Reminder: Constrained variation and non-variational wave functions

- If wave function is constructed via constrained variation or in a non-variational manner, in principle response of wave-function parameters needs to be calculated

$$\frac{dE(x)}{dx} = \frac{\partial E}{\partial x} + \frac{\partial E}{\partial c}\frac{\partial c}{\partial x}$$

doesn't vanish

needs hence to be calculated!

- Possible…., will need a set of equations per perturbation → we chose method of Lagrange multipliers instead → avoid to calculate dc/dx

Reminder: method of Lagrange multipliers

- Set up energy functional (Lagrangian L) with side condition f
- Side condition written such that

$$f(x, c(x)) = 0$$

- If those side conditions are fulfilled, Lagrangian is equal to the energy itself: $L = E$
- Lagrangian:

$$L = E + \lambda f$$

side condition

Lagrange multiplier

- Enforce stationarity $\frac{\partial L}{\partial c} \stackrel{!}{=} 0$ and $\frac{\partial L}{\partial \lambda} \stackrel{!}{=} 0$

notice: L, not E!

Gives back side condition f

Reminder: method of Lagrange multipliers

- Hence for the gradient:

$$\frac{dL(x)}{dx} = \frac{\partial L}{\partial x} + \cancel{\frac{\partial L}{\partial c}\frac{\partial c}{\partial x}} + \cancel{\frac{\partial L}{\partial \lambda}\frac{\partial \lambda}{\partial x}}$$

$\frac{\partial L}{\partial c}$ → =0 ; $\frac{\partial L}{\partial \lambda}$ → =0

→We managed to avoid having to solve for response of wave function parameters to perturbation!

$$\frac{dL(x)}{dx} = \frac{\partial L}{\partial x} = \frac{\partial E}{\partial x} + \lambda\frac{\partial f}{\partial x}$$

In addition, as compared to expression for variational methods.

Only contributions from explicit dependence (perturbed integrals) needed

Reminder CC Lagrangian

$$L^{\mathrm{CC}} = \langle \Psi^{\mathrm{HF}} \mid \exp(-\hat{T})\hat{H}\exp(\hat{T}) \mid \Psi^{\mathrm{HF}} \rangle$$

CC energy

$$+ \sum_{p} \lambda_p \langle \Psi_p \mid \exp(-\hat{T})\hat{H}\exp(\hat{T}) \mid \Psi^{\mathrm{HF}} \rangle$$

CC amplitude eqs.

$$+ \sum_{ai} Z_{ai} f_{ai}$$

$$+ \sum_{pq} I_{pq}(S_{pq} - \delta_{pq})$$

Orbital relaxation terms

Brillouin condition (HF eqs. fulfilled)

Orthonormality of MOs (HF side condition)

Wigner's (2*n*+1) rule for wave-function parameters

- One can show that the *n*-th derivative of the wave-function parameters is sufficient for the calculation up to the (2*n*+1)-th derivative of the energy!

$c^{(n)} \rightarrow E^{(2n+1)}$

no response of the wave function parameters required

n=0 → 1st derivative of energy

n=1 → 2nd and 3rd derivative of the energy

n=2 → 4th and 5th derivative of the energy

- Holds for variational wave functions
- Holds for constrained variation and non-variational methods when Lagrangian is used

(2*n*+2) rule for Lagrange multipliers

- Similarly, one can show that the *n*-th derivative of the Lagrange multipliers is sufficient for the calculation up to the (2*n*+2)-th derivative of the energy!

$$\lambda^{(n)} \rightarrow E^{(2n+2)}$$

n=0 → 1st and 2nd derivative of energy

n=1 → 3rd and 4th derivative of the energy

n=2 → 5th and 6th derivative of the energy

First contribution appears for third derivative of the energy!

Second derivatives

- For the second derivative, according to the (2*n*+1) and (2*n*+2) rules, the first derivative of the wave-function parameters $c^{(1)}$ is required, no derivatives with respect to the Lagrange multipliers $\lambda^{(0)}$.

$$\frac{d^2E}{dxdy} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial y \partial c}\frac{\partial c}{\partial x} + \frac{\partial^2 L}{\partial c^2}\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}$$

- Equations for the perturbed wave-function parameters are obtained via differentiation of their conditional equations wrt to the perturbation.

Second derivatives

- Depending on the perturbation it can be advantageous to differentiate the first derivative leading to the so-called asymmetric expression

$$\frac{d^2E}{dxdy} = \frac{d}{dy}\frac{\partial L}{\partial x} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial x \partial \lambda}\frac{\partial \lambda}{\partial y}$$

- No derivative of c wrt to perturbation x needed.
- Instead, derivative of **λ** wrt to y needed.
- Order of differentiation: Example NMR shieldings:
  - Perturbation 1: Nuclear magnetic moment, N_{atom}*3 components
  - Perturbation 2: Magnetic field, 3 components, two sets

Harmonic frequencies

- Typical example: harmonic vibrational frequencies

- Taylor expansion of the BO potential around equilibrium geometry & cut after harmonic approximation

$$V^{\mathrm{BO}} \approx V_{\mathrm{eq}} + \frac{1}{2} \sum_{ij}^{3N_{\mathrm{atom}}} \left(\frac{\partial^2 V}{\partial X_i \partial X_j} \right)_{\mathrm{eq}} (X_i - X_i^{\mathrm{eq}})(X_j - X_j^{\mathrm{eq}})$$

elements H_{ij} of Hessian

$$\approx V_{\mathrm{eq}} + \frac{1}{2} \sum_{ij}^{3N_{\mathrm{atom}}} H_{ij} \Delta x_i \Delta x_j$$

- Insert into nuclear Hamiltonian $\hat{H}_{\mathrm{nuc}} = \hat{T}_{\mathrm{nuc}} + V^{\mathrm{BO}}$

$$\hat{H}_{\mathrm{nuc}} = -\frac{1}{2} \sum_{i}^{3N_{\mathrm{atom}}} \frac{1}{M_i} \frac{\partial^2}{\partial X_i^2} + \frac{1}{2} \sum_{i}^{3N_{\mathrm{atom}}} H_{ij} \Delta x_i \Delta x_j$$

couplings

Harmonic frequencies

- Introduce mass-weighted coordinates $\tilde{x}_i = \sqrt{M_i}\Delta x_i$

$$\hat{H}_{\text{nuc}} = -\frac{1}{2}\sum_{i}^{3N_{\text{atom}}} \frac{\partial^2}{\partial \tilde{x}_i^2} + \frac{1}{2}\sum_{ij}^{3N_{\text{atom}}} \underbrace{\frac{H_{ij}}{\sqrt{M_i M_j}}}_{K_{ij}} \tilde{x}_i \tilde{x}_j$$

