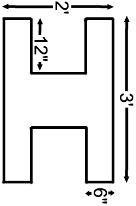


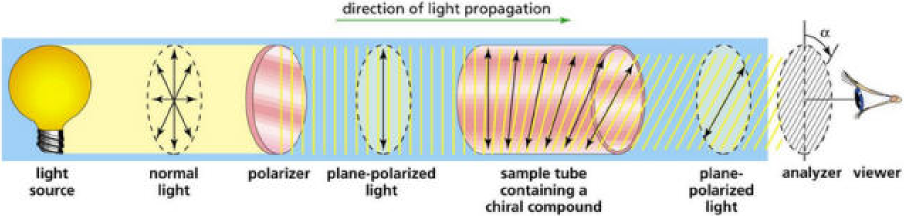

# Constructing the Hamiltonian

**Trond Saue**

Laboratoire de Chimie et Physique Quantiques
CNRS/Université de Toulouse (Paul Sabatier)
118 route de Narbonne, 31062 Toulouse (FRANCE)
e-mail: trond.saue@irsamc.ups-tlse.fr

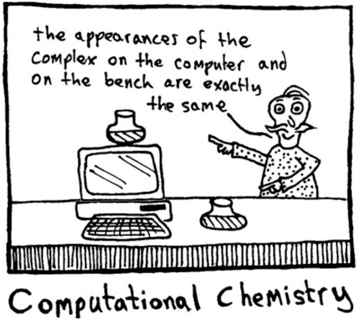
# Experiment vs. theory

Matter is typically probed by electromagnetic radiation.




- The experimentalist works at the **macroscopic level** and typically records the **reponse of the electromagnetic field**.
- The theoretician works at the **microscopic level** and typically calculates the **molecular response**.
- In order to connect experiment and theory
  we must reconcile these two different approaches.

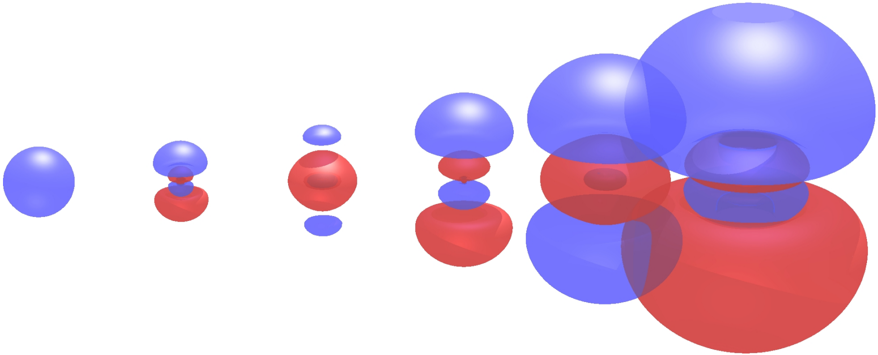
# Asking Nature ... and the computer




The quantum mechanical equivalent of the outcome of a series of experiments is an **expectation value**, e.g.

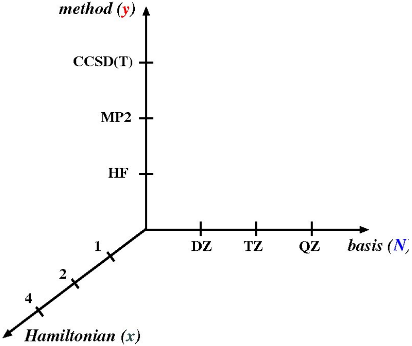
- dipole moment: $\boldsymbol{\mu} = \langle \Psi \left| -e\mathbf{r} \right| \Psi \rangle$
- charge density: $\rho(\mathbf{r}) = \langle \Psi \left| -e\delta(\mathbf{r} - \mathbf{r}') \right| \Psi \rangle$

# Molecular properties and response theory



- $\rho = \rho^{(0)} + \rho^{(1)} F_z + \frac{1}{2!}\rho^{(2)} F_z^2 + \frac{1}{3!}\rho^{(3)} F_z^3 + \frac{1}{4!}\rho^{(4)} F_z^4 + \frac{1}{5!}\rho^{(5)} F_z^5 + \ldots$
- $\mu_i = \int r_i \rho^{(0)} d\tau + \underbrace{\int r_i \rho^{(z)} d\tau}_{\alpha_{iz}} F_z + \frac{1}{2!} \underbrace{\int r_i \rho^{(zz)} d\tau}_{\beta_{izz}} F_z F_z + \ldots$

# Theoretical model chemistries




**Computational cost:** $xN^y$

The electronic Hamiltonian, relativistic or not, has the same generic form

$$\hat{H} = \sum_i \hat{h}(i) + \frac{1}{2}\sum_{i\neq j}\hat{g}(i,j) + V_{NN}; \quad V_{NN} = \frac{1}{2}\sum_{K\neq L}\frac{Z_K Z_L}{R_{KL}}$$

