymbol{\pi})\,\Psi &= (\mathbf{p}+e\mathbf{A})\times(\mathbf{p}+e\mathbf{A})\,\Psi\\ &= e\mathbf{p}\times\mathbf{A}\Psi + e\mathbf{A}\times\mathbf{p}\Psi\\ &= e\,(\mathbf{p}\times\mathbf{A})\,\Psi + e\,(\mathbf{p}\Psi)\times\mathbf{A} + e\mathbf{A}\times\mathbf{p}\Psi\\ &= -\mathrm{i}\hbar e\,(\boldsymbol{\nabla}\times\mathbf{A})\,\Psi = -\mathrm{i}\hbar e\mathbf{B}\Psi\end{aligned}$$

- In the Coulomb gauge, the kinetic energy operator is therefore given by:

$$T = \frac{1}{2m}\pi^2 + \frac{1}{2m}\mathrm{i}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\times\boldsymbol{\pi} = \frac{1}{2m}p^2 + \frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e}{m}\mathbf{B}\cdot\mathbf{s} + \frac{e^2}{2m}A^2$$

where we have used $\hbar\boldsymbol{\sigma} = 2\mathbf{s}$.

Detour VII: Electron spin

- The Dirac Hamiltonian does not commute with the orbital angular momentum operator but rather with the operator

$$\mathbf{l} + \frac{\hbar}{2}\boldsymbol{\sigma}$$

- We therefore assign to the electron an intrinsic spin angular momentum

$$\mathbf{s} = \frac{\hbar}{2}\boldsymbol{\sigma}$$

- Likewise, we interpret the Zeeman term by assigning to the electron a magnetic moment

$$\mu_{\mathbf{B}}\boldsymbol{\sigma}\cdot\mathbf{B} = -\mathbf{m}\cdot\mathbf{B}, \quad \mu_{\mathrm{B}} = \frac{e\hbar}{2m}$$

where we have introduced the anomalous spin magnetic moment:

$$\mathbf{m} = -2\mu_{\mathrm{B}}\mathbf{s}$$

- From quantum electrodynamics, one finds that the true spin magnetic moment differs slightly from that given by Dirac's theory:

$$\mathbf{m} = -g\mu_{\mathrm{B}}\mathbf{s}, \quad g \approx 2.002$$