- Diagonalize **K** matrix to construct new coordinates from the eigenvectors **L** $\mathbf{KL} = \mathbf{L}\boldsymbol{\lambda}$
- Build normal coordinates $Q_i = \sum_j L_{ji}\tilde{x}_j$

$$\hat{H}_{\text{nuc}} = -\frac{1}{2}\sum_{i}^{3N_{\text{atom}}} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\sum_{i}^{3N_{\text{atom}}} \lambda_i Q_i^2 = \sum_{i}^{3N_{\text{atom}}} \hat{H}_i^{\text{HO}}$$

separable harmonic oscillator

no couplings

- vibrational frequencies $\omega_i = \sqrt{\lambda_i}$ normal-coordinate analysis

Expression for HF second derivatives

asymmetric expression: $\frac{d^2E}{dxdy} = \frac{d}{dy}\frac{\partial L}{\partial x} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial x \partial \lambda}\frac{\partial \lambda}{\partial y}$

$$\frac{d^2E^{\mathrm{HF}}}{dxdy} = \frac{d}{dy}\frac{\partial L^{\mathrm{HF}}}{\partial x} = \sum_{\mu\nu} D_{\mu\nu}\frac{\partial^2 h_{\mu\nu}}{\partial x \partial y} + \frac{1}{2}\sum_{\mu\nu\sigma\rho} D_{\mu\nu}D_{\sigma\rho}\left(\frac{\partial^2\langle\mu\sigma \mid \nu\rho\rangle}{\partial x \partial y} - \frac{1}{2}\frac{\partial^2\langle\mu\sigma \mid \rho\nu\rangle}{\partial x \partial y}\right)$$
$$- \sum_{\mu\nu} W_{\mu\nu}\frac{\partial^2 S_{\mu\nu}}{\partial x \partial y}$$
$$+ \sum_{\mu\nu}\frac{\partial D_{\mu\nu}}{\partial y}\left(\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} P_{\sigma\rho}\left(\frac{\partial\langle\mu\sigma \mid \nu\rho\rangle}{\partial x} - \frac{1}{2}\frac{\partial\langle\mu\sigma \mid \rho\nu\rangle}{\partial x}\right)\right)$$
$$- \sum_{\mu\nu}\frac{\partial W_{\mu\nu}}{\partial y}\frac{\partial S_{\mu\nu}}{\partial x}$$

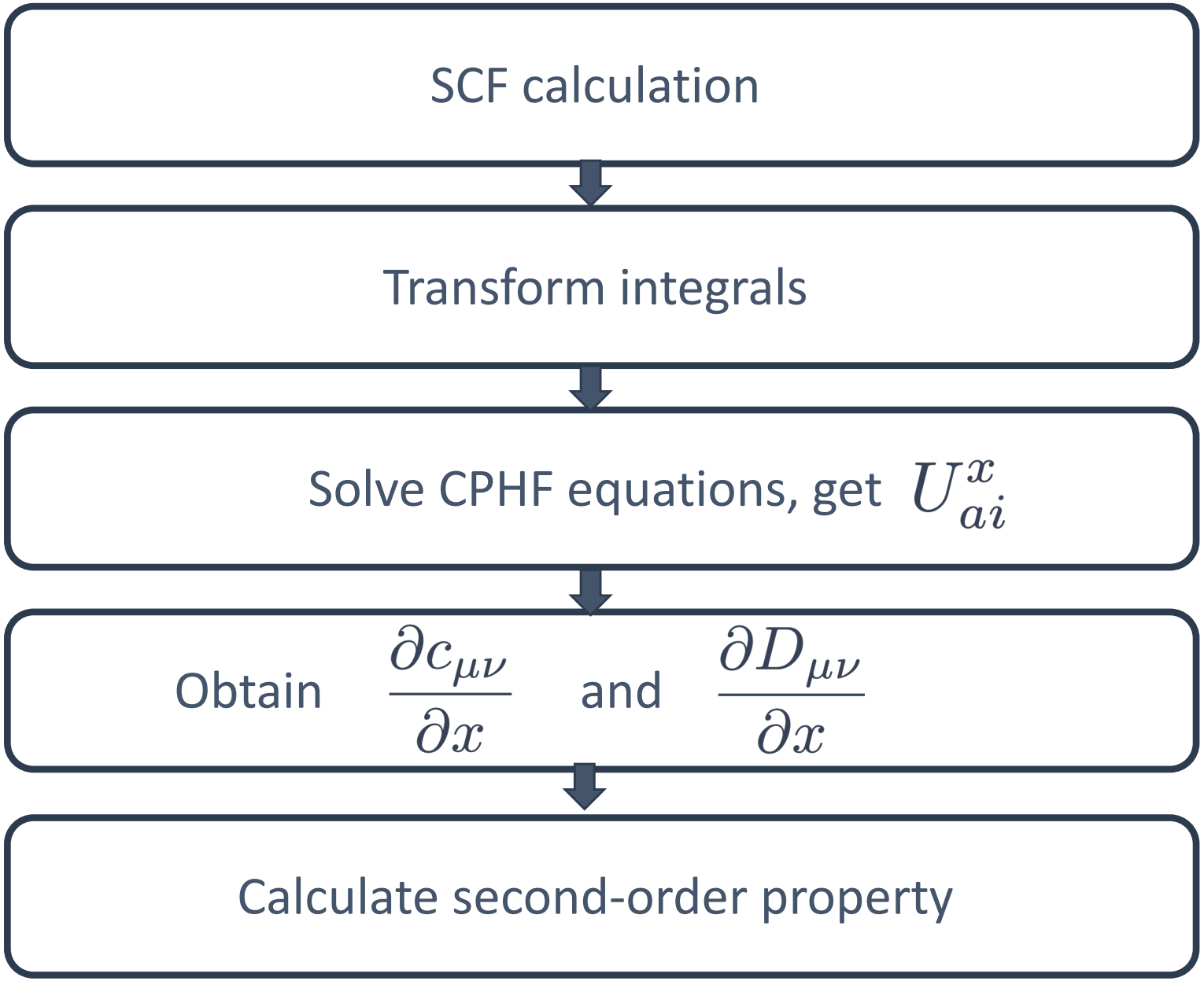
with

$$\frac{\partial D_{\mu\nu}}{\partial y} = 2\sum_i \left\{\frac{\partial c^*_{\mu i}}{\partial y}c_{\nu i} + c^*_{\mu i}\frac{\partial c_{\nu i}}{\partial y}\right\} \qquad \frac{\partial W_{\mu\nu}}{\partial y} = 2\sum_i \left\{\frac{\partial c^*_{\mu i}}{\partial y}\epsilon_i c_{\nu i} + c^*_{\mu i}\epsilon_i\frac{\partial c_{\nu i}}{\partial y}\right\} + \sum_{ij} c^*_{\mu i}\frac{\partial \epsilon_{ji}}{\partial y}c_{\nu}$$

(2n+1) → Derivative of MO coefficients needed → CPHF equations

Shown here: asymmetric expression

Flowchart HF second derivatives



Expression for CC second derivatives

- symmetric expression: $\frac{d^2E}{dxdy} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial y \partial c}\frac{\partial c}{\partial x} + \frac{\partial^2 L}{\partial c^2}\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}$

$$\frac{d^2E}{dxdy} = \langle 0|(1+\Lambda)\exp(-T)\frac{\partial^2 H}{\partial x \partial y}\exp(T)|0\rangle$$
$$+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial x}\exp(T), \frac{dT}{dy}]|0\rangle +$$
$$+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial y}\exp(T), \frac{dT}{dx}]|0\rangle +$$
$$+\langle 0|(1+\Lambda)[[\exp(-T)H\exp(T), \frac{dT}{dx}], \frac{dT}{dy}]|0\rangle.$$

Skipping here the contributions from orbital relaxation.

