

Time-independent molecular properties

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Section 1

Introduction

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Time-Independent Molecular Properties

- ▶ When a molecular system is perturbed, its total energy changes

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

- ▶ 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

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

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

- ▶ 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 spin 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)

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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)

λ : electronic (wave-function) parameters (MOs, cluster amplitudes)

- ▶ The Hamiltonian (here in second quantization)

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

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 λ for each value of x :

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

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

$$\frac{d\mathcal{E}(x)}{dx} = \underbrace{\frac{\partial E(x, \lambda^*)}{\partial x}}_{\text{explicit dependence}} + \underbrace{\left. \frac{\partial E(x, \lambda)}{\partial \lambda} \right|_{\lambda=\lambda^*} \left. \frac{\partial \lambda}{\partial x} \right|_{\lambda=\lambda^*}}_{\text{implicit dependence}}$$

- ▶ 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:

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

- ▶ **example:** the Hartree–Fock energy in an unconstrained exponential parameterization

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

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

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

Nonvariational wave functions

- ▶ the optimized energy does not fulfil the stationary (variational) condition:

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

- ▶ **example:** the Hartree–Fock and Kohn–Sham energies in a constrained LCAO parameterization (orthonormality)

$$|\text{HF}\rangle = \frac{1}{\sqrt{N!}} \det|\phi_1, \phi_2, \dots, \phi_N|, \quad \phi_p(\mathbf{r}; \mathbf{x}) = \sum_{\mu} C_{\mu p} \chi_{\mu}(\mathbf{r}; \mathbf{x}), \quad \langle \phi_p | \phi_q \rangle = \delta_{pq}$$

- ▶ **example:** the truncated CI energy with respect to orbital rotations:

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

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Derivatives for Variational Wave Functions

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Molecular Gradients for Variational Wave Functions

- ▶ Applying the **chain rule**, we obtain for the total derivative of the energy:

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

- ▶ 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**:

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

- ▶ The molecular gradient then simplifies to

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

- ▶ 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**:

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

- ▶ Relationship to **first-order perturbation theory**:

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

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

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

- ▶ Classical interpretation: **integration over the force operator**

Molecular Hessians for Variational Wave Functions

- ▶ Differentiating the molecular gradient, we obtain the **molecular Hessian**:

$$\begin{aligned}\frac{d^2\mathcal{E}(x)}{dx^2} &= \frac{d}{dx} \frac{\partial E(x, \lambda)}{\partial x} = \left(\frac{\partial}{\partial x} + \frac{\partial \lambda}{\partial x} \frac{\partial}{\partial \lambda} \right) \frac{\partial E(x, \lambda)}{\partial x} \\ &= \frac{\partial^2 E(x, \lambda)}{\partial x^2} + \frac{\partial^2 E(x, \lambda)}{\partial x \partial \lambda} \frac{\partial \lambda}{\partial x}\end{aligned}$$

- ▶ 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**:

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

- ▶ These are the **first-order response equations**:

$$\underbrace{\frac{\partial^2 E}{\partial \lambda^2}}_{\text{electronic Hessian}} \frac{\partial \lambda}{\partial x} = - \underbrace{\frac{\partial^2 E}{\partial x \partial \lambda}}_{\text{right-hand side}}$$

Response Equations

- ▶ The **molecular Hessian** for stationary energies:

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

- ▶ The **response equations**:

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

- ▶ 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**:

$$\text{force constant} \rightarrow kx = -F \leftarrow \text{force}$$

- ▶ the wave function relaxes by an amount proportional to the perturbation

2n + 1 Rule

- ▶ For molecular gradients and Hessians, we have the expressions

$$\frac{d\mathcal{E}}{dx} = \frac{\partial E}{\partial x} \quad \leftarrow \text{zero-order response needed}$$

$$\frac{d^2\mathcal{E}}{dx^2} = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial x \partial \lambda} \frac{\partial \lambda}{\partial x} \quad \leftarrow \text{first-order response needed}$$

- ▶ In 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	$\lambda^{(0)}$	$\lambda^{(0)}$	$\lambda^{(0)}, \lambda^{(1)}$	$\lambda^{(0)}, \lambda^{(1)}$	$\lambda^{(0)}, \lambda^{(1)}, \lambda^{(2)}$

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Nonvariational Wave Functions

- ▶ The $2n + 1$ 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:

