# The molecular Hamiltonian

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# The electronic Hamiltonian in an electromagnetic field

- Classical mechanics of particles
  - Newtonian mechanics (1687)
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- Electromagnetic fields
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- Spin-free electron in an electromagnetic field
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  - the Schrödinger equation (1925)
- Spinning electron in an electromagnetic field
  - the Schrödinger–Pauli equation (Pauli, 1927)
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# Classical mechanics

- The motion of matter is described by Newton's equations:

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

  - the force $\mathbf{F}$ defines the system and is obtained from experiment
  - $m$ and $\mathbf{a}$ are the mass and acceleration of the particle
  - conservative forces (e.g., gravitational forces) are obtained from a potential $V(\mathbf{r})$:

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

- 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:

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

  - $z$ is the charge of the particle

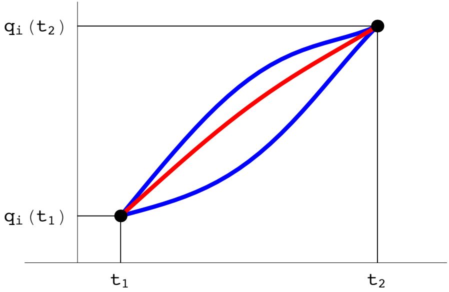
# Lagrangian mechanics: the principle of least action

- 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

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

  is an extremum for the trajectory taken by the system in configuration space



# Lagrange's equations

- From the principle of least action, we obtain

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

- The Lagrangian therefore satisfies the following second-order differential equations:

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

  - there is one such equation for each degree of freedom
- The scalar Lagrangian defines the system:
  - it is determined to reproduce the equations of motion consistent with experiment
  - Lagrange's equations preserve their form in any coordinate system
- The Lagrangian formulation is more general than the Newtonian one:
  - it provides a unified description of matter and fields
  - it represents the springboard for quantum mechanics

# The arbitrariness of the Lagrangian and gauge transformations

- The Lagrangian is not uniquely defined
- Let us 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 $\dot{q}$:

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

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

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

- 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,

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

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

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

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

# Energy and energy conservation

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

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

- Example: for a conservative Cartesian system with $L = \frac{1}{2}mv^2 - V(\mathbf{r})$ we obtain:

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

- $h$ is the total energy whenever $T(\dot{q})$ is quadratic in $\dot{q}$ and $V(q)$ is independent of $\dot{q}$
- The energy function $h$ is conserved if $L$ does not depend explicitly on time:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = -\frac{\partial L}{\partial t} = 0 \quad \leftarrow \text{if } L \text{ is independent of } t$$

  - proof:

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

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

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \quad \leftarrow \text{generalized momentum conjugate to } q$$

- For a conservative system in Cartesian coordinates with Lagrangian

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

the conjugate momentum corresponds to the linear momentum:

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

- The momentum $p_i$ conjugate to $q_i$ is conserved if $L$ does not depend on $q_i$:

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

  - 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:

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

  - the motion is fully specified by the initial values of the $n$ coordinates and $n$ 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:

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

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

- This can be achieved by convex conjugation since:
  - $L$ is convex in $\dot{q}$
  - $p$ is the derivative of $L$ with respect to $\dot{q}$:

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

# Hamiltonian mechanics

- The Lagrangian is convex in $\dot{q}$ and may be represented by its Legendre transform:

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

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

- The two stationary conditions establish the reciprocal relations:

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

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

- The 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

- The Hamiltonian is the energy, whose derivates are the equations of motion:

$$\boxed{\dot{p} = -\frac{\partial H}{\partial q}, \qquad \dot{q} = \frac{\partial H}{\partial p}}$$

# 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, $\dot{q}_i$ are 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 |

- 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 are:

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

- 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

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

- The equations of motion:

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

# 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, in a general electromagnetic field

# Review: Hamiltonian mechanics

- A system of particles is described by their positions $q_i$ and conjugate momenta $p_i$
- For each system, a Hamiltonian $H(q_i, p_i)$ exists with the equations of motion:

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

- 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 equation:

$$\left.\begin{aligned} \dot{q} &= \tfrac{\partial H(q,p)}{\partial p} = \tfrac{p}{m} \\ \dot{p} &= -\tfrac{\partial H(q,p)}{\partial q} = -\tfrac{\partial V(q)}{\partial q} \end{aligned}\right\} \implies m\ddot{q} = F(q) \quad \text{(Newton's equation of motion)}$$

- Newton's equations are second order, 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:

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

  - 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 $\mathbf{B}(\mathbf{r}, t)$

- 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 $\mathbf{E}$ and $\mathbf{B}$:

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

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

1. Equation (1) is satisfied by introducing the vector potential $\mathbf{A}$:

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

2. Inserting Eq. (3) in Eq. (2) and introducing the scalar potential $\phi$, we obtain

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

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

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

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

- 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 $\rho$ and $\mathbf{J}$

- The scalar and vector potentials $\phi$ 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:

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

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

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

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

- In the following, we shall assume the Coulomb gauge (without loss of generality)

# 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

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

- 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 $U$ is given by

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

and the Lagrangian becomes

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

# Conjugate momentum in an electromagnetic field

- We recall that, for a conservative system described by a 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 $\boldsymbol{\pi}$:

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

- 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 different

- In particular, for a particle in an electromagnetic field

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

we obtain the following conjugate momentum:

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} + z\mathbf{A} \implies \mathbf{p} = \boldsymbol{\pi} + z\mathbf{A}$$

# 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:

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

# Quantization of a particle in an electromagnetic field

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

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

- To this end, we introduced scalar and vector potentials $\phi$ 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 gives the 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

- The nonrelativistic Hamiltonian for an electron in an electromagnetic field is:

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

- 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

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

  - spin is therefore not a relativistic property of the electron
  - but we note that, in the nonrelativistic limit, all magnetic fields disappear...
- 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
- To interpret $\boldsymbol{\sigma}$ we associate 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 $\pi^2$ 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 nuclei:

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

- 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

- Relativistic 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 $(v/c)^2 \to 0$

# 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

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

- 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 $\alpha_i$, we note that

$$\begin{aligned}(\alpha_x\pi_x + \alpha_y\pi_y + \cdots)^2 &= \alpha_x^2\pi_x^2 + \alpha_y^2\pi_y^2 + (\alpha_x\alpha_y + \alpha_y\alpha_x)\,\pi_x\pi_y + \cdots \\ &= \pi_x^2 + \pi_y^2 + \cdots\end{aligned}$$

if the $\alpha_i$ operators anticommute

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

- The Hamiltonian may now be written as

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

- In matrix representation, the $\alpha_i$ are represented by four $4 \times 4$ 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 $2 \times 2$ unit matrix and the $\sigma_i$ 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 ($\alpha$ and $\beta$), negative with positrons

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

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

- 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 $\chi$

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

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

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

- 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 $\hbar\boldsymbol{\sigma} = 2\mathbf{s}$.