(2n+1) rule → first derivatives of t amplitudes

(2n+2) rule → no derivative of λ amplitudes

Expression for CC second derivatives

- asymmetric expression: $\frac{d^2E}{dxdy} = \frac{d}{dy}\frac{\partial L}{\partial x} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial x \partial \lambda}\frac{\partial \lambda}{\partial y}$

$$\frac{d^2E}{dxdy} = \langle 0|(1+\Lambda)\exp(-T)\frac{\partial^2 H}{\partial x \partial y}\exp(T)|0\rangle$$
$$+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial x}\exp(T), \frac{dT}{dy}]|0\rangle +$$
$$+\langle 0|\frac{d\Lambda}{dy}\exp(-T)\frac{\partial H}{\partial x}\exp(T)|0\rangle.$$

Skipping here the contributions from orbital relaxation

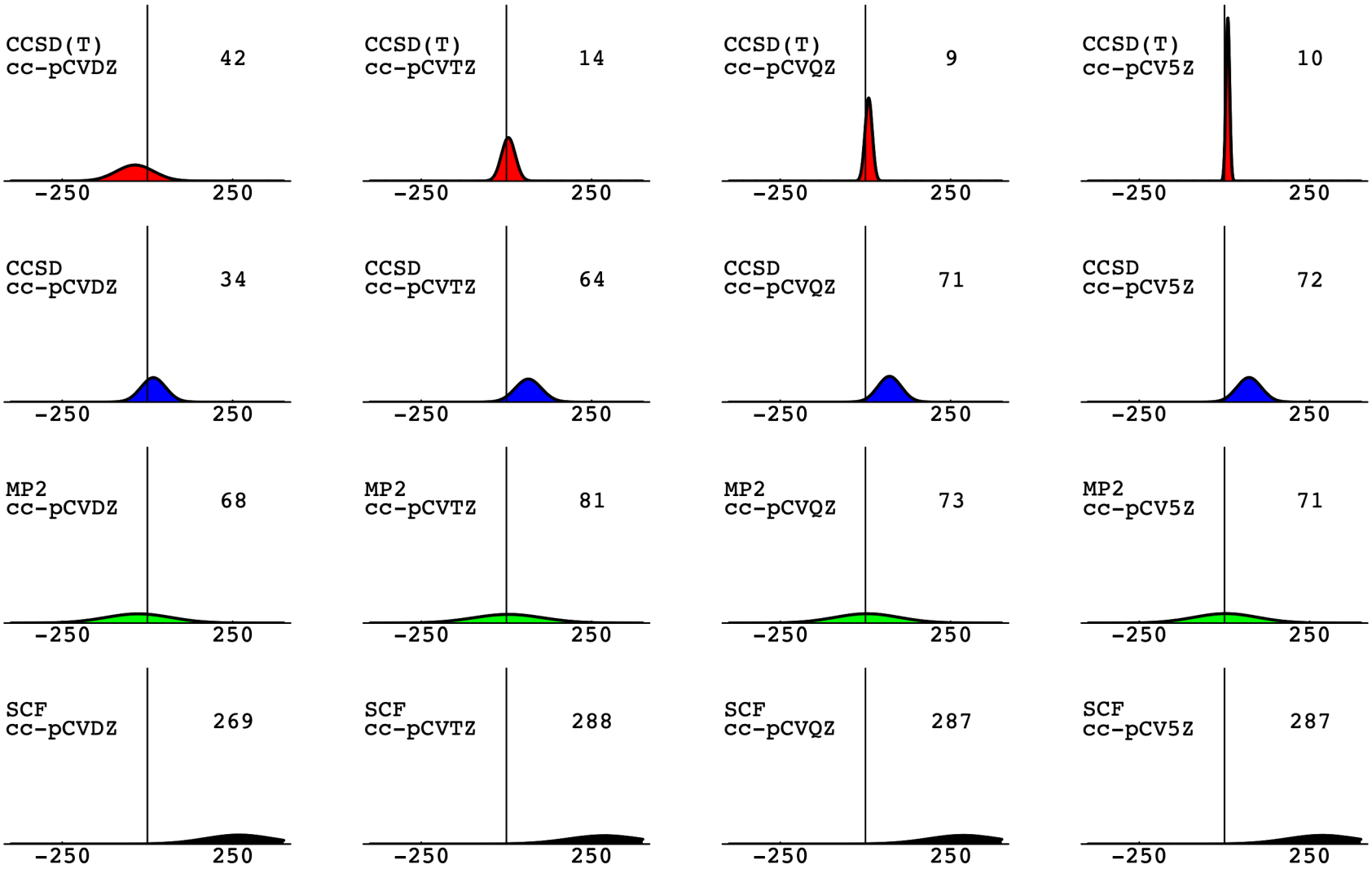
full differentiation of the gradient expression :

→ perturbed CC equations wrt *x*

→ perturbed λ equations wrt *y*

Harmonic constants ω_e of BH, CO, N_2, HF, F_2

in cm^{-1}



from T. Helgaker lecture notes on derivatives

Summary

- Properties as derivatives
- Numerical vs. analytical derivatives
- Lagrangian techniques for constrained variation and non-variational wave functions
  - Avoid calculation of response of wave function parameters if possible
- Expressions for gradients and second derivatives

Part 2
Magnetic properties and molecules in magnetic fields

Contents

- Introduction into electromagnetic fields
- Derivation of Hamiltonian with electromagnetic fields
- Magnetizabilities
- Gauge-origin dependence in quantum-chemical calculations
- Further magnetic properties
- Strong magnetic fields

Fields, Forces, and Potentials

- Particles can be charged
- Charged particles interact

Coulomb force
(SI units)

$$\underline{F}^{\mathrm{Coul}} = \frac{1}{4\pi\varepsilon_0}\frac{z_1 z_2}{r^3}\underline{r}$$

charges z_1 and z_2

vacuum permittivity

- Charge generates electric field
- Second charge interacts with electric field (feels force in the electric field generated by z_1)

$$\underline{E} = \frac{\underline{F}}{z_2} = \frac{1}{4\pi\varepsilon_0}\frac{z_1}{r^3}\underline{r}$$

A quick reminder...