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

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

$$\frac{\partial E_{\text{CI}}(x, c, \kappa)}{\partial c} = 0 \leftarrow \text{stationary}$$

$$\frac{\partial E_{\text{CI}}(x, c, \kappa)}{\partial \kappa} \neq 0 \leftarrow \text{nonstationary}$$

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

CI Molecular Gradients the Straightforward Way

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

$$\begin{aligned} \frac{dE_{\text{CI}}}{dx} &= \frac{\partial E_{\text{CI}}}{\partial x} + \frac{\partial E_{\text{CI}}}{\partial c} \frac{\partial c}{\partial x} + \frac{\partial E_{\text{CI}}}{\partial \kappa} \frac{\partial \kappa}{\partial x} \\ &= \frac{\partial E_{\text{CI}}}{\partial x} + \frac{\partial E_{\text{CI}}}{\partial \kappa} \frac{\partial \kappa}{\partial x} \quad \leftarrow \kappa \text{ contribution does not vanish} \end{aligned}$$

- ▶ 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:

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

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

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

- ▶ 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 κ :

$$\min_{c, \kappa} E_{\text{CI}}(x, c, \kappa) \quad \text{subject to the constraints} \quad \frac{\partial E_{\text{HF}}(x, \kappa)}{\partial \kappa} = 0$$

- ▶ Use Lagrange's method of undetermined multipliers:

- ▶ construct the CI Lagrangian by adding these constraints with multipliers to the energy:

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

- ▶ adjust the Lagrange multipliers $\bar{\kappa}$ such that the Lagrangian becomes stationary:

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

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

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

- ▶ note the duality between κ and $\bar{\kappa}$
- ▶ Note that $E_{\text{CI}} = L_{\text{CI}}$ when the Lagrangian is stationary
 - ▶ we now have a stationary CI energy expression L_{CI}

CI Molecular Gradients the Easy Way

- ▶ The CI Lagrangian is given by

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

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

$$\frac{dE_{\text{CI}}}{dx} = \frac{dL_{\text{CI}}}{dx} = \frac{\partial L_{\text{CI}}}{\partial x} = \frac{\partial E_{\text{CI}}}{\partial x} + \bar{\kappa} \frac{\partial^2 E_{\text{HF}}}{\partial \kappa \partial x}$$

$$\text{zero-order response equations} \rightarrow \bar{\kappa} \frac{\partial^2 E_{\text{HF}}}{\partial \kappa^2} = - \frac{\partial E_{\text{CI}}}{\partial \kappa}$$

- ▶ This result should be contrasted with the original expression

$$\frac{dE_{\text{CI}}}{dx} = \frac{\partial E_{\text{CI}}}{\partial x} + \frac{\partial E_{\text{CI}}}{\partial \kappa} \frac{\partial \kappa}{\partial x}$$

$$\text{first-order response equations} \rightarrow \frac{\partial^2 E_{\text{HF}}}{\partial \kappa^2} \frac{\partial \kappa}{\partial x} = - \frac{\partial^2 E_{\text{HF}}}{\partial \kappa \partial x}$$

- ▶ 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**:

$$\underbrace{L(x, \lambda, \bar{\lambda})}_{\text{Lagrangian}} = \underbrace{E(x, \lambda)}_{\text{energy function}} + \bar{\lambda} \underbrace{(e(x, \lambda) - 0)}_{\text{constraints}}$$

- ▶ (3) Satisfy the **stationary conditions** for the variables and their multipliers:

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

$$\frac{\partial L}{\partial \lambda} = \frac{\partial E}{\partial \lambda} + \bar{\lambda} \frac{\partial e}{\partial \lambda} = 0 \quad \leftarrow \text{condition for } \lambda \text{ determines } \bar{\lambda}$$

- ▶ note the **duality** between λ and $\bar{\lambda}$!
- ▶ (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:

$\bar{\lambda}^{(n)}$ 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
$\bar{\lambda}^{(k)}$	0	0	0	1	1	2	2	3	3	4	4

