

# Time-Independent Molecular Properties

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- Examples of derivatives (geometrical and other)
- Energy functions
- Derivatives for variational wave functions
  - molecular gradients and Hessians
  - the  $2n + 1$  rule
- Derivatives for nonvariational wave functions
  - Lagrangian method
- Hartree–Fock molecular gradient
- Hamiltonian derivatives
- Uses of geometrical derivatives
  - molecular equilibrium structures
  - vibrational harmonic and fundamental frequencies

## Time-independent molecular properties

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

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

- 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

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

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

- such properties are said to be **time independent**
- We do not here consider time-dependent molecular properties

## Example: Geometrical derivatives

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

$$\varepsilon(x) = \varepsilon_0 + \varepsilon^{(1)} \Delta x + \frac{1}{2} \varepsilon^{(2)} \Delta x^2 + \dots \leftarrow \text{expansion around the reference geometry}$$

- The derivatives of this surface are therefore important:

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

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

- 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, but in some cases low-order expansions are inadequate or useless.

## Example: Interaction with an external electric field

- The energy of interaction in an external electrostatic field is given by

$$\varepsilon_{\text{int}} = qV - p\bar{E} - \frac{1}{2}Q\bar{F} - \dots$$

where

$V$	potential	$q = \frac{d\varepsilon}{dV}$	charge
$\bar{E}$	field	$p = -\frac{d\varepsilon}{d\bar{E}}$	dipole moment
$\bar{F}$	field gradient	$Q = -2\frac{d\varepsilon}{d\bar{F}}$	quadrupole moment

- The permanent and induced moments are given by

$$p(\bar{E}) = \underbrace{p_0}_{\text{permanent moment}} + \underbrace{\alpha\bar{E}}_{\text{induced moment}} + \dots$$

where

$p_0 = -\left.\frac{d\varepsilon}{d\bar{E}}\right _{\bar{E}=0}$	permanent dipole moment
$\alpha = \left.\frac{dp}{d\bar{E}}\right _{\bar{E}=0} = -\left.\frac{d^2\varepsilon}{d\bar{E}^2}\right _{\bar{E}=0}$	dipole polarizability

### Example: Magnetic resonance parameters

- Energy expansion in nuclear magnetic moments  $m$  and external magnetic field  $B$ :

$$\varepsilon(m, B) = \varepsilon_0 + \varepsilon^{(10)}m + \varepsilon^{(01)}B + \frac{1}{2}\varepsilon^{(20)}m^2 + \varepsilon^{(11)}Bm + \frac{1}{2}\varepsilon^{(02)}B^2 + \dots$$

- In NMR spectroscopy, we measure the coupling between  $m$  and  $B$ :

$$\varepsilon^{(11)} = \frac{d^2\varepsilon}{dm dB}$$

- in vacuum, the coupling is equal to  $-1$  since  $\varepsilon_{\text{vac}} = -m \cdot B$
- in the presence of electrons, it is modified by a few ppm:

$$\varepsilon_{\text{mol}}^{(11)} = -I + \sigma \quad \leftarrow \text{shielding constant}$$

- We also measure the coupling between magnetic nuclei

$$\varepsilon^{(20)} = \frac{d^2\varepsilon}{dm^2} = J \quad \leftarrow \text{nuclear spin-spin coupling}$$

- in solution, only the indirect coupling (mediated by electrons) survives

## 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 and ESR parameters
- 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
- Analytical techniques have been developed and widely implemented for first-order properties (e.g., dipole moments and molecular gradients) and for second-order properties (e.g., polarizabilities and molecular Hessians)

## 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)

$\lambda$ : electronic (wave-function) parameters (MOs, cluster amplitudes)

- The Hamiltonian (here in second quantization)

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

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  $\varepsilon(x)$  is obtained by optimizing the energy function  $E(x, \lambda)$  with respect to  $\lambda$  for each value of  $x$ :

$$\varepsilon(x) = E(x, \lambda^*)$$

- note: the optimization is not necessarily variational!
- Our task is to calculate derivatives of  $\varepsilon(x)$  with respect to  $x$ :

