#### Time-independent molecular properties

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#### European Summer School in Quantum Chemistry (ESQC) 2017 Torre Normanna, Sicily, Italy September 10–23, 2017

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# Section 1

Introduction

#### Introduction

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#### Time-Independent Molecular Properties

When a molecular system is perturbed, its total energy changes

 $\mathcal{E}(\mu) = \mathcal{E}^{(0)} + \mathcal{E}^{(1)}\mu + \frac{1}{2}\mathcal{E}^{(2)}\mu^2 + \cdots$ 

The expansion coefficients are characteristic of the molecule and its quantum state

- we refer to these coefficients as molecular properties
- When the perturbation is static, the properties may be calculated by differentiation

$$\mathcal{E}^{(1)} = \left. \frac{\mathrm{d}\mathcal{E}}{\mathrm{d}\mu} \right|_{\mu=0}$$
$$\mathcal{E}^{(2)} = \left. \frac{\mathrm{d}^2\mathcal{E}}{\mathrm{d}\mu^2} \right|_{\mu=0}$$

- such properties are said to be time independent
- We do not here consider time-dependent molecular properties
  - ▶ if periodic, these can be calculated in similar way using the quasi-energy

#### Examples of Derivatives

- Responses to geometrical perturbations
  - forces and force constants
  - spectroscopic constants
- Responses to external electromagnetic fields
  - permanent and induced moments
  - polarizabilities and magnetizabilities
  - optical activity
- Responses to external magnetic fields and nuclear magnetic moments
  - NMR shielding and indirect spin-spin coupling constants
  - EPR hyperfine coupling constants and g values
- Responses to nuclear quadrupole moments
  - nuclear field gradients, quadrupole coupling constants
- Responses to molecular rotation
  - spin-rotation constants and molecular g values

#### Numerical vs. analytical differentiation

- Numerical differentiation (finite differences and polynomial fitting)
  - often simple to implement (at least for real singlet perturbations)
  - difficulties related to numerical accuracy and computational efficiency
- Analytical differentiation (derivatives calculated from analytical expressions)
  - considerable programming effort required
  - greater speed, precision, and convenience
- Implementations of analytical techniques
  - first-order properties (dipole moments and gradients)
  - second-order properties (polarizabilities and Hessians, NMR parameters)

# Section 2

**Energy Functions** 

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### Electronic Energy Function

> The electronic energy function contains the Hamiltonian and the wave function:

 $E(x,\lambda) = \langle \lambda | H(x) | \lambda \rangle$ 

It depends on two distinct sets of parameters:

x: external (perturbation) parameters (geometry, external field)  $\lambda$ : electronic (wave-function) parameters (MOs, cluster amplitudes)

The Hamiltonian (here in second quantization)

$$H(x) = \sum_{pq} h_{pq}(x) E_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs}(x) e_{pqrs} + h_{nuc}(x)$$

depends explicitly on the external parameters:

 $h_{pq}(x) = \langle \phi_p(x) | h(x) | \phi_q(x) \rangle$ 

• The wave function  $|\lambda\rangle$  depends implicitly on the external parameters  $\lambda(x)$ .

#### Electronic Energy and its Derivatives

• The electronic energy  $\mathcal{E}(x)$  is obtained by optimizing the energy function  $E(x, \lambda)$  with respect to  $\lambda$  for each value of x:

$$\mathcal{E}(x) = \mathbf{E}(x, \lambda^*)$$

- > note: the optimization is not necessarily a variational minimization
- Our task is to calculate derivatives of  $\mathcal{E}(x)$  with respect to x:



- the implicit as well as explicit dependence must be accounted for
- The quantity  $\partial \lambda / \partial x$  is the wave-function response
  - it tells us how the electronic structure changes when the system is perturbed
- To proceed, we need to make a distinction between
  - variationally determined wave functions
  - nonvariationally determined wave functions

## Variational and Nonvariational Wave Functions

#### Variational wave functions

the optimized energy fulfils the stationary (variational) condition:

$$\frac{\partial E(x,\lambda)}{\partial \lambda} = 0 \quad \text{(for all } x\text{)}$$

the Hartree–Fock energy in an unconstrained exponential parameterization

$$|\mathsf{HF}\rangle = \exp(-\kappa)|0\rangle, \quad \kappa^{\dagger} = -\kappa$$

• the energy of the full CI (FCI) wave function  $|\text{FCI}\rangle = \sum_i c_i |i\rangle$  as an expectation value:

$$\frac{\partial E_{\mathsf{FCI}}(x,c)}{\partial c} = 0$$

#### Nonvariational wave functions

wave functions whose energy does not fulfil the stationary condition:

$$\frac{\partial E(x,\lambda)}{\partial \lambda} \neq 0$$

the Hartree–Fock and Kohn–Sham energies in a constrained LCAO parameterization (orthonormality)

$$|\mathsf{HF}\rangle = \frac{1}{\sqrt{N!}}\mathsf{det}|\phi_1,\phi_2,\ldots\phi_N|, \quad \phi_p(\mathbf{r};\mathbf{x}) = \sum_{\mu} C_{\mu\rho}\chi_{\mu}(\mathbf{r};\mathbf{x}), \quad \left\langle \phi_p | \phi_q \right\rangle = \delta_{\rho q}$$

the truncated CI energy with respect to orbital rotations:

$$\frac{\partial E_{\mathsf{CI}}(x, c, \kappa)}{\partial c} = 0, \quad \frac{\partial E_{\mathsf{CI}}(x, c, \kappa)}{\partial \kappa} \neq 0$$