Section 5

Examples of derivatives

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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

$$E_{\text{HF}} = \sum_{ij} D_{ij} h_{ij} + \frac{1}{2} \sum_{ijkl} d_{ijkl} g_{ijkl} + \sum_{K>L} \frac{Z_K Z_L}{R_{KL}}$$

where the one- and two-electron integrals are given by

$$h_{ij}(\mathbf{x}) = \int \phi_i(\mathbf{r}, \mathbf{x}) \left(-\frac{1}{2} \nabla^2 - \sum_K \frac{Z_K}{r_K} \right) \phi_j(\mathbf{r}, \mathbf{x}) d\mathbf{r}$$

$$g_{ijkl}(\mathbf{x}) = \iint \frac{\phi_i(\mathbf{r}_1, \mathbf{x}) \phi_j(\mathbf{r}_1, \mathbf{x}) \phi_k(\mathbf{r}_2, \mathbf{x}) \phi_l(\mathbf{r}_2, \mathbf{x})}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

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

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

- ▶ summations over doubly occupied orbitals

Hartree–Fock Equations

- ▶ The HF energy is minimized subject to **orthonormality constraints**

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

- ▶ We therefore introduce the **HF Lagrangian**:

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

- ▶ The **stationary conditions** on the Lagrangian become:

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

- ▶ Note:

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

$$\frac{\partial E_{\text{HF}}}{\partial C_{\mu i}} = \sum_{kl} \varepsilon_{kl} \frac{\partial S_{kl}}{\partial C_{\mu i}} \quad \implies \quad \mathbf{F}^{\text{AO}} \mathbf{C} = \mathbf{S}^{\text{AO}} \mathbf{C} \boldsymbol{\varepsilon}$$

Hartree–Fock Molecular Gradient

- ▶ From the $2n + 1$ rule, we obtain the **RHF molecular gradient**:

$$\frac{dE_{\text{HF}}}{d\mathbf{x}} = \frac{dL_{\text{HF}}}{d\mathbf{x}} = \frac{\partial L_{\text{HF}}}{\partial \mathbf{x}} = \frac{\partial E_{\text{HF}}}{\partial \mathbf{x}} - \sum_{ij} \varepsilon_{ij} \frac{\partial S_{ij}}{\partial \mathbf{x}}$$

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

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

- ▶ We then express the gradient in terms of **AO integrals**:

$$\frac{dE_{\text{HF}}}{d\mathbf{x}} = \sum_{\mu\nu} D_{\mu\nu}^{\text{AO}} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial \mathbf{x}} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} d_{\mu\nu\rho\sigma}^{\text{AO}} \frac{\partial g_{\mu\nu\rho\sigma}^{\text{AO}}}{\partial \mathbf{x}} - \sum_{\mu\nu} \varepsilon_{\mu\nu}^{\text{AO}} \frac{\partial S_{\mu\nu}^{\text{AO}}}{\partial \mathbf{x}} + \mathbf{F}_{\text{nuc}}$$

- ▶ 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**:

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

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

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

- ▶ 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

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

$$\frac{\partial L(x, y, \mathbf{c}, \mu)}{\partial \mu} = 0 \implies \sum_n c_n^2 - 1 = 0 \implies \mathbf{c}^T \mathbf{c} = 1$$

- ▶ 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:

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

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

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

- ▶ We next evaluate the various partial derivatives at $x = y = 0$ where $|c\rangle = |0\rangle$:

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

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

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

Section 6

Derivatives in second quantization

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Second-Quantization Hamiltonian

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

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q + h_{\text{nuc}}$$

$$h_{pq} = \langle \phi_p^*(\mathbf{r}) | h(\mathbf{r}) | \phi_q(\mathbf{r}) \rangle$$

$$g_{pqrs} = \langle \phi_p^*(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) | r_{12}^{-1} | \phi_q(\mathbf{r}_1) \phi_s(\mathbf{r}_2) \rangle$$

- ▶ Its construction assumes an **orthonormal basis of MOs** ϕ_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**:

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

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

MOs and Hamiltonian at Distorted geometries

1. Orthonormal MOs at the reference geometry:

$$\phi(x_0) = \mathbf{C}^{(0)}\chi(x_0)$$

$$\mathbf{S}(x_0) = \langle \phi(x_0) | \phi^\dagger(x_0) \rangle = \mathbf{I}$$

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

$$\phi(x) = \mathbf{C}^{(0)}\chi(x)$$

$$\mathbf{S}(x) = \langle \phi(x) | \phi^\dagger(x) \rangle \neq \mathbf{I}$$

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)** ψ_p , construct Hamiltonian in the usual manner

