

Time-independent molecular properties

Trygve Helgaker

Centre for Theoretical and Computational Chemistry
Department of Chemistry, University of Oslo, Norway

The 12th Sostrup Summer School
Quantum Chemistry and Molecular Properties
July 1–13 2012

- ▶ Introduction
- ▶ Energy functions
 - ▶ variational wave functions
 - ▶ nonvariational wave functions
- ▶ Derivatives for variational wave functions
 - ▶ molecular gradients and Hessians
 - ▶ the $2n + 1$ rule
- ▶ Derivatives for nonvariational wave functions
 - ▶ the Lagrangian method
 - ▶ the $2n + 1$ and $2n + 2$ rules
- ▶ The molecular gradient
 - ▶ the Hartree–Fock molecular gradient in first quantization
 - ▶ Hamiltonian derivatives in second quantization
 - ▶ the Hartree–Fock molecular gradient in second quantization
- ▶ Geometrical properties: uses and benchmarking
 - ▶ molecular equilibrium structures
 - ▶ vibrational harmonic and fundamental frequencies

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

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

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)

Overview: Calculation of derivatives

- ▶ Energy functionals:
 - ▶ variational and nonvariational energies
- ▶ Variational wave functions:
 - ▶ gradients and Hessians
 - ▶ response equations
 - ▶ the $2n + 1$ rule
- ▶ Nonvariational wave functions:
 - ▶ Lagrange's method of undetermined multipliers
 - ▶ the $2n + 1$ and $2n + 2$ rules
- ▶ Derivatives in more detail:
 - ▶ Hartree–Fock molecular gradients
- ▶ Hamiltonian derivatives in second quantization:
 - ▶ perturbation-dependent basis sets

The 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 $\lambda(x)$.

The 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 variational!
- ▶ 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 dependence as well as the 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

Variational and nonvariational wave functions

- ▶ Variational wave functions:

- ▶ the optimized energy fulfils the stationary (variational) condition:

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

where x is the geometry and λ the electronic parameters.

- ▶ the stationary condition determines λ as a function of the geometry $\lambda(x)$
- ▶ for the ground state, the energy is typically obtained by minimization:

$$\mathcal{E}(x) = \min_{\lambda} E(x, \lambda) \quad (\text{for all } x)$$

- ▶ Nonvariational wave functions:

- ▶ wave functions whose energy does not fulfil the stationary condition

Examples of variational wave functions

- ▶ Hartree–Fock and Kohn–Sham energies in an exponential parametrization:

$$\frac{\partial E_{\text{SCF}}}{\partial \kappa_{ia}} = 0 \quad \text{orbital-rotation parameters}$$

- ▶ expressed in terms of MO coefficients, the HF energy is nonstationary

$$\frac{\partial E_{\text{SCF}}}{\partial C_{\mu i}} \neq 0 \quad \text{MO coefficients}$$

- ▶ The MCSCF energy in an exponential parametrization:

$$\frac{\partial E_{\text{MC}}}{\partial \kappa_{pq}} = 0 \quad \text{orbital-rotation parameters}$$

$$\frac{\partial E_{\text{MC}}}{\partial p_k} = 0 \quad \text{state-transfer parameters}$$

- ▶ expressed in terms of MO and CI coefficients, the energy is nonstationary
- ▶ We note the importance of the parametrization!

Examples of nonvariational wave functions

- ▶ The CI energy is nonvariational with respect to the orbital-rotation parameters:

$$\frac{\partial E_{\text{CI}}}{\partial \kappa_{pq}} \neq 0 \quad \text{orbital-rotation parameters}$$

$$\frac{\partial E_{\text{CI}}}{\partial P_k} = 0 \quad \text{state-transfer parameters}$$

- ▶ The CI orbitals instead satisfy the HF/MCSCF stationary conditions:

$$\frac{\partial E_{\text{MC}}}{\partial \kappa_{pq}} = 0 \quad \text{orbital-rotation parameters}$$

- ▶ The CI energy is often referred to as variational:
 - ▶ it represents an upper bound to the exact ground-state energy
 - ▶ it is not stationary with respect to variations in the MOs
- ▶ Other examples: coupled-cluster and perturbation theories