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Time-independent molecular properties

# Section 3

# Derivatives for Variational Wave Functions

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#### Molecular gradients

## Molecular Gradients for Variational Wave Functions

• Applying the chain rule, we obtain for the total derivative of the energy:

$$\frac{\mathrm{d}\mathcal{E}(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x} + \frac{\partial E(x,\lambda)}{\partial \lambda} \frac{\partial \lambda}{\partial x}$$

- the first term accounts for the explicit dependence on x
- the last term accounts for the implicit dependence on x
- We now invoke the stationary condition:

$$rac{\partial E(x,\lambda)}{\partial \lambda} = 0$$
 (zero electronic gradient for all x)

The molecular gradient then simplifies to

$$\frac{\mathrm{d}\mathcal{E}(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x}$$

examples: HF/KS and MCSCF molecular gradients (exponential parameterization)

For variational wave functions, we do not need the response of the wave function  $\partial \lambda / \partial x$  to calculate the molecular gradient  $d\mathcal{E}/dx$ .

#### Hellmann-Feynman Theorem

Assume that the (stationary) energy is an expectation value:

 $E(x,\lambda) = \langle \lambda | H(x) | \lambda \rangle$ 

▶ The gradient is then given by the expectation-value expression:

 $\frac{\mathrm{d}\mathcal{E}(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x} = \left\langle \lambda \left| \frac{\partial H}{\partial x} \right| \lambda \right\rangle \quad \leftarrow \text{the Hellmann-Feynman theorem}$ 

Relationship to first-order perturbation theory:

 $E^{(1)} = \left\langle 0 \left| H^{(1)} \right| 0 \right\rangle$ 

▶ The Hellmann–Feynman theorem was originally stated for geometrical distortions:

$$\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}\mathbf{R}_{K}} = -\left\langle\lambda\left|\sum_{i}\frac{Z_{K}\mathbf{r}_{iK}}{r_{iK}^{3}}\right|\lambda\right\rangle + \sum_{I\neq K}\frac{Z_{I}Z_{K}\mathbf{R}_{IK}}{R_{IK}^{3}}$$

Classical interpretation: integration over the force operator

#### Molecular Hessians for Variational Wave Functions

Differentiating the molecular gradient, we obtain the molecular Hessian:

$$\frac{\mathrm{d}^{2}\mathcal{E}(x)}{\mathrm{d}x^{2}} = \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial E(x,\lambda)}{\partial x} = \left(\frac{\partial}{\partial x} + \frac{\partial\lambda}{\partial x}\frac{\partial}{\partial\lambda}\right)\frac{\partial E(x,\lambda)}{\partial x}$$
$$= \frac{\partial^{2}E(x,\lambda)}{\partial x^{2}} + \frac{\partial^{2}E(x,\lambda)}{\partial x\partial\lambda}\frac{\partial\lambda}{\partial x}$$

- we need the first-order response  $\partial \lambda / \partial x$  to calculate the Hessian
- but we do not need the second-order response  $\partial^2 \lambda / \partial x^2$  for stationary energies
- ► To determine the response, we differentiate the stationary condition:

$$\frac{\partial E(x,\lambda)}{\partial \lambda} = 0 \quad (\text{all } x) \implies \frac{d}{dx} \frac{\partial E(x,\lambda)}{\partial \lambda} = 0$$
$$\implies \frac{\partial^2 E(x,\lambda)}{\partial x \partial \lambda} + \frac{\partial^2 E(x,\lambda)}{\partial \lambda^2} \frac{\partial \lambda}{\partial x} = 0$$

These are the first-order response equations:



#### Molecular Hessians

## **Response Equations**

The molecular Hessian for stationary energies:

$d^2 \mathcal{E}$	$\partial^2 E$	$\partial^2 E$	$\partial \lambda$
$\frac{dx^2}{dx^2}$ –	$\partial x^2$ +	$\partial x \partial \lambda$	$\partial x$

The response equations:

$$\begin{array}{c} \text{electronic} \\ \text{Hessian} \end{array} \rightarrow \begin{array}{c} \frac{\partial^2 E}{\partial \lambda^2} \end{array} \begin{array}{c} \frac{\partial \lambda}{\partial x} \end{array} = - \begin{array}{c} \frac{\partial^2 E}{\partial \lambda \partial x} \end{array} \leftarrow \begin{array}{c} \text{perturbed} \\ \text{electronic gradient} \end{array}$$

- the electronic Hessian is a Hermitian matrix, independent of the perturbation
- its dimensions are usually large and it cannot be constructed explicitly
- the response equations are typically solved by iterative techniques
- key step: multiplication of the Hessian with a trial vector
- Analogy with Hooke's law:

#### force constant $\rightarrow kx = -F \leftarrow$ force

the wave function relaxes by an amount proportional to the perturbation

## 2n + 1 Rule

- > For molecular gradients and Hessians, we have the expressions
  - $\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}x} = \frac{\partial E}{\partial x} \qquad \leftarrow \text{zero-order response needed}$  $\frac{\mathrm{d}^2 \mathcal{E}}{\mathrm{d}x^2} = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial x \partial \lambda} \frac{\partial \lambda}{\partial x} \qquad \leftarrow \text{first-order response needed}$
- ln general, we have the 2n + 1 rule:

For variational wave functions, the derivatives of the wave function to order n determine the derivatives of the energy to order 2n + 1.