Nabla-operator (vector) $\nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}$

Gradient (on scalar) → vector $\nabla f = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{pmatrix}$

Divergence (on vector) → scalar $\nabla \underline{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$

Curl $\nabla \times \underline{A} = \begin{pmatrix} \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \\ \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \\ \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \end{pmatrix}$

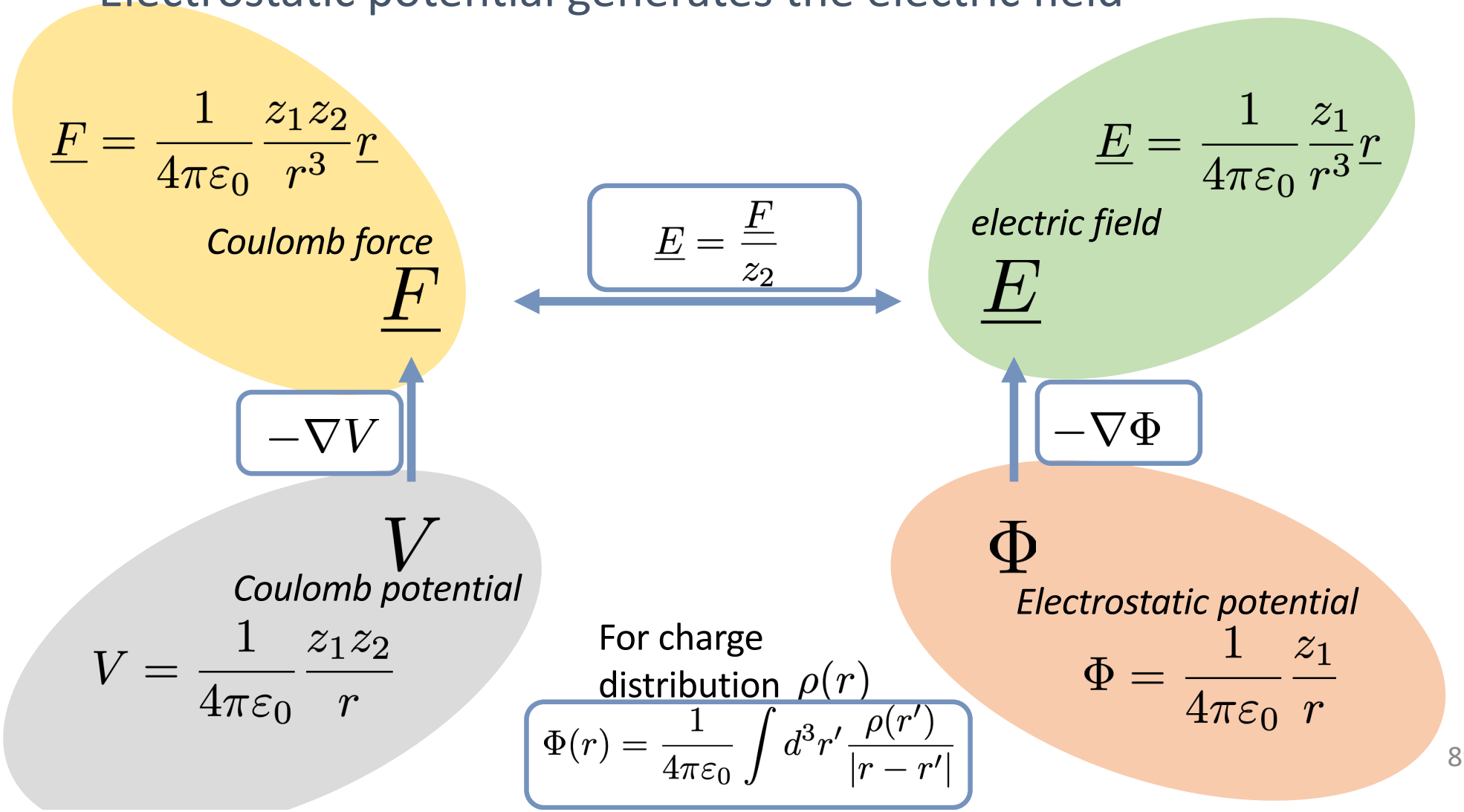
Curl of gradient $\nabla \times \nabla f = \underline{0}$

Divergence of curl $\nabla \cdot (\nabla \times \underline{A}) = 0$

Fields, Forces, and Potentials

$$\underline{F} = -\nabla V$$

- Coulomb force is conservative → can be deduced from potential
- Electrostatic potential generates the electric field



Fields, Forces, and Potentials

- Fields are associated with forces
- In quantum-mechanics we work with potentials rather than forces (see Hamiltonian…)
- For conservative forces, the potential is related to the force simply via $F = -\nabla V$

→ Easy to work with potentials

Moving charges and magnetic fields

- A moving charge furthermore experiences a Lorentz-force

$$\underline{F}^{\text{Lorentz}} = z(\underline{v} \times \underline{B})$$

force is dependent on velocity! deflection perpendicular to B magnetic field

- Additional non-conservative force!
- Forces on matter through $\underline{E}$ and $\underline{B}$
  → Coulomb- and Lorentz forces

$$\underline{F}^{\text{tot}} = z(\underline{E} + \underline{v} \times \underline{B})$$

electric part magnetic part

often referred to as Lorentz force

Straightforward to be used within Newton‘s formulation of classical mechanics!

Moving charges and magnetic fields

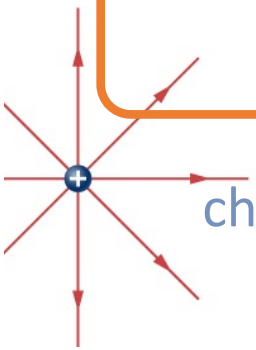
- In the case of a non-conservative force, the relationship with the potential is not as simple…

$$F \neq -\nabla V$$

- How can we then get access to the potentials?