Molecular gradients

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

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

- ▶ 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**:

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

- ▶ The molecular gradient then simplifies to

$$\frac{d\mathcal{E}}{dx} = \frac{\partial E}{\partial x}$$

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

- ▶ Examples: HF/KS and MCSCF molecular gradients (exponential parametrization)

The 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 expression:

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

- ▶ 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

- ▶ Differentiating the molecular gradient, we obtain:

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

- ▶ Note:

- ▶ we need the **first-order response** $\partial\lambda/\partial x$ to calculate the Hessian
- ▶ 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**:

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

- ▶ These are the first-order (time-independent) **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 independent of the perturbation
 - ▶ its dimensions are usually large and it cannot be constructed explicitly
 - ▶ the response equations are usually 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

The molecular Hessian for FCI wave functions

- ▶ The **molecular Hessian** may be written in the general form

$$\frac{d^2\mathcal{E}}{dx^2} = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial x \partial \lambda} \frac{\partial \lambda}{\partial x} = \frac{\partial^2 E}{\partial x^2} - \frac{\partial^2 E}{\partial x \partial \lambda} \left[\frac{\partial^2 E}{\partial \lambda^2} \right]^{-1} \frac{\partial^2 E}{\partial \lambda \partial x}$$

- ▶ For **FCI wave functions**, we make the following identifications:

$$\begin{aligned} \frac{\partial^2 E}{\partial x \partial \lambda_n} &= 2 \langle 0 | H^{(1)} | n \rangle \\ \frac{\partial^2 E}{\partial \lambda_m \partial \lambda_n} &= 2 \delta_{mn} (E_n - E_0) \quad \leftarrow \text{diagonal representation} \end{aligned}$$

- ▶ This gives the following expression for the **FCI molecular Hessian**:

$$\mathcal{E}^{(2)} = \langle 0 | H^{(2)} | 0 \rangle - 2 \sum_n \frac{\langle 0 | H^{(1)} | n \rangle \langle n | H^{(1)} | 0 \rangle}{E_n - E_0}$$

- ▶ compare with **second-order perturbation theory**

The $2n + 1$ 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 energy derivatives 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	$\lambda^{(0)}$	$\lambda^{(0)}$	$\lambda^{(0)}, \lambda^{(1)}$	$\lambda^{(0)}, \lambda^{(1)}$	$\lambda^{(0)}, \lambda^{(1)}, \lambda^{(2)}$

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:

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

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

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

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

- ▶ We shall now consider its **molecular gradient**:
 - 1 by straightforward differentiation of the CI energy
 - 2 by differentiation of the CI Lagrangian

CI molecular gradients the straightforward way

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

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

- ▶ 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 HF response equations must be solved for **each perturbation**
- ▶ Calculated in this manner, the CI gradient becomes **expensive**

Lagrange's method of undetermined multipliers

- ▶ When calculating the CI energy, we minimize E_{CI} with respect to P and κ :

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

- ▶ Use Lagrange's method of undetermined multipliers:

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

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

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

$$\frac{\partial L_{\text{CI}}}{\partial P} = \frac{\partial E_{\text{CI}}}{\partial P} = 0 \quad \leftarrow \text{CI stationary conditions}$$

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

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

- ▶ note the duality between κ and $\bar{\kappa}$.
- ▶ We now have a stationary CI energy expression

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:

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

one set of 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

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

$3N$ sets of 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

- ▶ The Lagrangian energy function:

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

- ▶ The stationary conditions for variables and their multipliers:

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

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

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

The $2n + 2$ rule

- ▶ 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

Derivatives so far . . .