Examples: wave-function responses needed to fourth order:

energy	$\mathcal{E}^{(0)}$	$\mathcal{E}^{(1)}$	$\mathcal{E}^{(2)}$	$\mathcal{E}^{(3)}$	$\mathcal{E}^{(4)}$
wave function	$\lambda^{(0)}$	$\lambda^{(0)}$	$\lambda^{(0)}, \lambda^{(1)}$	$\lambda^{(0)}, \lambda^{(1)}$	$\lambda^{(0)}$ , $\lambda^{(1)}$ , $\lambda^{(2)}$

# Section 4

# Derivatives for Nonvariational Wave Functions

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#### Nonvariational Wave Functions

- ▶ The 2*n* + 1 rule simplifies property evaluation for variational wave functions
- What about the nonvariational wave functions?
  - any energy may be made stationary by Lagrange's method of undetermined multipliers
  - ▶ the 2n + 1 rule is therefore of general interest
- Example: the CI energy
  - the CI energy function is given by:

 $E_{CI}(x, c, \kappa) \leftarrow CI \text{ parameters } c \text{ orbital-rotation parameters } \kappa$ 

it is nonstationary with respect to the orbital-rotation parameters:

 $\begin{array}{l} \displaystyle \frac{\partial E_{\mathsf{CI}}(x,c,\kappa)}{\partial c} = 0 & \leftarrow \text{stationary} \\ \displaystyle \frac{\partial E_{\mathsf{CI}}(x,c,\kappa)}{\partial \kappa} \neq 0 & \leftarrow \text{nonstationary} \end{array}$ 

- We shall now consider its molecular gradient:
  - by straightforward differentiation of the CI energy
  - Ø by differentiation of the CI Lagrangian
- In coupled-cluster theory, all parameters are nonvariationally determined

#### CI Molecular Gradients the Straightforward Way

• Straightforward differentiation of  $E_{CI}(x, c, \kappa)$  gives the expression

$$\begin{aligned} \frac{\mathrm{d}\mathcal{E}_{\mathsf{CI}}}{\mathrm{d}x} &= \frac{\partial E_{\mathsf{CI}}}{\partial x} + \frac{\partial E_{\mathsf{CI}}}{\partial c} \frac{\partial c}{\partial x} + \frac{\partial E_{\mathsf{CI}}}{\partial \kappa} \frac{\partial \kappa}{\partial x} \\ &= \frac{\partial E_{\mathsf{CI}}}{\partial x} + \frac{\partial E_{\mathsf{CI}}}{\partial \kappa} \frac{\partial \kappa}{\partial x} \quad \leftarrow \kappa \text{ contribution does not vanish} \end{aligned}$$

- it appears that we need the first-order response of the orbitals
- ▶ The HF orbitals used in CI theory fulfil the following conditions at all geometries:

 $\frac{\partial E_{\rm HF}}{\partial \kappa} = 0 \quad \leftarrow {\rm HF \ stationary \ conditions}$ 

we obtain the orbital responses by differentiating this equation with respect to x:

 $\frac{\partial^2 E_{\rm HF}}{\partial \kappa^2} \frac{\partial \kappa}{\partial x} = -\frac{\partial^2 E_{\rm HF}}{\partial x \partial \kappa} \quad \leftarrow \text{1st-order response equations}$ 

one such set of equations must be solved for each perturbation

Calculated in this manner, the CI gradient becomes expensive

## Lagrange's Method of Undetermined Multipliers

• To calculate the CI energy, we minimize  $E_{CI}$  with respect to c and  $\kappa$ :

 $\min_{c,\kappa} E_{Cl}(x,c,\kappa) \quad \text{subject to the constraints} \quad \stackrel{\diamond}{-}$ 

$$\frac{\partial E_{\mathsf{HF}}(x,\kappa)}{\partial \kappa} = 0$$

- Use Lagrange's method of undetermined multipliers:
  - construct the CI Lagrangian by adding these constraints with multipliers to the energy:

$$L_{\mathsf{CI}}(x, c, \kappa, \overline{\kappa}) = E_{\mathsf{CI}}(x, c, \kappa) + \overline{\kappa} \left( \frac{\partial E_{\mathsf{HF}}(x, \kappa)}{\partial \kappa} - 0 \right)$$

• adjust the Lagrange multipliers  $\overline{\kappa}$  such that the Lagrangian becomes stationary:

$$\frac{\partial L_{CI}}{\partial c} = 0 \implies \frac{\partial E_{CI}}{\partial c} = 0 \qquad \leftarrow \text{ CI conditions}$$

$$\frac{\partial L_{CI}}{\partial \kappa} = 0 \implies \frac{\partial E_{CI}}{\partial \kappa} + \overline{\kappa} \frac{\partial^2 E_{HF}}{\partial \kappa^2} = 0 \qquad \leftarrow \text{ linear set of equations for } \overline{\kappa}$$

$$\frac{\partial L_{CI}}{\partial \overline{\kappa}} = 0 \implies \frac{\partial E_{HF}}{\partial \kappa} = 0 \qquad \leftarrow \text{ HF conditions}$$