Maxwell Equations

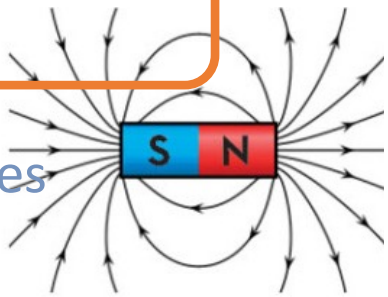
- Maxwell equations provide basis for electrodynamics
  connect $\underline{\boldsymbol{E}}$ and $\underline{\boldsymbol{B}}$ as well as charge density $\underline{\rho}$ and current $\underline{\boldsymbol{j}}$



$$\nabla \underline{E} = \frac{1}{\varepsilon_0}\rho$$

charges create electric field

$$\nabla \underline{B} = 0$$



no magnetic monopoles

$$\nabla \times \underline{E} = -\frac{\partial \underline{B}}{\partial t}$$

time-dependent magnetic field generates electric field

$$\nabla \times \underline{B} = -\mu_0 \underline{j} + \frac{1}{c^2}\frac{\partial \underline{E}}{\partial t}$$

currents generate magnetic field

Lorentz invariant (same value in all inertial reference frames)

Potentials of electromagnetic fields

- Lorentz force not conservative → cannot be traced back to a simple scalar potential!
- Limiting cases:
  - E≠0, B=0 $\underline{E} = -\nabla\Phi$ (as before)
  - B≠0, E=0 $\underline{B} = \nabla \times \underline{A}$ fulfills 2.Maxwell eq: $\nabla \underline{B} = 0$

$\underline{A}$ is the so-called vector potential which is associated with the magnetic field. We define it such that it gives back $\underline{B}$

Potentials of electromagnetic fields

- Lorentz force not conservative → cannot be traced back to a simple scalar potential!
- Limiting cases:
  - E≠0, B=0 $\underline{E} = -\nabla\Phi$ (as before)
  - B≠0, E=0 $\underline{B} = \nabla \times \underline{A}$ (fulfills 2.MEQ: $\nabla \underline{B} = 0$)
  - E≠0, B≠0 using 3. MEQ: $\nabla \times \underline{E} = -\frac{\partial}{\partial t}\underline{B}$

rearrange rhs

$$\nabla \times \underline{E} = -\frac{\partial}{\partial t}(\nabla \times \underline{A})$$

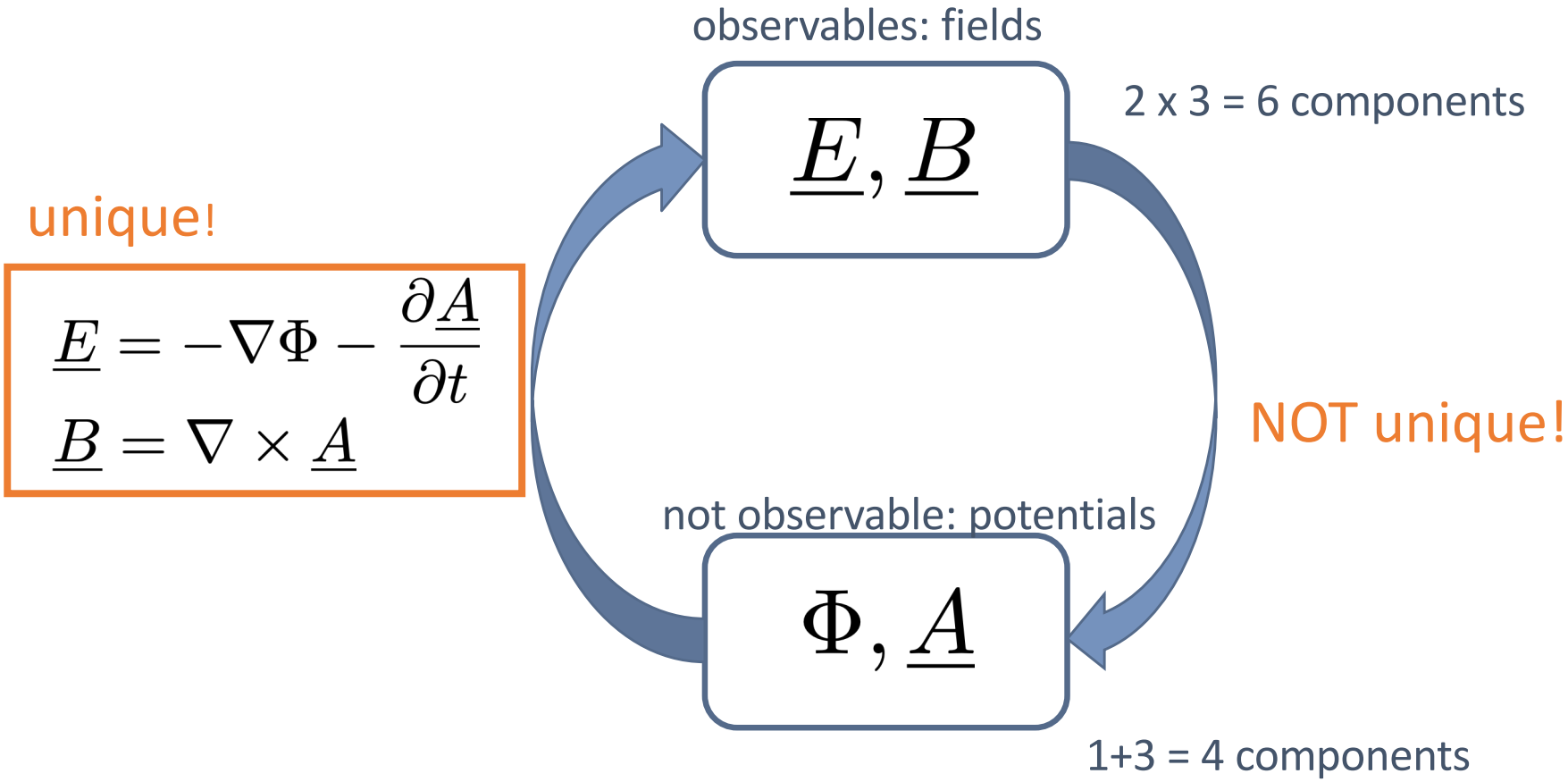
$$\nabla \times \underline{E} = \nabla \times \left(-\frac{\partial \underline{A}}{\partial t}\right)$$

$$\underline{E} = -\frac{\partial \underline{A}}{\partial t} + \nabla f$$

can be added since $\nabla \times \nabla f = 0$ hence no impact on 3. MEQ

$$\underline{E} = -\nabla\Phi - \frac{\partial \underline{A}}{\partial t}$$

Potentials of electromagnetic fields



This means: Many choices of vector potential and electrostatic potential lead to same observable electric and magnetic fields!