- ▶ The $2n + 1$ rule greatly simplifies derivatives for variational wave functions.
 - ▶ simple example: molecular gradients for variational wave functions

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

- ▶ the Lagrangian techniques extends this rule to all wave functions
- ▶ We shall now apply this theory to the calculation of gradients
 - ▶ using first quantization
 - ▶ using second quantization

The 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

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

where

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

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

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

- ▶ summations over doubly occupied orbitals

The Hartree–Fock equations

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

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

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

$$L_{\text{HF}} = E_{\text{HF}} - \sum_{ij} \varepsilon_{ij} (S_{ij} - \delta_{ij})$$

- ▶ 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

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

The 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 transform to the AO basis:

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

- ▶ 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

The 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**:

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

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

MOs at distorted geometries

1. Orthonormal MOs at the reference geometry:

$$\begin{aligned}\phi(\mathbf{r}; x_0) &= \mathbf{C}^{(0)} \chi(\mathbf{r}; x_0) \\ \mathbf{S}(x_0) &= \langle \phi(x_0) | \phi^\dagger(x_0) \rangle = \mathbf{I}\end{aligned}$$

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

$$\begin{aligned}\phi(\mathbf{r}; x) &= \mathbf{C}^{(0)} \chi(\mathbf{r}; x) \\ \mathbf{S}(x) &= \langle \phi(x) | \phi^\dagger(x) \rangle \neq \mathbf{I}\end{aligned}$$

This basis is **nonorthogonal** and not useful for setting up the Hamiltonian.

3. Orthonormalize the basis set:

$$\begin{aligned}\psi(\mathbf{r}; x) &= \mathbf{S}^{-1/2}(x) \phi(\mathbf{r}; x) \\ \tilde{\mathbf{S}}(x) &= \mathbf{S}^{-1/2}(x) \mathbf{S}(x) \mathbf{S}^{-1/2}(x) = \mathbf{I}\end{aligned}$$

- ▶ From such **orthonormalized MOs (OMOs)**, the Hamiltonian is constructed as before

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

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

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**:

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

- ▶ We need the derivatives of the OMO integrals:

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

- ▶ After some algebra, the molecular gradient may be written in the form

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

where the **generalized Fock matrix** is given by:

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

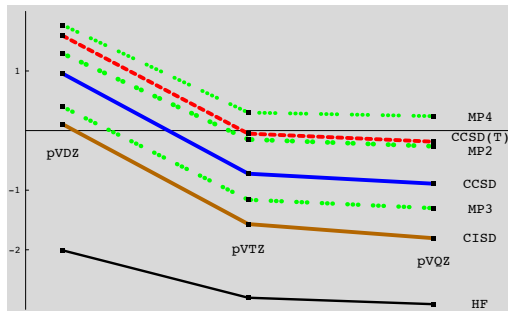
- ▶ For RHF theory, this result is equivalent to that derived in first quantization

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 I

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

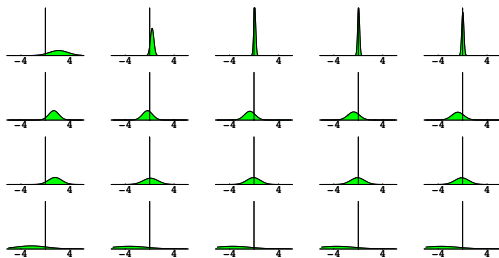


$ \bar{\Delta} $	DZ	TZ	QZ
CCSD	1.2	0.6	0.8
CCSD(T)	1.7	0.2	0.2

- ▶ 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 II

- ▶ **Normal distributions** of errors (pm) relative to experiment for HF, MP2, CCSD, and CCSD(T) at the valence-electron cc-pVXZ level of theory:



- ▶ CCSD(T) bond distances compared with experiment (pm):

	DZ	TZ	QZ
$\overline{\Delta}$	1.68	0.01	-0.12
$ \overline{\Delta} $	1.68	0.20	0.16

- ▶ However, the high accuracy arises in part because of **error cancellation**
 - ▶ basis-set extension QZ \rightarrow 6Z: ≈ -0.10 pm
 - ▶ triples relaxation CCSD(T) \rightarrow CCSDT: ≈ -0.02 pm
- ▶ Intrinsic error of the CCSDT model: ≈ -0.2 pm

Bond distances III (pm)