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

- 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

## Variational 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  $\lambda$  the electronic parameters.

- the stationary condition determines  $\lambda$  as a function of the geometry  $\lambda(x)$
- for the ground state, the variational energy is typically an upper bound

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

- we shall only use the stationary condition

- Nonvariational wave functions:

- wave functions whose energy does not fulfil the stationary condition

## Examples of variational wave functions

- The Hartree–Fock energy in an exponential parametrization:

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

- however, when parametrized in terms of MO coefficients, the HF energy is nonstationary: orthonormality conditions must then be imposed
  - the Kohn–Sham energy behaves in the same manner
- 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 wave functions and perturbation theory

## Molecular gradients

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

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

- 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

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

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

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

## The Hellmann–Feynman theorem

- Assume that the (variational) energy is an expectation value:

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

- The gradient is then given by the expression:

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

- Relationship to first-order perturbation theory:

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

- The theorem was originally stated for geometrical distortions:

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

– simple classical interpretation: integration over the force operator

## Molecular Hessians

- Differentiating the molecular gradient, we obtain:

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

- 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 variational 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 **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

- Molecular Hessian for variational energies:

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

- 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
- 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

## Hessian for full CI (FCI) wave functions

- The molecular Hessian may be written in the general form

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

- For full CI (FCI) wave functions, we may make the 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 us the following expression for the FCI molecular Hessian (compare with second-order perturbation theory):

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

## The $2n + 1$ rule

- For molecular gradients and Hessians, we have

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

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

- 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  $2n + 1$ .

- Responses needed to fourth order:

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

## Nonvariational wave functions

- This is all very nice for variational wave functions, but what about the nonvariational ones?
- It turns out that we may use **Lagrange's method of undetermined multipliers** to make any energy variational. The  $2n + 1$  rule is therefore of general interest.
- Example: CI molecular gradients
  - 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 nonvariational with respect to the orbital-rotation parameters:

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

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

- We shall now consider its gradients:
  1. by straightforward differentiation of the CI energy
  2. by differentiation of the CI Lagrangian

## CI gradients the straightforward way

- Straightforward differentiation of  $E_{\text{CI}}(x, P, \kappa)$  gives us:

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

- It looks as if we need the first-order response of the orbitals.
- The HF orbitals used in CI theory fulfil the following condition at all geometries:

$$\frac{\partial E_{\text{SCF}}}{\partial \kappa} = 0$$

- we obtain the orbital responses by differentiating this equation wrt  $x$ :

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

- one such set of equations must be solved for **each** perturbation.
- Calculated in this manner, the CI gradient becomes expensive.

## Lagrange's method

- To calculate the CI energy, we minimize  $E_{\text{CI}}$  with respect to  $P$  and  $\kappa$ :

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

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

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

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

$$\frac{\partial L_{\text{CI}}}{\partial P} = \frac{\partial E_{\text{CI}}}{\partial P} = 0$$

← CI conditions

$$\frac{\partial L_{\text{CI}}}{\partial \kappa} = \frac{\partial E_{\text{CI}}}{\partial \kappa} + \bar{\kappa} \frac{\partial^2 E_{\text{SCF}}}{\partial \kappa^2} = 0$$

← linear set of equations for  $\bar{\kappa}$

$$\frac{\partial L_{\text{CI}}}{\partial \bar{\kappa}} = \frac{\partial E_{\text{SCF}}}{\partial \kappa} = 0$$

← HF conditions

- note the duality between  $\kappa$  and  $\bar{\kappa}$ .

## CI gradients the easy way

- The CI Lagrangian is given by

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

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

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

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

- This result should be contrasted with the original expression

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

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

- We have (greatly) reduced the number of response equations to be solved.