Choice of gauge

- Different choices of $\underline{A}$ and ϕ can generate same $\underline{E}$ and $\underline{B}$
  - Case 1: $\underline{E} = -\nabla\Phi, \quad \underline{B} = 0$

    can add a constant to ϕ (because gradient is taken)
  - Case 2: $\underline{E} = 0, \quad \underline{B} = \nabla \times \underline{A}$

    can add gradient of a scalar function to $\underline{A}$
  - General case: $\underline{E} = -\nabla\Phi - \frac{\partial \underline{A}}{\partial t}, \quad \underline{B} = \nabla \times \underline{A}$

Allowed trans-formations

$$\underline{A}' = \underline{A} + \nabla f$$

$$\Phi' = \Phi - \frac{\partial}{\partial t} f$$

no change in $\underline{B}$: $\underline{B}(\underline{A}) = \underline{B}(\underline{A}')$
but change in $\underline{E}$, compensate by choice of arbitrary scalar function f → choice of gauge!

$$\underline{E}(\Phi, \underline{A}) = \underline{E}(\Phi', \underline{A}')$$

$$\underline{B}(\underline{A}) = \underline{B}(\underline{A}')$$

electric and magnetic fields unchanged!

Concereteley: choosig a set of $\underline{A}$ and ϕ for given $\underline{E}$ and $\underline{B}$ is the choice auf gauge

Choice of gauge

observables

$\underline{E}, \underline{B}$

unique!

$$\underline{E} = -\nabla\Phi - \frac{\partial \underline{A}}{\partial t}$$
$$B = \nabla \times \underline{A}$$

NOT unique!

not observable

$\Phi, \underline{A}$

Gauge transformations:

$$\Phi' = \Phi - \frac{\partial}{\partial t} f$$
$$\underline{A}' = \underline{A} + \nabla f$$

Using Φ' and $\underline{A}'$ instead of Φ and $\underline{A}$ will describe the same fields $\underline{E}$ and $\underline{B}$

Usually we require the vector potential to obey: $\nabla \underline{A} = 0$ „Coulomb gauge“ implies also $\nabla^2 f = 0$

Choice of gauge-origin

- Example: Static homogenous magnetic field (independent of time and position)

$$\underline{B} = \underline{\text{const.}} \qquad \underline{B} = \nabla \times \underline{A}$$

$$\underline{A} = \frac{1}{2}(\underline{B} \times \underline{r})$$

Choice of gauge-origin

- Example: B in z-direction

$$\underline{B} = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix} \qquad \underline{A} = \frac{1}{2}(\underline{B} \times \underline{r}) \qquad \underline{A} = \frac{1}{2}\begin{pmatrix} -B_z y \\ B_z x \\ 0 \end{pmatrix}$$

$$B = \nabla \times \underline{A} = \frac{1}{2}\begin{pmatrix} 0 \\ 0 \\ \frac{\partial}{\partial x}A_y - \frac{\partial}{\partial y}A_x \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 \\ 0 \\ B_z + B_z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix}$$

Choice of gauge-origin

- Example: Static homogenous magnetic field (independent of time and position)

$$\underline{B} = \underline{\text{const.}} \qquad \underline{B} = \nabla \times \underline{A}$$

$$\underline{A} = \frac{1}{2}(\underline{B} \times \underline{r})$$

- Equivalent:

$$\underline{A}' = \frac{1}{2}(\underline{B} \times (\underline{r} - \underline{R}_\mathrm{O}))$$

$$\underline{A}' = \frac{1}{2}\underline{B} \times \underline{r} - \frac{1}{2}\underline{B} \times \underline{R}_\mathrm{O}$$

$$\underline{A}' = \underline{A} + \nabla f \qquad f = -\frac{1}{2}(\underline{B} \times \underline{R}_\mathrm{O})\underline{r}$$

- Any choice of $\underline{R}_\mathrm{O}$ is valid as it yields the *same magnetic field*!

gauge origin

Recipe to get the Hamiltonian for magnetic interactions

Newton formulation of classical mechanics
(with Lorentz force, non-conservative!)

↓

Lagrange formulation of classical mechanics

↓

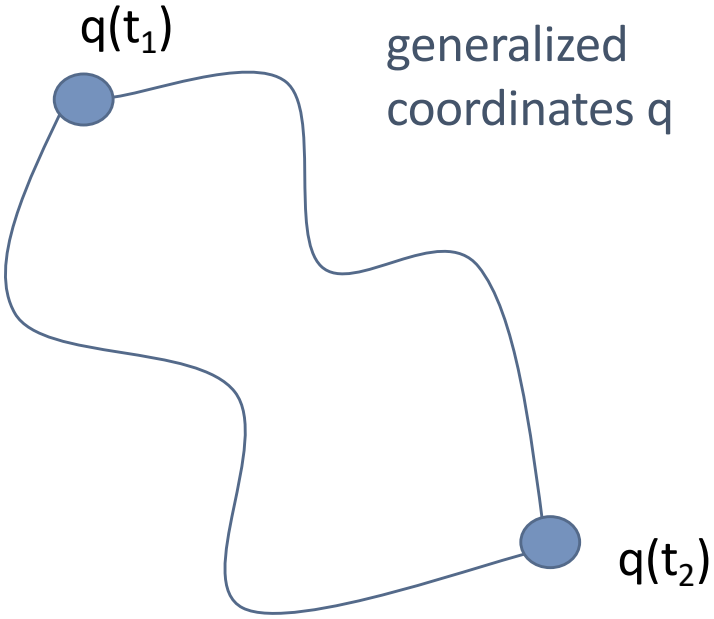
Hamilton formulation of classical mechanics

} equivalent formulations!

↓ quantization

Hamiltonian with magnetic interactions

Lagrangian mechanics



generalized coordinates q

Hamilton principle: (least action) path minimizes action integral

$$S = \int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt$$

Lagrange function L

meaning $\delta S = 0$

variation

Euler-Lagrange equations
(Lagrange equations of motion)

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \left(\frac{\partial L}{\partial q}\right) = 0$$

Q: Which path is taken for a particle moving from $q(t_1) \rightarrow q(t_2)$?

Note: Treat q and $\dot{q}$ as independent variables.

Note: For conservative force: $L(q, \dot{q}, t) = T(q, \dot{q}, t) - V(q)$
(does not hold for Lorentz force!)

Hamilton mechanics

Definition of conjugated canonical momentum $p = \frac{\partial L}{\partial \dot{q}}$

Hamilton function via Legendre transformation

$$H(q, p, t) = p\dot{q} - L(q, \dot{q}, t)$$

basis for quantization

Hamilton eqs. of motion $\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}$

Equivalence of the 3 formulations of classical mechanics

Particle with coordinate x=q in 1-dim. potential V(x)

Newton

$$F = m\ddot{x}$$

$$-\frac{\partial V}{\partial x} = m\ddot{x}$$

$$0 = -\frac{\partial V}{\partial x} - m\ddot{x}$$

Lagrange

$$L = T - V$$

$$L = \frac{1}{2}m\dot{x}^2 - V(x)$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \left(\frac{\partial L}{\partial x}\right) = 0$$

$$0 = -\frac{\partial V(x)}{\partial x} - m\ddot{x}$$

Hamilton

$$p = \frac{\partial L}{\partial \dot{q}} = m\dot{x}$$

$$H(q,p) = p\dot{q} - L$$

$$= m\dot{x}^2 - \frac{m\dot{x}^2}{2} + V(x)$$

$$= \frac{p^2}{2m} + V(x)$$

$$\dot{p} = -\frac{\partial H}{\partial q} = -\frac{\partial V}{\partial x}$$

$$\dot{p} \rightarrow m\ddot{x}$$

$$0 = -\frac{\partial V}{\partial x} - m\ddot{x}$$

Lagrangian in an electromagnetic field

Task: Set up Hamilton function! Needs Lagrange function L

→ Not known for non-conservative force!