- note the duality between  $\kappa$  and  $\overline{\kappa}$
- Note that  $E_{CI} = L_{CI}$  when the Lagrangian is stationary
  - we now have a stationary CI energy expression L<sub>CI</sub>

# CI Molecular Gradients the Easy Way

• The CI Lagrangian is given by

 $L_{\rm CI} = E_{\rm CI} + \overline{\kappa} \frac{\partial E_{\rm HF}}{\partial \kappa} \quad \leftarrow \text{stationary with respect to all variables}$ 

Since the Lagrangian is stationary, we may invoke the 2n + 1 rule:

$$\frac{\mathrm{d}E_{\mathrm{CI}}}{\mathrm{d}x} = \frac{\mathrm{d}L_{\mathrm{CI}}}{\mathrm{d}x} = \frac{\partial L_{\mathrm{CI}}}{\partial x} = \frac{\partial E_{\mathrm{CI}}}{\partial x} + \overline{\kappa} \frac{\partial^2 E_{\mathrm{HF}}}{\partial \kappa \partial x}$$
zero-order response equations  $\rightarrow \overline{\kappa} \frac{\partial^2 E_{\mathrm{HF}}}{\partial \kappa^2} = -\frac{\partial E_{\mathrm{CI}}}{\partial \kappa}$ 

This result should be contrasted with the original expression

$$\frac{\mathrm{d}E_{\mathsf{CI}}}{\mathrm{d}x} = \frac{\partial E_{\mathsf{CI}}}{\partial x} + \frac{\partial E_{\mathsf{CI}}}{\partial \kappa} \frac{\partial \kappa}{\partial x}$$
first-order response equations  $\rightarrow \frac{\partial^2 E_{\mathsf{HF}}}{\partial \kappa^2} \frac{\partial \kappa}{\partial x} = -\frac{\partial^2 E_{\mathsf{HF}}}{\partial \kappa \partial x}$ 

We have greatly reduced the number of response equations to be solved

# Lagrange's Method Summarized

(1) Establish the energy function  $E(x, \lambda)$  and identify conditions on the variables

 $e(x,\lambda) = 0$ 

(2) Set up the Lagrangian energy function:



• (3) Satisfy the stationary conditions for the variables and their multipliers:

 $\frac{\partial L}{\partial \overline{\lambda}} = e(x, \lambda) = 0 \qquad \leftarrow \text{ condition for } \overline{\lambda} \text{ determines } \lambda$  $\frac{\partial L}{\partial \lambda} = \frac{\partial E}{\partial \lambda} + \overline{\lambda} \frac{\partial e}{\partial \lambda} = 0 \quad \leftarrow \text{ condition for } \lambda \text{ determines } \overline{\lambda}$ 

- note the duality between  $\lambda$  and  $\overline{\lambda}$ !
- (4) Calculate derivatives from the stationary Lagrangian
- ▶ The Lagrangian approach is generally applicable:
  - it gives the Hylleraas functional when applied to a perturbation expression
  - it may be generalized to time-dependent properties

### 2n+1 and 2n+2 Rules

For variational wave functions, we have the 2n + 1 rule:

 $\lambda^{(n)}$  determines the energy to order 2n + 1.

- The Lagrangian technique extends this rule to nonvariational wave functions
- For the new variables—the multipliers—the stronger 2n + 2 rule applies:

 $\overline{\lambda}^{(n)}$  determines the energy to order 2n + 2.

Responses required to order 10:

$\mathcal{E}^{(n)}$	0	1	2	3	4	5	6	7	8	9	10
$\lambda^{(k)}$	0	0	1	1	2	2	3	3	4	4	5
$\overline{\lambda}^{(k)}$	0	0	0	1	1	2	2	3	3	4	4

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Derivatives in second quantization • Second-quantization Hamiltonian • Molecular gradients

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#### Hartree–Fock Molecular Gradient

#### Hartree–Fock Energy

The MOs are expanded in atom-fixed AOs

$$\phi_p(\mathbf{r};\mathbf{x}) = \sum_{\mu} C_{\mu p} \chi_{\mu}(\mathbf{r};\mathbf{x})$$

The HF energy may be written in the general form

$$E_{\mathsf{HF}} = \sum_{pq} D_{pq} h_{pq} + \frac{1}{2} \sum_{pqrs} d_{pqrs} g_{pqrs} + \sum_{K>L} \frac{Z_K Z_L}{R_{KL}}$$

where

$$h_{pq}(\mathbf{x}) = \int \phi_p(\mathbf{r}, \mathbf{x}) \left( -\frac{1}{2} \nabla^2 - \sum_K \frac{Z_K}{r_K} \right) \phi_q(\mathbf{r}, \mathbf{x}) \, \mathrm{d}\mathbf{r}$$
$$g_{pqrs}(\mathbf{x}) = \iint \frac{\phi_p(\mathbf{r}_1, \mathbf{x}) \phi_q(\mathbf{r}_1, \mathbf{x}) \phi_r(\mathbf{r}_2, \mathbf{x}) \phi_s(\mathbf{r}_2, \mathbf{x})}{r_{12}} \, \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