## Lagrange's method

- The Lagrangian energy function:

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

- The stationary (variational) conditions for variables and their multipliers:

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

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

– note the duality between  $\lambda$  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



### Trivial example

- Find  $x$  such that  $f(x) = 1$  when  $f(x) = x$ .
- Construct a Lagrangian:

$$L(x, \bar{x}) = f(x) + \bar{x} [f(x) - 1] = x + x\bar{x} - \bar{x}$$

- Determine the stationary point:

$$\frac{dL}{dx} = 0 \Rightarrow 1 + \bar{x} = 0 \Rightarrow \bar{x} = -1$$

$$\frac{dL}{d\bar{x}} = 0 \Rightarrow x - 1 = 0 \Rightarrow x = 1$$

- Value of the Lagrangian at the stationary point  $\{1, -1\}$ :

$$L(1, -1) = 1 = f(1)$$

- Note: the stationary point is a saddle point.

## The $2n + 2$ rule

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

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

- For nonvariational wave functions, the  $2n + 1$  rule is retained **provided** the energy is expressed as a Lagrangian.

- 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:

$\varepsilon^{(n)}$	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

## Review

- For variational wave functions, the wave function to order  $n$  determines the energy to order  $2n + 1$  (the  $2n + 1$  rule):

$$\frac{d\varepsilon}{dx} = \frac{\partial E}{\partial x} \quad \leftarrow \text{Hellmann-Feynman} \quad \Leftarrow \frac{\partial E}{\partial \lambda} = 0$$

- For nonvariational wave functions, we may use the  $2n + 1$  rule if the energy is expressed as a variational Lagrangian

$$L(x, \lambda, \bar{\lambda}) = E(x, \lambda) + \bar{\lambda} e(x, \lambda) \quad \leftarrow \text{Lagrangian}$$
$$e(x, \lambda) = 0 \quad (\text{all } x) \quad \leftarrow \text{constraints}$$

The molecular gradient may then be calculated as

$$\frac{d\varepsilon}{dx} = \frac{\partial E}{\partial x} + \bar{\lambda} \frac{\partial e}{\partial x} \quad \leftarrow \text{zero-order multiplier needed}$$
$$\frac{\partial E}{\partial \lambda} + \bar{\lambda} \frac{\partial e}{\partial \lambda} = 0 \quad \leftarrow \text{zero-order response equations}$$

## Derivatives so far ...

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

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

- It may be extended to nonvariational wave functions by Lagrange's method of undetermined multipliers.
- We shall now apply this theory to the calculation of gradients
  - first quantization first
  - second quantization second

## 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

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

$$g_{pqrs}(\mathbf{x}) = \iint \frac{\phi_p(\mathbf{r}_1, \mathbf{x}) \phi_q(\mathbf{r}_1, \mathbf{x}) \phi_s(\mathbf{r}_2, \mathbf{x}) \phi_r(\mathbf{r}_2, \mathbf{x})}{r_{12}} \, d\mathbf{r}_1 d\mathbf{r}_2$$

- integrals depend explicitly on the geometry
- For closed-shell restricted HF (RHF), the energy becomes

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

- summations over doubly occupied orbitals

## 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

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

- Stationary conditions on the Lagrangian:

$$\frac{\partial L_{\text{SCF}}}{\partial \varepsilon_{ij}} = S_{ij} - \delta_{ij} = 0$$

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

- the multiplier conditions are equivalent to the orthonormality conditions
- the MO conditions may be written in the matrix form

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

## The Hartree–Fock gradient

- According to the general theory, we obtain the gradient

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

- In terms of integrals, we obtain in the MO basis

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

- In the AO basis, we then find

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

- density matrices transformed to AO basis
- derivative integrals added directly to gradient elements
- Important points:
  - the gradient does not involve MO differentiation
  - the time-consuming step is integral differentiation

## Second-quantization Hamiltonian

- The Hamiltonian operator in second quantization:

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

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

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

- its construction assumes an **orthonormal MO basis**  $\phi_p$ :

$$[a_p, a_q]_+ = 0, \quad [a_p^\dagger, a_q^\dagger]_+ = 0, \quad [a_p, a_q^\dagger]_+ = \delta_{pq}$$

- The MOs are expanded in AOs, which frequently depend explicitly on the perturbation—**perturbation-dependent basis sets**:

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

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



## MOs 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  $x = x_0 + \Delta x$ :

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

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

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

3. Orthonormalize the basis set:

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

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

From these orthonormalized MOs (OMOs), we may construct the Hamiltonian in the usual manner.