# Components of the electronic Hamiltonian

- **One-electron part:** $\hat{h} = \hat{h}_0 + V_{eN}$
  - non-relativistic case:

$$\hat{h}_0 = \frac{p^2}{2m}$$

  - relativistic case:

$$\hat{h}_0 = \left[ \begin{array}{cc} +mc^2 & c\,(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c\,(\boldsymbol{\sigma} \cdot \mathbf{p}) & -mc^2 \end{array} \right]$$

- **Two-electron part:**
  - non-relativistic case:

$$\hat{g}(1,2) = \frac{1}{r_{12}}$$

  - relativistic case:

$$\hat{g}(1,2) = \frac{1}{r_{12}} + \left\{ \begin{array}{c} \text{magnetic interactions} \\ \text{retardation} \end{array} \right.$$

# Particles and fields

$$H = H_p + H_{\text{int}} + H_f$$

- $H_p$ : Hamiltonian of particle
- $H_f$ : Hamiltonian of electromagnetic field
- $H_{\text{int}}$ : Hamiltonian of interaction
- **In the following we will consider the construction of our Hamiltonian**

# Principle of stationary action

- **The action**

$$S[\mathbf{r}] = \int_{t_a}^{t_b} L(\mathbf{r}, \mathbf{v}, t)\, dt; \quad \mathbf{v} = \frac{d\mathbf{r}}{dt}$$

  - is a *functional* of the particle trajectory $\mathbf{r}(t)$
  - is an integral over the Lagrangian from initial time $t_a$ to final time $t_b$

- The actual trajectory leads to stationary action

$$\delta S = S[\mathbf{r} + \delta\mathbf{r}] - S[\mathbf{r}] = 0; \quad \delta\mathbf{r}(t_a) = \delta\mathbf{r}(t_b) = \mathbf{0}$$

- Derivative of a function

$$f(x) \quad \Rightarrow \quad df = \left(\frac{df}{dx}\right) dx$$

- Derivative of a functional

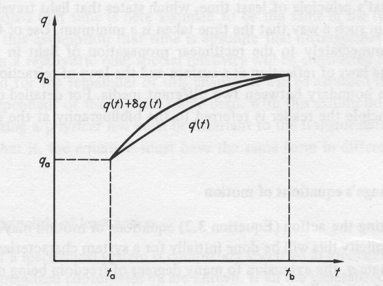
$$E\left[\rho(\mathbf{r})\right] \quad \Rightarrow \quad \delta E = \int \left(\frac{\delta E}{\delta \rho\left(\mathbf{r}\right)}\right) \delta \rho\left(\mathbf{r}\right) d^3\mathbf{r}$$

# Variational calculus

## Stationary action

We seek the minimum:

$$\frac{\delta S}{\delta \mathbf{r}(t)} = 0$$




$$\begin{aligned}
\delta S &= \int_{t_a}^{t_b} \left(\frac{\delta S}{\delta \mathbf{r}(t)}\right) \delta \mathbf{r}(t) dt \\
&= \int_{t_a}^{t_b} \left[L(\mathbf{r}+\delta\mathbf{r}, \mathbf{v}+\delta\mathbf{v}, t) - L(\mathbf{r}, \mathbf{v}, t)\right] dt; \quad \delta\mathbf{r}(t_a) = \delta\mathbf{r}(t_b) = 0 \\
&= \int_{t_a}^{t_b} \left[\left(\frac{\partial L}{\partial \mathbf{r}}\right)\delta\mathbf{r} + \left(\frac{\partial L}{\partial \mathbf{v}}\right)\delta\mathbf{v}\right] dt = 0
\end{aligned}$$

# Variational calculus
## Stationary action

- By partial integration

$$\int_{t_a}^{t_b}\left(\frac{\partial L}{\partial \mathbf{v}}\right)\delta\mathbf{v}dt = \underbrace{\left(\frac{\partial L}{\partial \mathbf{v}}\right)\delta\mathbf{r}\Big|_{t_a}^{t_b}}_{=0} - \int_{t_a}^{t_b}\frac{d}{dt}\left(\frac{\partial L}{\partial \mathbf{v}}\right)\delta\mathbf{r}dt$$

- ...one obtains

$$\delta S = \int_{t_a}^{t_b}\left(\frac{\delta S}{\delta\mathbf{r}(t)}\right)\delta\mathbf{r}(t)dt = \int_{t_a}^{t_b}\left[\left(\frac{\partial L}{\partial \mathbf{r}}\right) - \frac{d}{dt}\left(\frac{\partial L}{\partial \mathbf{v}}\right)\right]\delta\mathbf{r}dt = 0$$