		HF	MP2	CCSD	CCSD(T)	emp.	exp.
H ₂	<i>R</i> _{HH}	73.4	73.6	74.2	74.2	74.1	74.1
HF	<i>R</i> _{FH}	89.7	91.7	91.3	91.6	91.7	91.7
H ₂ O	<i>R</i> _{OH}	94.0	95.7	95.4	95.7	95.8	95.7
HOF	<i>R</i> _{OH}	94.5	96.6	96.2	96.6	96.9	96.6
HNC	<i>R</i> _{NH}	98.2	99.5	99.3	99.5	99.5	99.4
NH ₃	<i>R</i> _{NH}	99.8	100.8	100.9	101.1	101.1	101.1
N ₂ H ₂	<i>R</i> _{NH}	101.1	102.6	102.5	102.8	102.9	102.9
C ₂ H ₂	<i>R</i> _{CH}	105.4	106.0	106.0	106.2	106.2	106.2
HCN	<i>R</i> _{CH}	105.7	106.3	106.3	106.6	106.5	106.5
C ₂ H ₄	<i>R</i> _{CH}	107.4	107.8	107.9	108.1	108.1	108.1
CH ₄	<i>R</i> _{CH}	108.2	108.3	108.5	108.6	108.6	108.6
N ₂	<i>R</i> _{NN}	106.6	110.8	109.1	109.8	109.8	109.8
CH ₂ O	<i>R</i> _{CH}	109.3	109.8	109.9	110.1	110.1	110.1
CH ₂	<i>R</i> _{CH}	109.5	110.1	110.5	110.7	110.6	110.7
CO	<i>R</i> _{CO}	110.2	113.2	112.2	112.9	112.8	112.8
HCN	<i>R</i> _{CN}	112.3	116.0	114.6	115.4	115.3	115.3
CO ₂	<i>R</i> _{CO}	113.4	116.4	115.3	116.0	116.0	116.0
HNC	<i>R</i> _{CN}	114.4	117.0	116.2	116.9	116.9	116.9
C ₂ H ₂	<i>R</i> _{CC}	117.9	120.5	119.7	120.4	120.4	120.3
CH ₂ O	<i>R</i> _{CO}	117.6	120.6	119.7	120.4	120.5	120.3
N ₂ H ₂	<i>R</i> _{NN}	120.8	124.9	123.6	124.7	124.6	124.7
C ₂ H ₄	<i>R</i> _{CC}	131.3	132.6	132.5	133.1	133.1	133.1
F ₂	<i>R</i> _{FF}	132.7	139.5	138.8	141.1	141.3	141.2
HOF	<i>R</i> _{OF}	136.2	142.0	141.2	143.3	143.4	143.4

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
 - ▶ approximate 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

Calculation of harmonic frequencies

- ▶ Generate parabolic potential by calculating the molecular Hessian at equilibrium:

$$V(\mathbf{x}) = \frac{1}{2} \mathbf{x}^T \mathbf{G} \mathbf{x}$$

- ▶ Calculate mass-weighted Hessian:

$$H_{ij} = \frac{G_{ij}}{\sqrt{m_i m_j}}$$

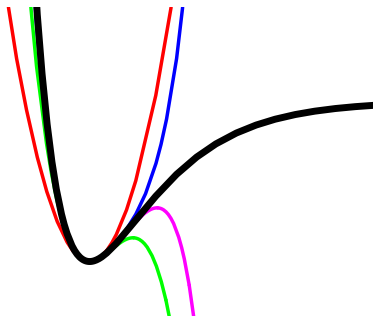
- ▶ Diagonalize the Hessian \mathbf{H} to obtain **normal coordinates** and **harmonic frequencies**:

$$\mathbf{H} \mathbf{q} = \lambda \mathbf{q}, \quad \omega_i = 2\pi \nu_i = \sqrt{\lambda_i}$$

- ▶ Harmonic frequencies are too high (by a few percent) but often qualitatively useful

Anharmonic potentials

- ▶ Anharmonic potentials may be generated by:
 - ▶ higher-order Taylor expansions
 - ▶ numerical fitting
 - ▶ analytical functions (e.g., Morse potential)
- ▶ Taylor expansion of Morse potential up to fifth order:



- ▶ odd-order expansions are unbounded from below.