- the integrals depend explicitly on the geometry
- ▶ In closed-shell restricted HF (RHF) theory, the energy is given by

$$E_{\mathsf{RHF}} = 2\sum_{i} h_{ii} + \sum_{ij} \left( 2g_{iijj} - g_{ijji} \right) + \sum_{K > L} \frac{Z_K Z_L}{R_{KL}}$$

summations over doubly occupied orbitals

#### Hartree–Fock Equations

The HF energy is minimized subject to orthonormality constraints

$$S_{ij} = \left\langle \phi_i | \phi_j \right\rangle = \delta_{ij}$$

We therefore introduce the HF Lagrangian:

$$L_{\rm HF} = E_{\rm HF} - \sum_{ij} \varepsilon_{ij} \left( S_{ij} - \delta_{ij} \right)$$
$$= \sum_{ij} D_{ij} h_{ij} + \frac{1}{2} \sum_{ijkl} d_{ijkl} g_{ijkl} - \sum_{ij} \varepsilon_{ij} \left( S_{ij} - \delta_{ij} \right) + \sum_{K>L} \frac{Z_K Z_L}{R_{KL}}$$

The stationary conditions on the Lagrangian become:

$$\frac{\partial L_{\text{HF}}}{\partial \varepsilon_{ij}} = S_{ij} - \delta_{ij} = 0$$
$$\frac{\partial L_{\text{HF}}}{\partial C_{\mu i}} = \frac{\partial E_{\text{HF}}}{\partial C_{\mu i}} - \sum_{kl} \varepsilon_{kl} \frac{\partial S_{kl}}{\partial C_{\mu i}} = 0$$

- the multiplier conditions are the orthonormality constraints
- the MO stationary conditions are the Roothaan–Hall equations

$$\frac{\partial E_{\mathsf{HF}}}{\partial C_{\mu i}} = \sum_{kl} \varepsilon_{kl} \frac{\partial S_{kl}}{\partial C_{\mu i}} \quad \Longrightarrow \quad \mathsf{F}^{\mathsf{AO}}\mathsf{C} = \mathsf{S}^{\mathsf{AO}}\mathsf{C}\varepsilon$$

# Hartree–Fock Molecular Gradient

From the 2n + 1 rule, we obtain the RHF molecular gradient:

$$\frac{\mathrm{d}E_{\mathsf{HF}}}{\mathrm{d}\mathbf{x}} = \frac{\mathrm{d}L_{\mathsf{HF}}}{\mathrm{d}\mathbf{x}} = \frac{\partial L_{\mathsf{HF}}}{\partial \mathbf{x}} = \frac{\partial E_{\mathsf{HF}}}{\partial \mathbf{x}} - \sum_{ii} \varepsilon_{ij} \frac{\partial S_{ij}}{\partial \mathbf{x}}$$

▶ In terms of MO integrals and density-matrix elements, we obtain the expression

$$\frac{\mathrm{d}E_{\mathsf{HF}}}{\mathrm{d}\mathbf{x}} = \sum_{ij} D_{ij} \frac{\partial h_{ij}}{\partial \mathbf{x}} + \frac{1}{2} \sum_{ijkl} d_{ijkl} \frac{\partial g_{ijkl}}{\partial \mathbf{x}} - \sum_{ij} \varepsilon_{ij} \frac{\partial S_{ij}}{\partial \mathbf{x}} + \mathbf{F}_{\mathsf{nuc}}$$

We then transform to the AO basis:

$$\frac{\mathrm{d}E_{\mathsf{HF}}}{\mathrm{d}\mathbf{x}} = \sum_{\mu\nu} D^{\mathsf{AO}}_{\mu\nu} \frac{\partial h^{\mathsf{AO}}_{\mu\nu}}{\partial \mathbf{x}} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} d^{\mathsf{AO}}_{\mu\nu\rho\sigma} \frac{\partial g^{\mathsf{AO}}_{\mu\nu\rho\sigma}}{\partial \mathbf{x}} - \sum_{\mu\nu} \varepsilon^{\mathsf{AO}}_{\mu\nu} \frac{\partial S^{\mathsf{AO}}_{\mu\nu}}{\partial \mathbf{x}} + \mathbf{F}_{\mathsf{nuc}}$$

- density matrices transformed to AO basis
- derivative integrals added directly to gradient elements
- Important points:
  - the gradient does not involve MO differentiation because of the 2n + 1 rule
  - the time-consuming step is integral differentiation

# FCI Energy

Consider a normalized CI wave function:

$$|\mathbf{c}
angle = \sum_{n=0}^{\infty} c_n |n
angle, \quad \mathbf{c}^{\mathrm{T}}\mathbf{c} = 1, \quad \langle m|n
angle = \delta_{mn}$$