$$H = \sum_{pq} \tilde{h}_{pq} a_p^\dagger a_q + \sum_{pqrs} \tilde{g}_{pqrs} a_p^\dagger a_r^\dagger a_s a_q + h_{\text{nuc}}$$

$$\tilde{h}_{pq} = \langle \psi_p^*(\mathbf{r}) | h(\mathbf{r}) | \psi_q(\mathbf{r}) \rangle$$

$$\tilde{g}_{pqrs} = \langle \psi_p^*(\mathbf{r}_1) \psi_r^*(\mathbf{r}_2) | r_{12}^{-1} | \psi_q(\mathbf{r}_1) \psi_s(\mathbf{r}_2) \rangle$$

Hamiltonian at all Geometries

- ▶ The Hamiltonian is now well defined at **all geometries**:

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

- ▶ 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

$$h_{mn}(x) = \sum_{\mu\nu} C_{m\mu}^{(0)} C_{n\nu}^{(0)} h_{\mu\nu}^{\text{AO}}(x), \quad S_{mn}(x) = \sum_{\mu\nu} C_{m\mu}^{(0)} C_{n\nu}^{(0)} S_{\mu\nu}^{\text{AO}}(x),$$

with $S_{mn}(x_0) = \delta_{mn}$ 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,

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

HF Molecular Gradients in Second Quantization

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

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

- ▶ We need the derivatives of the OMO integrals:

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

since $S^{-1/2} = I$ and $[S^{-1/2}]^{(1)} = -\frac{1}{2} S^{(1)}$ at $x = x_0$.

- ▶ The gradient may therefore be written in the form

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

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 $\mathcal{E}(x)$, which is a function of the nuclear geometry:

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

- ▶ The derivatives of this surface are therefore important:

$$\mathcal{E}^{(1)} = \frac{d\mathcal{E}}{dx} \leftarrow \text{molecular gradient}$$

$$\mathcal{E}^{(2)} = \frac{d^2\mathcal{E}}{dx^2} \leftarrow \text{molecular Hessian}$$

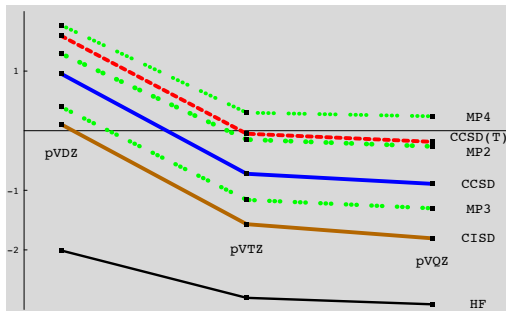
- ▶ The geometrical derivatives are
 - ▶ used for **locating and characterizing critical points**
 - ▶ related to **spectroscopic constants**, vibrational frequencies, and intensities
- ▶ Usually, only a few terms are needed in the expansions
 - ▶ in some cases low-order expansions are inadequate or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

Uses of Geometrical Derivatives

- ▶ To explore molecular potential-energy surfaces ($3N - 6$ dimensions)
 - ▶ localization and characterization of stationary points
 - ▶ localization 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

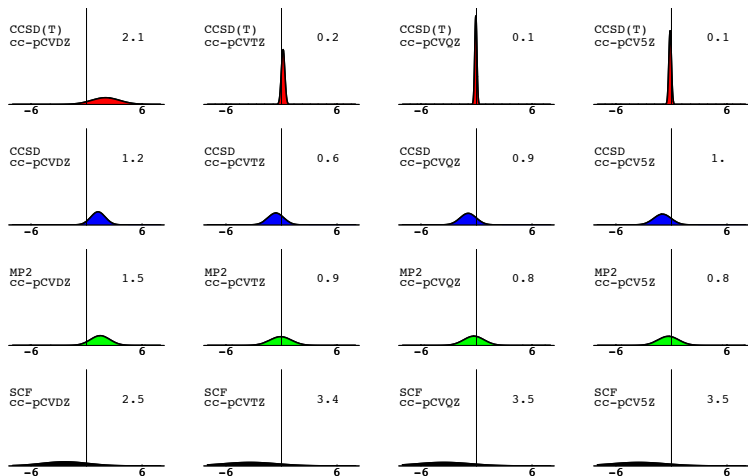
Bond Distances

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



$ \overline{\Delta} $	DZ	TZ	QZ
CCSD	1.2	0.6	0.8
CCSD(T)	1.7	0.2	0.2

- ▶ 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 < ...
- ▶ There is considerable scope for error cancellation: CISD/DZ, MP3/DZ