# The Euler-Lagrange equations

$$\left(\frac{\partial L}{\partial \mathbf{r}}\right) - \frac{d}{dt}\left(\frac{\partial L}{\partial \mathbf{v}}\right) = \mathbf{0}$$

- The Lagrangian is chosen so as to give trajectories in accordance with experiments
- General form: $L = T - U$ $\left\{\begin{array}{lll} T(\mathbf{v}) & - & \text{kinetic energy} \\ & & \\ U(\mathbf{r}, \mathbf{v}, t) & - & \text{generalized potential} \end{array}\right.$
- We may re-write the Euler–Lagrange equations as

$$\mathbf{F} = \frac{d}{dt}\left(\frac{\partial T}{\partial \mathbf{v}}\right) = m\mathbf{a} = -\frac{\partial U}{\partial \mathbf{r}} + \frac{d}{dt}\left(\frac{\partial U}{\partial \mathbf{v}}\right)$$

# Choosing the Lagrangian

## Free particle

- Homogeneity of space: no dependence on position $\mathbf{r}$
- Isotropy of space: no dependence on direction of movement
- Homogeneity of time: no dependence on time

$$L(\mathbf{r}, \mathbf{v}, t) \quad \rightarrow \quad L(v) \sim v^2$$

- (Non-relativistic) free particle: $L = T = \frac{1}{2}mv^2 \quad \Rightarrow \quad \mathbf{F} = m\mathbf{a} = 0$

# Hamiltonian

- Legendre transformation

$$H(\mathbf{r},\mathbf{p},t) = \mathbf{p}\cdot\mathbf{v} - L(\mathbf{r},\mathbf{v},t)$$

- Momentum:

$$\frac{\partial H}{\partial \mathbf{v}} = 0; \quad \Rightarrow \quad \mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} - \frac{\partial U}{\partial \mathbf{v}}$$

- Equations of motion:

$$\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial L}{\partial \mathbf{r}} = -\frac{d\mathbf{p}}{dt}; \quad \frac{\partial H}{\partial \mathbf{p}} = \mathbf{v} = \frac{d\mathbf{r}}{dt}$$

- Total time derivative:

$$\frac{dH}{dt} = \frac{\partial H}{\partial \mathbf{r}}\cdot\frac{d\mathbf{r}}{dt} + \frac{\partial H}{\partial \mathbf{p}}\cdot\frac{d\mathbf{p}}{dt} + \frac{\partial H}{\partial t} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$$

- The Hamiltonian is a constant of motion (energy is conserved) when the Lagrangian has no explicit time dependence

# Quantization

## Non-relativistic free particle

1. Determine the Lagrangian who, according to the principle of stationary action, gives the correct equations of motion

$$L_p = \frac{1}{2}mv^2$$

2. Determine momentum $\mathbf{p} = \frac{\partial L_p}{\partial \mathbf{v}} = m\mathbf{v}$
3. Construct the Hamiltonian by a Legendre transform

$$H_p = \mathbf{p}\cdot\mathbf{v} - L_p = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

4. Quantize by replacing classical variables by quantized operators

$$\mathbf{p} \rightarrow \hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}; \quad \mathbf{r} \rightarrow \hat{\mathbf{r}} = \mathbf{r}; \quad E \rightarrow i\hbar\frac{\partial}{\partial t}$$

# Quantization

## Relativistic free particle

1. Lagrangian:

$$L_p^R = -\gamma^{-1} mc^2 = -mc^2 + \frac{1}{2} mv^2 + \frac{1}{8} mv^2 \frac{v^2}{c^2} + \ldots; \quad \gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

2. Momentum: $\mathbf{p} = \gamma m \mathbf{v}$
3. Hamiltonian:

$$H_p^R = \gamma mc^2 = \sqrt{m^2 c^4 + c^2 p^2} = \underbrace{mc^2}_{\text{rest mass}} + \underbrace{\frac{p^2}{2m} - \frac{p^4}{8m^3 c^4} + \ldots}_{\text{kinetic energy}}$$

4. Quantization:
   - ask Dirac

# Equations for particles or fields

- Complete Lagrangian:

$$L = L_{\mathrm{p(articles)}} + L_{\mathrm{int(eraction)}} + L_{\mathrm{f(ields)}}$$

- Interaction term:

$$L_{\text{int}} = \int j_\mu A_\mu d^3\mathbf{r}' = \int \left[\mathbf{j}\left(\mathbf{r}', t\right) \cdot \mathbf{A}\left(\mathbf{r}', t\right) - \rho\left(\mathbf{r}', t\right)\phi\left(\mathbf{r}', t\right)\right] d^3\mathbf{r}'$$

- Fixing the particles (as sources), the term $L_{\mathrm{p}}$ drop out of the equations of motion, and we obtain Maxwell's equations.
- Let us now consider the equations of motion obtained for a single point charge in fixed fields