• The basis functions  $|n\rangle$  are the normalized CI eigenstates of the unperturbed problem:

$$\langle m|H|n \rangle = \delta_{mn}E_n, \quad E_0 \leq E_1 \leq E_2 \cdots$$

▶ We assume that the ground-state energy function depends on two external parameters:

$$\langle \mathbf{c}|H(x,y)|\mathbf{c}\rangle = \sum_{mn} c_m \langle m|H(x,y)|n \rangle c_n, \quad \sum_n c_n^2 = 1$$

We construct a variational CI Lagrangian:

$$L(x, y, \mathbf{c}, \mu) = \sum_{mn} c_m \langle m | H(x, y) | n \rangle c_n - \mu \left( \sum_n c_n^2 - 1 \right)$$

The stationary conditions are given by

$$\frac{\partial L(x, y, \mathbf{c}, \mu)}{\partial c_n} = 0 \implies 2\langle n | H(x, y) | \mathbf{c} \rangle - 2\mu c_n = 0 \implies \mathbf{H}(x, y) \mathbf{c} = E_0(x, y) \mathbf{c}$$
$$\frac{\partial L(x, y, \mathbf{c}, \mu)}{\partial \mu} = 0 \implies \sum_n c_n^2 - 1 = 0 \implies \mathbf{c}^{\mathrm{T}} \mathbf{c} = 1$$

- the first condition is the CI eigenvalue problem with ground-state energy  $E_0(x, y) = \mu$
- the second condition is the CI normalization condition

### FCI Molecular Gradient and Hessian

• Using the CI Lagrangian, we calculate CI energy derivative in the usual way:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\partial L}{\partial x}, \quad \frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x\partial y} + \sum_n \frac{\partial^2 L}{\partial x\partial c_n} \frac{\partial c_n}{\partial x}, \quad \sum_n \frac{\partial^2 L}{\partial c_m \partial c_n} \frac{\partial c_n}{\partial x} = -\frac{\partial^2 L}{\partial x\partial c_m}$$

▶ By inverting the electronic Hessian, we obtain the more compact expression:

$$\frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x \partial y} - \sum_{mn} \frac{\partial^2 L}{\partial x \partial c_m} \left[ \frac{\partial^2 L}{\partial c_m \partial c_n} \right]^{-1} \frac{\partial^2 L}{\partial c_n \partial y}$$

• We next evaluate the various partial derivatives at x = y = 0 where  $|\mathbf{c}\rangle = |0\rangle$ :

$$\frac{\partial L}{\partial x} = \left\langle 0 \left| \frac{\partial H}{\partial x} \right| 0 \right\rangle, \quad \frac{\partial^2 L}{\partial x \partial y} = \left\langle 0 \left| \frac{\partial^2 H}{\partial x \partial y} \right| 0 \right\rangle, \quad \frac{\partial^2 L}{\partial x \partial c_n} = 2 \left\langle n \left| \frac{\partial H}{\partial x} \right| 0 \right\rangle$$
$$\frac{\partial^2 L}{\partial c_m \partial c_n} = 2 \left\langle m \left| H - E_0 \right| n \right\rangle = 2(E_n - E_0) \delta_{mn}$$

Inserted above, we recover Rayleigh–Schrödinger perturbation theory to second order:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \left\langle 0 \left| \frac{\partial H}{\partial x} \right| 0 \right\rangle, \quad \frac{\mathrm{d}^2 E}{\mathrm{d}x \mathrm{d}y} = \left\langle 0 \left| \frac{\partial^2 H}{\partial x \partial y} \right| 0 \right\rangle - 2 \sum_n \frac{\left\langle 0 \left| \frac{\partial H}{\partial x} \right| n \right\rangle \left\langle n \left| \frac{\partial H}{\partial y} \right| 0 \right\rangle}{E_n - E_0}$$

# Section 6

## Derivatives in second quantization

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# Second-Quantization Hamiltonian

▶ In second quantization, the Hamiltonian operator is given by:

$$H = \sum_{pq} h_{pq} a_p^{\dagger} a_q + \sum_{pqrs} g_{pqrs} a_p^{\dagger} a_r^{\dagger} a_s a_q + h_{nuc}$$
$$h_{pq} = \langle \phi_p^*(\mathbf{r}) | h(\mathbf{r}) | \phi_q(\mathbf{r}) \rangle$$
$$g_{pqrs} = \langle \phi_p^*(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) | r_{12}^{-1} | \phi_q(\mathbf{r}_1) \phi_s(\mathbf{r}_2) \rangle$$

• Its construction assumes an orthonormal basis of MOs  $\phi_p$ :

$$[a_{p},a_{q}]_{+}=0, \quad [a_{p}^{\dagger},a_{q}^{\dagger}]_{+}=0, \quad [a_{p},a_{q}^{\dagger}]_{+}=\delta_{pq}$$

- > The MOs are expanded in AOs, which often depend explicitly on the perturbation
  - such basis sets are said to be perturbation-dependent:

$$\phi_{p}(\mathbf{r}) = \sum_{\mu} C_{p\mu} \, \chi_{\mu}(\mathbf{r}, x)$$

- we must make sure that the MOs remain orthonormal for all x
- this introduces complications as we take derivatives with respect to x

## MOs and Hamiltonian at Distorted geometries

1. Orthonormal MOs at the reference geometry:

$$egin{aligned} \phi(\mathbf{x}_0) &= \mathbf{C}^{(0)} oldsymbol{\chi}(\mathbf{x}_0) \ \mathbf{S}(\mathbf{x}_0) &= ig\langle \phi(\mathbf{x}_0) \,|\, \phi^\dagger(\mathbf{x}_0) ig
angle = \mathbf{I} \end{aligned}$$

2. Geometrical distortion  $x = x_0 + \Delta x$ :

$$\phi(x) = \mathbf{C}^{(0)} \boldsymbol{\chi}(x)$$
$$\mathbf{S}(x) = \langle \phi(x) \, | \, \phi^{\dagger}(x) \rangle \neq \mathbf{I}$$

note: this basis is nonorthogonal and not useful for setting up the Hamiltonian.