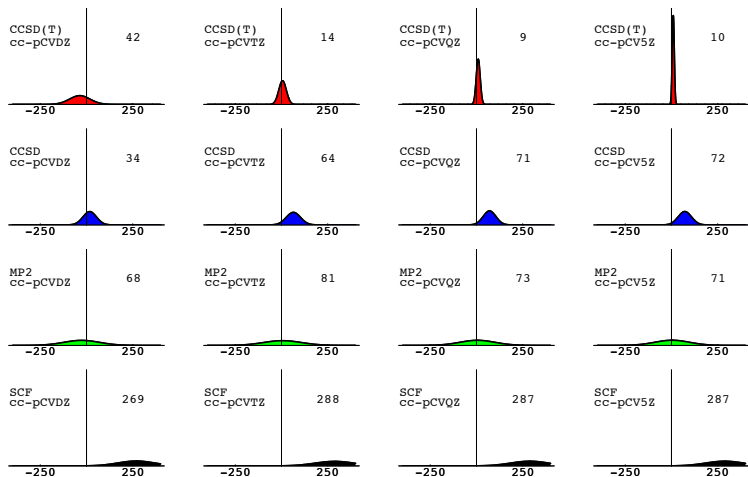
Bond Distances R_e of BH, CO, N₂, HF, and F₂ (pm)

Contributions to Equilibrium Bond Distances (pm)

	RHF	SD	T	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 ₂	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 F₂
- ▶ Hartree–Fock theory underestimates bond distances by up to 8.6 pm (for F₂)
- ▶ All correlation contributions are positive
 - ▶ approximately linear convergence, slowest for F₂
 - ▶ 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 F₂ (0.05 pm)
 - ▶ of the same magnitude and direction as the quintuples

Harmonic Constants ω_e of BH, CO, N₂, HF, and F₂ (cm⁻¹)



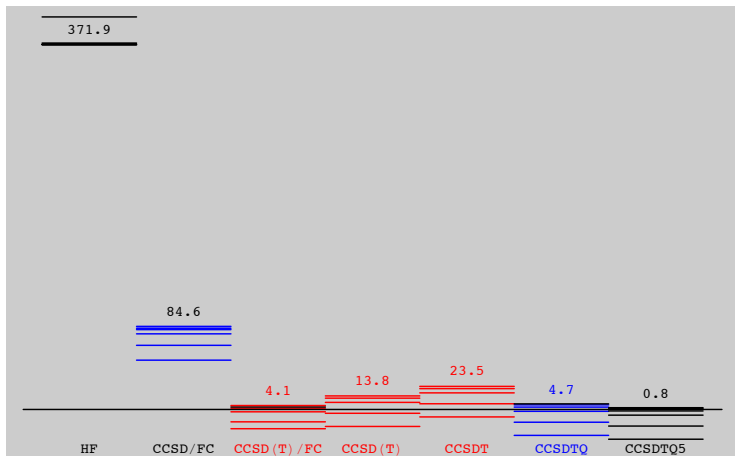
Contributions to Harmonic Frequencies ω_e (cm^{-1})

	RHF	SD	T	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 cm^{-1} except for F₂
- ▶ Hartree–Fock theory overestimates harmonic frequencies by up to 38% (in F₂).
- ▶ All correlation contributions are large and negative
 - ▶ triples contribute up to 95 cm^{-1} , quadruples 20 cm^{-1} , and quintuples 4 cm^{-1}
 - ▶ sextuples are sometimes needed for convergence to within 1 cm^{-1}
- ▶ The relativistic corrections are of the order of 1 cm^{-1}
 - ▶ of the same magnitude and direction as the quadruples or quintuples

Higher-Order Connected Contributions to ω_e in N_2 (cm^{-1})

- ▶ There are substantial higher-order corrections:



- ▶ connected triples relaxation contributes 9.7 cm^{-1} (total triples -70.5 cm^{-1})
- ▶ connected quadruples contribute -18.8 cm^{-1}
- ▶ connected quintuples contribute -3.9 cm^{-1}

Anharmonic Constants $\omega_e x_e$ of BH, CO, N₂, HF, and F₂ (cm⁻¹)