→ But Newtonian eqs. of motion known!

Set up *L* in terms of Φ and $\underline{A}$ *such that* resulting Lagrange eqs. of motion are equivalent

Lorentz force

$$\underline{F}^{\mathrm{tot}} = z(\underline{E} + \underline{v} \times \underline{B})$$

Newton's equation with Lorentz force and potentials

$$m\ddot{\underline{r}} = z\left(-\nabla\Phi - \frac{\partial \underline{A}}{\partial t}\right) + z\underline{v} \times (\nabla \times \underline{A}))$$

Lagrange function that leads to Newton's equation

$$L = \frac{mv^2}{2} - z\Phi + z\underline{v} \cdot \underline{A}$$

Hamiltonian in an electromagnetic field

Define conj. canonical momentum:

$$L = \frac{mv^2}{2} - z\Phi + z\underline{v}\cdot\underline{A}$$

$$p = \frac{\partial L}{\partial \dot{q}} = m\underline{v} + z\underline{A}$$

$\underline{v}$

no longer just $m\underline{v}$!

Legendre trafo to get Hamilton function

$$H(q,p,t) = p\dot{q} - L$$

$$= (m\underline{v} + z\underline{A})\underline{v} - \frac{m\underline{v}^2}{2} + z\Phi - z\underline{v}\,\underline{A}$$

$$= \frac{m\underline{v}^2}{2} + z\Phi$$

No dependence on $\underline{A}$

Express using canonical momentum

$$= \frac{(p - z\underline{A})^2}{2m} + z\Phi$$

Basis for quantization!

Hamiltonian in an electromagnetic field

$$H = \frac{(p - z\underline{A})^2}{2m} + z\Phi$$

For electrons: z=-e, in atomic units: z=-1, m=m_e=1. Quantize!

$$\hat{p} = -i\nabla$$

$$\hat{H} = \frac{(\hat{p} + \underline{A})^2}{2} - \Phi$$

$$= \frac{\hat{\pi}^2}{2} - \Phi$$

Comment: no quantization of fields here

$$\hat{\pi} = \hat{p} + \underline{A}$$

kinetic momentum

Non-relativistic Hamiltonian for electron in electromagnetic field!

Spin contribution in electromagnetic field

- Schrödinger equation does not contain spin
- Ad-hoc introduction of spin by Pauli (1927)

$$\hat{H} = \frac{(\underline{\sigma}\hat{\pi})^2}{2} - \Phi$$

vector of the Pauli spin matrices (2x2)

$$\underline{\sigma} = \begin{pmatrix} \boldsymbol{\sigma}_x \\ \boldsymbol{\sigma}_y \\ \boldsymbol{\sigma}_z \end{pmatrix} \qquad \boldsymbol{\sigma_x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \boldsymbol{\sigma_y} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \boldsymbol{\sigma_z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$(\underline{\sigma}\hat{\pi})^2 = \hat{\pi}^2 + i\underline{\sigma}(\hat{\pi} \times \hat{\pi}) \quad \textit{Dirac identity}$$

$$= \hat{\pi}^2 + i\underline{\sigma}(\hat{p} \times \hat{p} + \underline{A} \times \underline{A} + \hat{p} \times \underline{A} + \underline{A} \times \hat{p})$$

$\hat{p} \times \hat{p}$ and $\underline{A} \times \underline{A}$: 0

$$\hat{p} \times \underline{A} f = (\hat{p} \times \underline{A}) f - \underline{A} \times \hat{p} f$$

$\hat{p} = -i\nabla$

$$= \hat{\pi}^2 + \underline{\sigma}\underbrace{(\nabla \times \underline{A})}_{\underline{B}}$$

$\sigma = 2\hat{s}$

$$\Longrightarrow \quad \hat{H} = \frac{\hat{\pi}^2}{2} + \underline{B}\hat{s} - \Phi$$

Spin contribution in electromagnetic field

$$H = \frac{(\underline{\sigma\pi})^2}{2} - \Phi \quad \xrightarrow{\boldsymbol{\sigma}_i = 2\hat{s}_i} \quad H = \frac{\pi^2}{2} + \underline{B\hat{s}} - \Phi$$

- **same result** is obtained when taking non-relativistic limit ($c \to \infty$) of the (modified) Dirac equation
  - → arguments whether or not spin is a relativistic effect
  - → see Trond's lectures

- Note: magnetic field defines spin-quantization axis. Spin parallel or antiparallel wrt field (α & β).

Hamiltonian in electromagnetic field

$$\frac{\hat{p}^2}{2} \rightarrow \frac{\hat{\pi}^2}{2} - \Phi \rightarrow \frac{\hat{\pi}^2}{2} + \underline{B}\,\underline{\hat{s}} - \Phi$$

field-free

$\hat{p} = -i\nabla$

electromagn. field

$\hat{\pi} = \hat{p} + \underline{A}$

consideration of spin

- Expanding $\hat{\pi}^2$

$$\hat{\pi}^2 = (\hat{p} + \underline{A})^2$$

$$= \hat{p}^2 + \underline{A}^2 + \hat{p}\underline{A} + \underline{A}\hat{p}$$

be aware that the momentum operator does in general not commute with the vector potential!

Hamiltonian in electromagnetic field

$$\frac{\hat{p}^2}{2} \rightarrow \frac{\hat{\pi}^2}{2} - \Phi \rightarrow \frac{\hat{\pi}^2}{2} + \underline{B}\,\underline{\hat{s}} - \Phi$$

field-free

$\hat{p} = -i\nabla$

electromagn. field

$\hat{\pi} = \hat{p} + \underline{A}$

consideration of spin

- Expanding $\hat{\pi}^2$

$$\hat{\pi}^2 = (\hat{p} + \underline{A})^2$$
$$= \hat{p}^2 + \underline{A}^2 + \hat{p}\underline{A} + \underline{A}\hat{p}$$
$$= \hat{p}^2 + \underline{A}^2 + 2\underline{A}\hat{p}$$

$$\hat{p}\underline{A}f = (\hat{p}\underline{A})f + \underline{A}\hat{p}f$$

Coulomb gauge! $\nabla \underline{A} = 0$

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2 - \Phi$$

Hamiltonian

- Goal: Derive molecular Hamiltonian in electromagnetic field
- So far: Hamiltonian for 1 electron via use of the equivalence of Newtonian and Lagrange eqs. of motion:
  - Find L such that Lagrange eqs. of motion yield

$$\underline{F}^{\mathrm{tot}} = z(\underline{E} + \underline{v} \times \underline{B})$$

$$m\ddot{\underline{r}} = z\left(-\nabla\Phi - \frac{\partial \underline{A}}{\partial t}\right) + z\underline{v} \times (\nabla \times \underline{A}))$$