3. Orthonormalize the basis set (e.g., by Löwdin orthonormalization):

$$\psi(x) = \mathbf{S}^{-1/2}(x)\phi(x)$$
  
$$\tilde{\mathbf{S}}(x) = \mathbf{S}^{-1/2}(x)\mathbf{S}(x)\mathbf{S}^{-1/2}(x) = \mathbf{I}$$

4. From these orthonormalized MOs (OMOs)  $\psi_p$ , construct Hamiltonian in the usual manner

$$\begin{split} H &= \sum_{pq} \tilde{h}_{pq} a_p^{\dagger} a_q + \sum_{pqrs} \tilde{g}_{pqrs} a_p^{\dagger} a_r^{\dagger} a_s a_q + h_{\text{nuc}} \\ \tilde{h}_{pq} &= \langle \psi_p^*(\mathbf{r}) | h(\mathbf{r}) | \psi_q(\mathbf{r}) \rangle \\ \tilde{g}_{pqrs} &= \langle \psi_p^*(\mathbf{r}_1) \psi_r^*(\mathbf{r}_2) | r_{12}^{-1} | \psi_q(\mathbf{r}_1) \psi_s(\mathbf{r}_2) \rangle \end{split}$$

### Hamiltonian at all Geometries

The Hamiltonian is now well defined at all geometries:

$$H(x) = \sum_{pq} \tilde{h}_{pq}(x) E_{pq}(x) + \frac{1}{2} \sum_{pqrs} \tilde{g}_{pqrs}(x) e_{pqrs}(x) + h_{nuc}(x)$$

• The OMO integrals are given by

$$\tilde{h}_{pq}(x) = \sum_{mn} h_{mn}(x) [S^{-1/2}]_{mp}(x) [S^{-1/2}]_{nq}(x)$$

in terms of the usual MO integrals

$$h_{mn}(x) = \sum_{\mu\nu} C^{(0)}_{m\mu} C^{(0)}_{n\nu} h^{AO}_{\mu\nu}(x), \quad S_{mn}(x) = \sum_{\mu\nu} C^{(0)}_{m\mu} C^{(0)}_{n\nu} S^{AO}_{\mu\nu}(x)$$

and similarly for the two-electron integrals.

- What about the geometry dependence of the excitation operators?
  - this may be neglected when calculating derivatives since, for all geometries,

$$\left[a_p(x), a_q^{\dagger}(x)
ight]_+ = ilde{S}_{pq}(x) = \delta_{pq}$$

## HF Molecular Gradients in Second Quantization

▶ The molecular gradient now follows from the Hellmann–Feynman theorem:

$$E^{(1)} = \langle 0|H^{(1)}|0\rangle = \sum_{pq} D_{pq}\tilde{h}_{pq}^{(1)} + \frac{1}{2}\sum_{pqrs} d_{pqrs}\tilde{g}_{pqrs}^{(1)} + h_{nuc}^{(1)}$$

We need the derivatives of the OMO integrals:

$$\tilde{h}_{pq}^{(1)} = \sum_{mn} \left[ h_{mn} (S^{-1/2})_{mp} (S^{-1/2})_{nq} \right]^{(1)} = h_{pq}^{(1)} - \frac{1}{2} \sum_{m} S_{pm}^{(1)} h_{mq}^{(0)} - \frac{1}{2} \sum_{m} h_{pm}^{(0)} S_{mq}^{(1)}$$

The gradient may therefore be written in the form

$$E^{(1)} = \sum_{pq} D_{pq} h_{pq}^{(1)} + \frac{1}{2} \sum_{pqrs} d_{pqrs} g_{pqrs}^{(1)} - \sum_{pq} F_{pq} S_{pq}^{(1)} + h_{nuc}^{(1)},$$

where the generalized Fock matrix is given by:

$$F_{pq} = \sum_{n} D_{pn} h_{qn} + \sum_{nrs} d_{pnrs} g_{qnrs}$$

▶ For RHF theory, this result is equivalent to that derived in first quantization

# Section 7

**Geometrical Properties** 

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#### Geometrical Derivatives

In the Born–Oppenheimer approximation, the nuclei move on the electronic potential-energy surface E(x), which is a function of the nuclear geometry:

 $\mathcal{E}(x) = \mathcal{E}_0 + \mathcal{E}^{(1)} \Delta x + \frac{1}{2} \mathcal{E}^{(2)} \Delta x^2 + \cdots \leftarrow$  expansion around the reference geometry