## Hamiltonian at all geometries

- The Hamiltonian is now 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

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

where

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

and similarly for the two-electron integrals.

- The geometry dependence of the excitation operators may be neglected when calculating derivatives since, for all geometries,

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

## Molecular gradients

- The gradient from the Hellmann–Feynman theorem:

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

- Derivatives of the OMO integrals:

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

- The gradient may now be written in the form

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

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

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

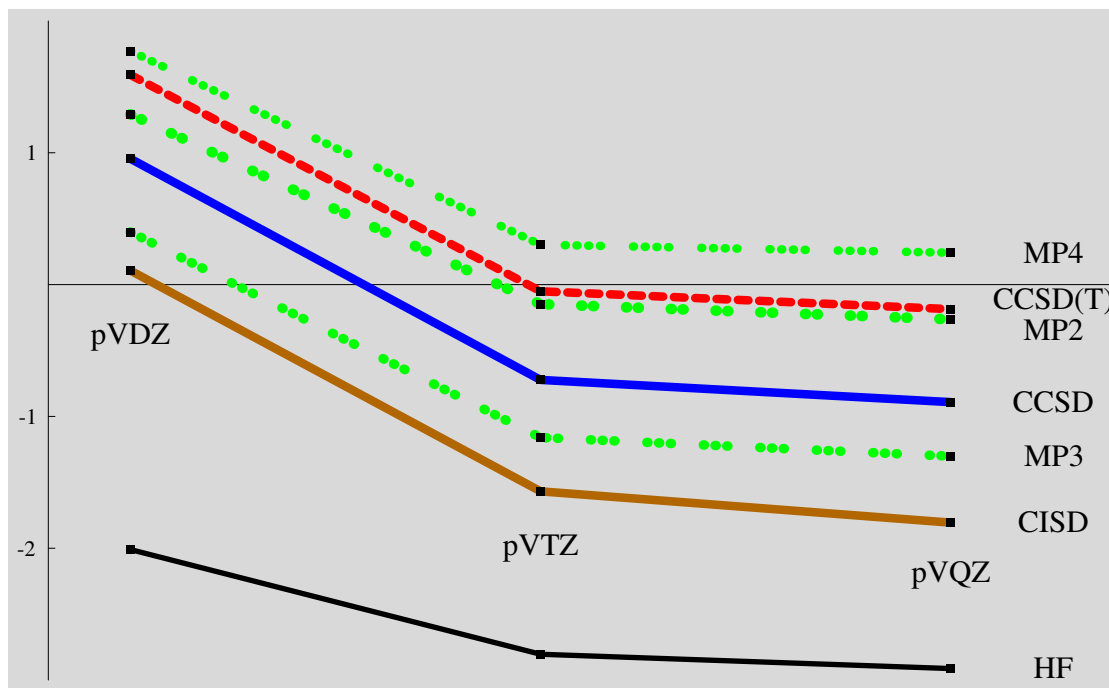
- In RHF theory, this expression is equivalent to that derived above.