Fundamental frequencies

- ▶ Vibrational energy levels of an **asymmetric top**:

$$E(\mathbf{n}) = V_0 + \sum_k \hbar \omega_k (n_k + \frac{1}{2}) + \sum_{k \leq l} x_{kl} (n_k + \frac{1}{2})(n_l + \frac{1}{2}).$$

- ▶ **harmonic constants** ω_k and **anharmonic constants** x_{kl}
- ▶ The **anharmonic constants** x_{kl} may be obtained from:
 - ▶ the harmonic constants ω_k ;
 - ▶ the cubic and quartic force constants with respect to the normal coordinates Q_k :

$$f_{klm} = \frac{d^3 V}{dQ_k dQ_l dQ_m}, \quad f_{klmn} = \frac{d^4 V}{dQ_k dQ_l dQ_m dQ_n},$$

- ▶ the rotational constants B_α and the Coriolis-coupling constants ζ_{kl}^α .
- ▶ The **fundamentals** are then given by:

$$\nu_k = \omega_k + \frac{2}{\hbar} x_{kk} + \frac{1}{2\hbar} \sum_{l \neq k} x_{kl}.$$

Anharmonic constants

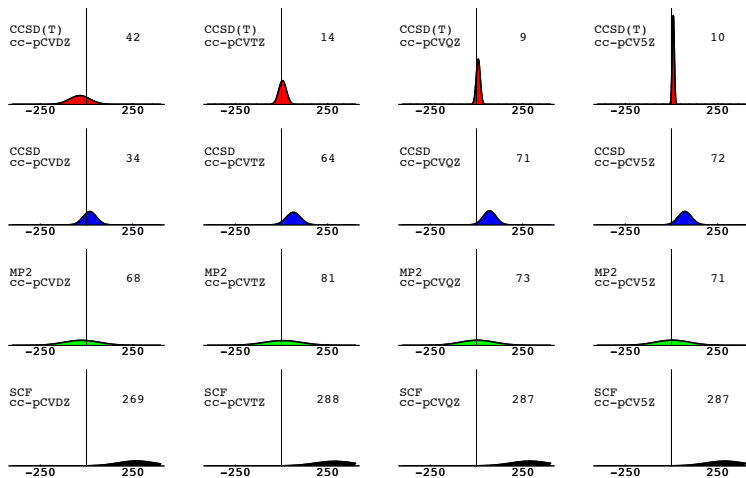
- ▶ Diagonal anharmonic constants (asymmetric top):

$$x_{kk} = \frac{\hbar^2}{16\omega_k^2} \left[f_{kkkk} - \sum_l \frac{f_{kkl}^2 (8\omega_k^2 - 3\omega_l^2)}{\omega_l^2 (4\omega_k^2 - \omega_l^2)} \right]$$

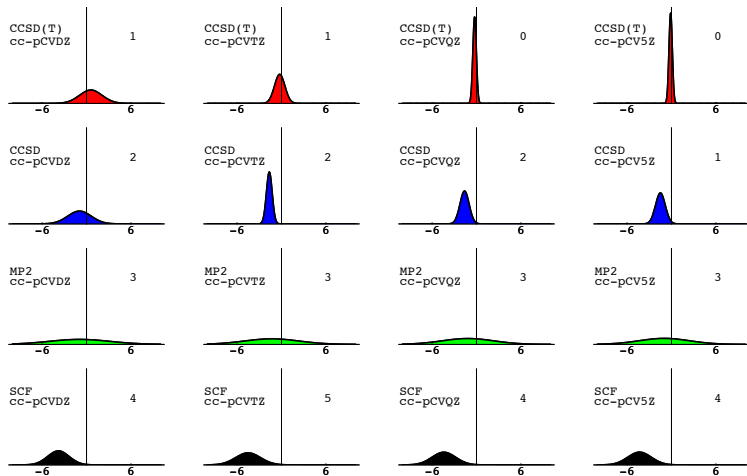
- ▶ Off-diagonal anharmonic constants (asymmetric top):

$$\begin{aligned} x_{kl} = \frac{\hbar^2}{4\omega_k\omega_l} & \left[f_{kkll} - \sum_m \frac{f_{kkm}f_{llm}}{\omega_m^2} \right. \\ & + \sum_m \frac{2f_{klm}^2(\omega_k^2 + \omega_l^2 - \omega_m^2)}{[(\omega_k + \omega_l)^2 - \omega_m^2][(\omega_k - \omega_l)^2 - \omega_m^2]} \\ & \left. + \left(\frac{\omega_k}{\omega_l} + \frac{\omega_l}{\omega_k} \right) \sum_{\alpha} B_{\alpha} (\zeta_{kl}^{\alpha})^2 \right] \end{aligned}$$