  - Determine p and set up Hamilton function H
  - Quantize $\hat{H} = \frac{(\hat{p} + \underline{A})^2}{2} - \Phi$
  - Consideration of spin and using Coulomb gauge

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2 - \Phi$$

Molecular Hamiltonian in electromagnetic field

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2 - \Phi$$

So far:

- 1 Electron in electromagnetic field

Now: Molecular Hamiltonian! (adding instantaneous Coulomb interaction, summing over all electrons)

$$\hat{H} = \sum_{\alpha} \frac{1}{2}\hat{p}_{\alpha}^2 - \sum_{K\alpha} \frac{Z_K}{r_{\alpha K}} + \sum_{\alpha<\beta} \frac{1}{r_{\alpha\beta}}$$

Zeroth-order Hamiltonian (non-relativistic)

$$+ \sum_{\alpha} \underline{A}_{\alpha}\hat{p}_{\alpha} + \sum_{\alpha} \underline{B}_{\alpha}\hat{s}_{\alpha} - \sum_{\alpha} \Phi_{\alpha}$$

First-order Hamiltonian

$$+ \frac{1}{2}\sum_{\alpha} \underline{A}_{\alpha}^2$$

Second-order Hamiltonian

Magnetic perturbations

$$\hat{H} = \hat{H}_0 + \sum_\alpha \underline{A}_\alpha \hat{p}_\alpha + \sum_\alpha \underline{B}_\alpha \hat{s}_\alpha - \sum_\alpha \Phi_\alpha + \frac{1}{2}\sum_\alpha \underline{A}_\alpha^2$$

Orbital Zeeman paramagnetic

Spin Zeeman paramagnetic

diamagnetic

- 1 atomic unit for B, B_0, corresponds to 235000 Tesla!
- 1 B_0 is very large in comparison to any field we would typically apply
- due to the "smallness" of typical magnet fields on Earth, perturbative treatment often sufficient

Magnetic perturbations

- For quantum chemistry with magnetic fields, we are typically interested in:
  - Uniform external magnetic field, with vector potential

$$\underline{A}^{\mathrm{ext}} = \frac{1}{2}\underline{B}^{\mathrm{ext}} \times \underline{r}$$

Or $\underline{r\text{-}R}_{\mathrm{O}} \rightarrow \underline{A}_{\mathrm{O}}$

→ *Zeeman interactions*

  - Nuclear magnetic moments M_K with vector potential

$$\underline{A}^{\mathrm{nuc}} = \sum_K \underline{A}_K = \sum_K \alpha^2 \frac{\underline{M}_K \times \underline{r}_K}{r_K^3}$$

α≈1/137 fine structure constant

→ *Hyperfine interactions*

  - Combination: NMR

Hamiltonian for static uniform magnetic field

Electronic Hamiltonian in static homogeneous magnetic field (in a.u.)

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2$$

$\underline{B} = \text{const}$ $\qquad$ $\underline{B} = \nabla \times \underline{A}$

$$\underline{A}_{\text{O}}(\underline{r}) = \frac{1}{2}(\underline{B} \times \underline{r}_{\text{O}})$$

$$\Phi = 0$$

$$\nabla \underline{A}_{\text{O}} = 0$$

Rewrite terms with vector potential $\underline{A}$ in terms of $\underline{B}$

Hamiltonian in uniform magnetic field

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2$$

Linear term (orbital Zeeman)

$$\underline{A}_{\mathrm{O}}\hat{p} = \frac{1}{2}(\underline{B} \times \underline{r}_{\mathrm{O}}) \cdot \hat{p} = \frac{1}{2}\underline{B} \cdot (\underline{r}_{\mathrm{O}} \times \hat{p}) = \frac{1}{2}\underline{B} \cdot \underline{\hat{l}}^{\mathrm{O}}$$

Angular momentum operator, dependent on gauge origin

Quadratic term (diamagnetic)

$$\frac{1}{2}\underline{A}_{\mathrm{O}}^2 = \frac{1}{8}(\underline{B} \times \underline{r}_{\mathrm{O}})^2 = \frac{1}{8}(\underline{B} \times \underline{r}_{\mathrm{O}})(\underline{B} \times \underline{r}_{\mathrm{O}}) = \frac{1}{8}[B^2 \cdot r_{\mathrm{O}}^2 - (\underline{B}\,\underline{r}_{\mathrm{O}})(\underline{B}\,\underline{r}_{\mathrm{O}})]$$

$$= \frac{1}{8}\underline{B}^T[\underline{r}_{\mathrm{O}} \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}\underline{r}_{\mathrm{O}}^T]\underline{B}$$

It follows for the Hamiltonian

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \frac{1}{2}\underline{B}\underline{l}^{\mathrm{O}} + \underline{B}s = \frac{1}{8}\underline{B}^T[\underline{r}_{\mathrm{O}} \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}\underline{r}_{\mathrm{O}}^T]\underline{B}$$

Hamiltonian in uniform magnetic field

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2$$

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \frac{1}{2}\underline{B}\,\underline{l}^{\mathrm{O}} + \underline{B}\,\hat{s} + \frac{1}{8}\underline{B}^T[\underline{r}_{\mathrm{O}} \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}\underline{r}_{\mathrm{O}}^T]\underline{B}$$

Molecular Hamiltonian

$$\hat{H} = \hat{H}_0 + \sum_\alpha \frac{1}{2}\underline{B}\,\underline{l}_\alpha^{\mathrm{O}} + \sum_\alpha \underline{B}\hat{s}_\alpha + \frac{1}{8}\sum_\alpha \underline{B}^T[\underline{r}_{\mathrm{O}}(\alpha) \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}(\alpha)\underline{r}_{\mathrm{O}}^T(\alpha)]\underline{B}$$

$\hat{H}^{(1)}$ — Linear in B

$\hat{H}^{(2)}$ — Quadratic in B

Take-Home messages from lecture 2

- For non-conservative forces, we cannot get the potential simply from $F = -\nabla V$
- Hamiltonian that involves electromagnetic-field interactions from Lorentz force → Newtonian mechanics → Lagrange → Hamilton → quantize
- Ad-hoc: spin → leads to spin-Zeeman contribution
- Observable: fields (E & B), not observable (A & Φ), gauge transformations allowed
- Static magnetic field: Free choice of gauge origin