## 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
  - 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):

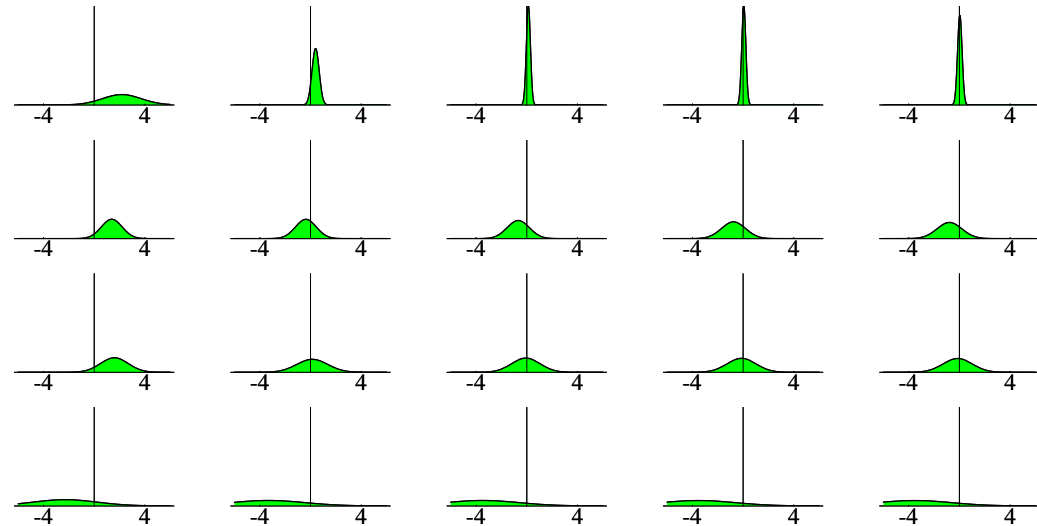


$ \bar{\Delta} $	DZ	TZ	QZ
MP4			
HF	1.9	2.6	2.7
CCSD(T)			
MP2	1.4	0.6	0.5
CCSD	1.2	0.6	0.8
MP3			
CISD	1.7	0.2	0.2

- 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 <  $\dots$
- There is considerable scope for error cancellation: CISD/DZ, MP3/DZ

## Bond distances II

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



- CCSD(T) bond distances compared with exp. (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.
- Bond distances are further reduced by
  - basis-set extension QZ  $\rightarrow$  6Z:  $\approx -0.10$  pm
  - triples relaxation CCSD(T)  $\rightarrow$  CCSDT:  $\approx -0.02$  pm
- Intrinsic error of the CCSDT model:  $\approx -0.2$  pm

## Bond distances III

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

- 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
  - approximate 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



## Calculation of harmonic frequencies

- Parabolic potential (lowest-order Taylor expansion of energy surface):

$$V(x) = \frac{1}{2}Gx^2$$

- Mass-weighted Hessian:

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

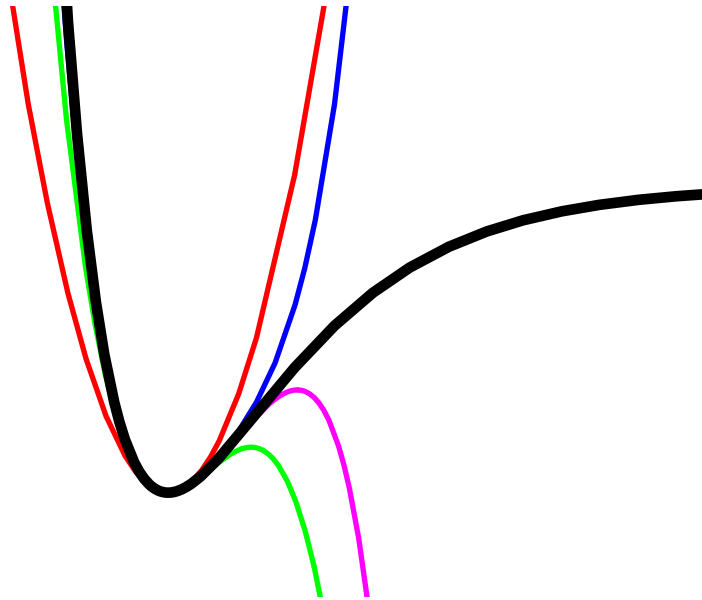
- Diagonalize mass-weighted Hessian to obtain normal coordinates and harmonic frequencies:

$$\omega = 2\pi\nu = \sqrt{\text{diagonalized } H}$$

- 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:

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

- The **anharmonic constants**  $x_{kl}$  may be obtained from:
  - the harmonic constants  $\omega_k$ ;
  - the cubic and quartic force constants

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

where  $Q_k$  are the normal coordinates;

- the rotational constants  $B_\alpha$  and the Coriolis-coupling constants  $\zeta_{kl}^\alpha$ .
- 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