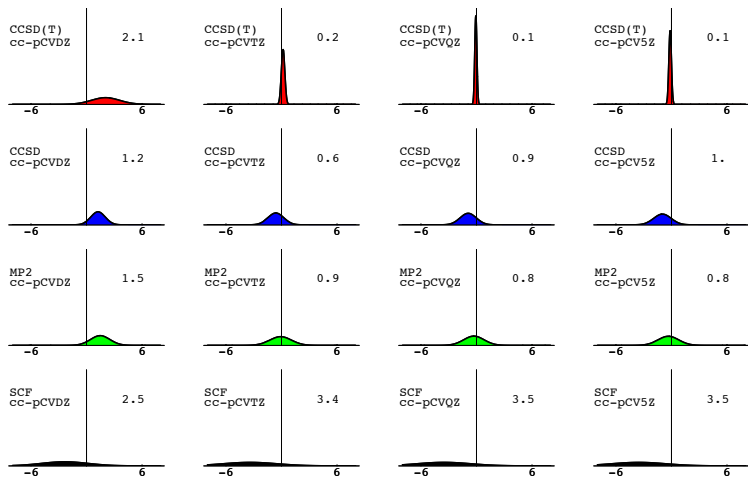
Harmonic constants ω_e of BH, CO, N₂, HF, and F₂ (cm⁻¹)



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



Bond distances R_e of BH, CO, N₂, HF, and F₂ (cm⁻¹)



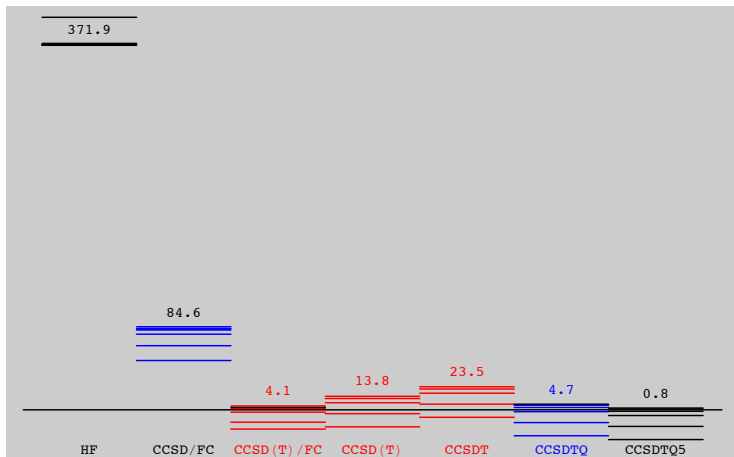
Contributions to harmonic frequencies ω_e (cm^{-1})

	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

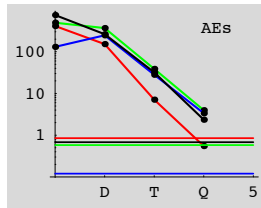
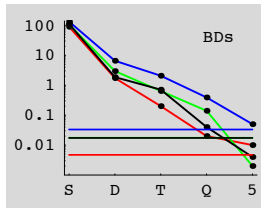
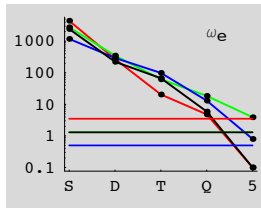
- ▶ There are substantial higher-order corrections:



- ▶ 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}

Excitation-level convergence

- ▶ Contributions to harmonic frequencies, bond lengths, and atomization energies:



- ▶ color code: HF (red), N_2 (green), F_2 (blue), and CO (black)
- ▶ straight lines indicate first-order relativistic corrections
- ▶ Excitation-level convergence is approximately exponential
- ▶ Relativity becomes important beyond connected quadruples
- ▶ Basis-set convergence is much slower: X^{-3}