The derivatives of this surface are therefore important:

$$\begin{split} \mathcal{E}^{(1)} &= \frac{\mathrm{d}\mathcal{E}}{\mathrm{d}x} & \leftarrow \text{molecular gradient} \\ \mathcal{E}^{(2)} &= \frac{\mathrm{d}^2 \mathcal{E}}{\mathrm{d}x^2} & \leftarrow \text{molecular Hessian} \end{split}$$

- The geometrical derivatives are
  - used for locating and characterizing critical points
  - related to spectroscopic constants, vibrational frequencies, and intensities
- Usually, only a few terms are needed in the expansions
  - in some cases low-order expansions are inadequate or useless

#### Uses of Geometrical Derivatives

- To explore molecular potential-energy surfaces (3N 6 dimensions)
  - Iocalization and characterization of stationary points
  - Iocalization of avoided crossings and conical intersections
  - calculation of reaction paths and reaction-path Hamiltonians
  - application to direct dynamics
- To calculate spectroscopic constants
  - molecular structure
  - quadratic force constants and harmonic frequencies
  - cubic and quartic force constants; fundamental frequencies
  - partition functions
  - dipole gradients and vibrational infrared intensities
  - polarizability gradients and Raman intensities

#### Bond Distances

Mean and mean abs. errors for 28 distances at the all-el. cc-pVXZ level (pm):



Bonds shorten with increasing basis:

- ▶ HF:  $DZ \rightarrow TZ$  0.8 pm;  $TZ \rightarrow QZ$  0.1 pm
- corr.: DZ  $\rightarrow$  TZ 1.6 pm; TZ  $\rightarrow$  QZ 0.1–0.2 pm
- Bonds lengthen with improvements in the N-electron model:
  - singles < doubles < triples <  $\cdots$
- There is considerable scope for error cancellation: CISD/DZ, MP3/DZ

# Bond Distances R<sub>e</sub> of BH, CO, N<sub>2</sub>, HF, and F<sub>2</sub> (pm)



# Contributions to Equilibrium Bond Distances (pm)

	RHF	SD	т	Q	5	rel.	adia.	theory	exp.	err.
HF	89.70	1.67	0.29	0.02	0.00	0.01	0.0	91.69	91.69	0.00
$N_2$	106.54	2.40	0.67	0.14	0.03	0.00	0.0	109.78	109.77	0.01
F <sub>2</sub>	132.64	6.04	2.02	0.44	0.03	0.05	0.0	141.22	141.27	-0.05
CO	110.18	1.87	0.75	0.04	0.00	0.00	0.0	112.84	112.84	0.00

We have agreement with experiment to within 0.01 pm except for F<sub>2</sub>

- ▶ Hartree–Fock theory underestimates bond distances by up to 8.6 pm (for F<sub>2</sub>)
- All correlation contributions are positive
  - approximately linear convergence, slowest for F<sub>2</sub>
  - triples contribute up to 2.0, quadruples up to 0.4, and quintuples 0.03 pm
  - sextuples are needed for convergence to within 0.01 pm
- Relativistic corrections are small except for F<sub>2</sub> (0.05 pm)
  - of the same magnitude and direction as the quintuples

# Harmonic Constants $\omega_e$ of BH, CO, N<sub>2</sub>, HF, and F<sub>2</sub> (cm<sup>-1</sup>)



# Contributions to Harmonic Frequencies $\omega_{e}$ (cm<sup>-1</sup>)

	RHF	SD	Т	Q	5	rel.	adia.	theory	exp.	err.
HF	4473.8	-277.4	-50.2	-4.1	-0.1	-3.5	0.4	4138.9	4138.3	0.1
$N_2$	2730.3	-275.8	-72.4	-18.8	-3.9	-1.4	0.0	2358.0	2358.6	-0.6
$F_2$	1266.9	-236.1	-95.3	-15.3	-0.8	-0.5	0.0	918.9	916.6	2.3
CO	2426.7	-177.4	-71.7	-7.2	0.0	-1.3	0.0	2169.1	2169.8	0.7

- We have agreement with experiment to within  $1 \text{ cm}^{-1}$  except for F<sub>2</sub>
- ▶ Hartree–Fock theory overestimates harmonic frequencies by up to 38% (in F<sub>2</sub>).
- All correlation contributions are large and negative
  - ▶ triples contribute up to 95 cm<sup>-1</sup>, quadruples 20 cm<sup>-1</sup>, and quintuples 4 cm<sup>-1</sup>
  - sextuples are sometimes needed for convergence to within 1 cm<sup>-1</sup>
- The relativistic corrections are of the order of 1 cm<sup>-1</sup>
  - of the same magnitude and direction as the quadruples or quintuples

# Higher-Order Connected Contributions to $\omega_e$ in N<sub>2</sub> (cm<sup>-1</sup>)

There are substantial higher-order corrections:



- connected triples relaxation contributes 9.7 cm<sup>-1</sup> (total triples -70.5 cm<sup>-1</sup>)
- connected quadruples contribute -18.8 cm<sup>-1</sup>
- connected quintuples contribute -3.9 cm<sup>-1</sup>

# Anharmonic Constants $\omega_e x_e$ of BH, CO, N<sub>2</sub>, HF, and F<sub>2</sub> (cm<sup>-1</sup>)