# Point charge in fixed fields

## Lagrangian

- Point charge with trajectory $\mathbf{r}(t)$:

$$\rho(\mathbf{r}') = q\delta\left(\mathbf{r}' - \mathbf{r}\left(t\right)\right); \quad \mathbf{j}(\mathbf{r}') = q\mathbf{v}'\delta\left(\mathbf{r}' - \mathbf{r}\left(t\right)\right)$$

- Interaction term:

$$\begin{aligned} L_{\text{int}} &= \int \left[\mathbf{j}\left(\mathbf{r}', t\right) \cdot \mathbf{A}\left(\mathbf{r}', t\right) - \rho\left(\mathbf{r}', t\right)\phi\left(\mathbf{r}', t\right)\right] d^3\mathbf{r}' \\ &= q\mathbf{v}(t) \cdot \mathbf{A}(\mathbf{r}\left(t\right), t) - q\phi(\mathbf{r}\left(t\right), t) \end{aligned}$$

- The Euler-Lagrange equation

$$\boldsymbol{\nabla} L - \frac{d}{dt}\left(\frac{\partial L}{\partial \mathbf{v}}\right) = 0; \quad L = L_p + L_{int}$$

- ..can be reformulated as

$$\boldsymbol{\nabla} L_{int} - \frac{d}{dt}\left(\frac{\partial L_{int}}{\partial \mathbf{v}}\right) = \frac{d}{dt}\left(\frac{\partial L_p}{\partial \mathbf{v}}\right) = \frac{d\boldsymbol{\pi}}{dt} = \mathbf{F}$$

# Lorentz force

- We start from

$$\mathbf{F}=\frac{d\boldsymbol{\pi}}{dt}=\boldsymbol{\nabla}L_{int}-\frac{d}{dt}\left(\frac{\partial L_{int}}{\partial\mathbf{v}}\right);\quad \boldsymbol{\pi}=\frac{\partial L_p}{\partial\mathbf{v}}$$

- Working component-wise
  - $\nabla_i L_{int}=q\sum_j v_j\nabla_i A_j-q\nabla_i\phi$
  - $\dfrac{\partial L_{int}}{\partial v_i}=qA_i(\mathbf{r}(t),t)$
  - $\dfrac{d}{dt}\left(\dfrac{\partial L_{int}}{\partial v_i}\right)=q\left[\dfrac{\partial A_i}{\partial t}+\sum_j\dfrac{\partial A_i}{\partial r_j}\dfrac{dr_j}{dt}\right]=q\left[\dfrac{\partial A_i}{\partial t}+\sum_j v_j\nabla_j A_i\right]$
- Putting all together

$$F=q\mathbf{E}+q\left(\mathbf{v}\times\mathbf{B}\right);\quad \begin{array}{rcl}\mathbf{E}&=&-\boldsymbol{\nabla}\phi-\frac{\partial\mathbf{A}}{\partial t}\\ \mathbf{B}&=&\boldsymbol{\nabla}\times\mathbf{A}\end{array}$$

# Point charge in fixed fields

## Hamiltonian

- Momentum

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \boldsymbol{\pi} + q\mathbf{A}; \quad \boldsymbol{\pi} = \frac{\partial L_p}{\partial \mathbf{v}} \quad \text{(mechanical momentum)}$$

- Hamiltonian

$$H(\mathbf{r}, \mathbf{p}, t) = \mathbf{p} \cdot \mathbf{v} - L(\mathbf{r}, \mathbf{v}, t)$$

- We split off
  - $H_p \quad = \boldsymbol{\pi} \cdot \mathbf{v} - L_p$
  - $H_{int} \quad = q\mathbf{A}(\mathbf{r}, t) \cdot \mathbf{v} - L_{int} = q\phi(\mathbf{r}, t)$
- Final result

$$H(\mathbf{r}, \mathbf{p}, t) = H_p(\mathbf{r}, \boldsymbol{\pi}, t) + q\phi(\mathbf{r}, t)$$

- Principle of minimal electromagnetic coupling

$$p_\mu \rightarrow p_\mu - qA_\mu$$

- This relativistic coupling of particles and fields is also used in the non-relativistic domain.

# Principle of minimal electromagnetic coupling

- First reference:
  - M. Gell-Mann, Nuovo Cimento Suppl. **4** (1956) 848 – 866.
- Verification:

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Dear Sir,
allow me to ask you: Are you the originator of the
"principle of minimal electromagnetic coupling", a term found in
a multitude of textbooks and papers, but never with any reference ?
  Best regards,
     Trond Saue
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From Murray Gell-Mann <mgm@santafe.edu>
Subject **Re: principle of minimal electromagnetic coupling** 11/16/2001 11:22 PM
To SAUE TROND

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Dear Trond SAVE,

Yes.

Murray Gell-Mann
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