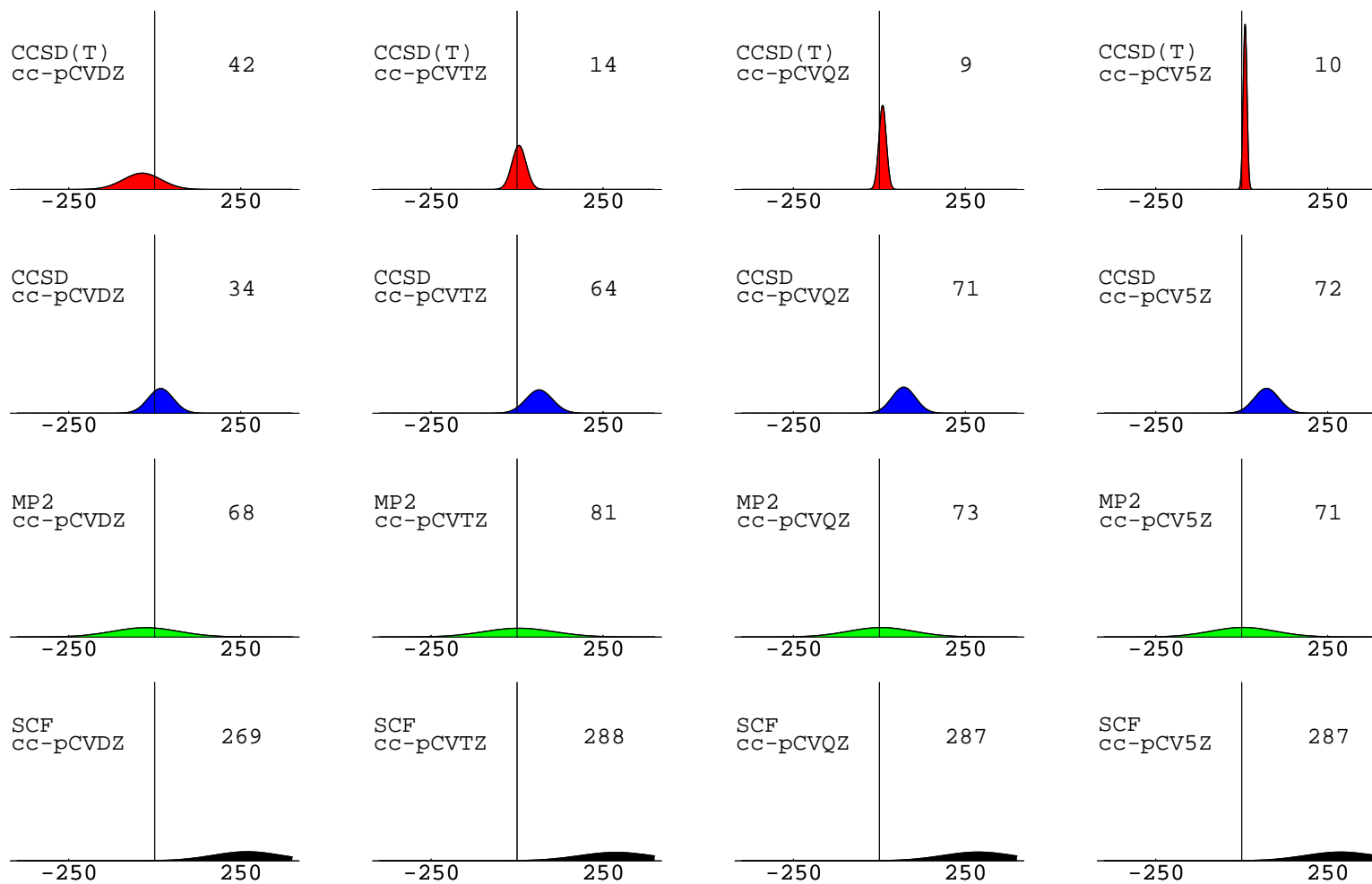
- Diagonal anharmonic constants (asymmetric top):

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

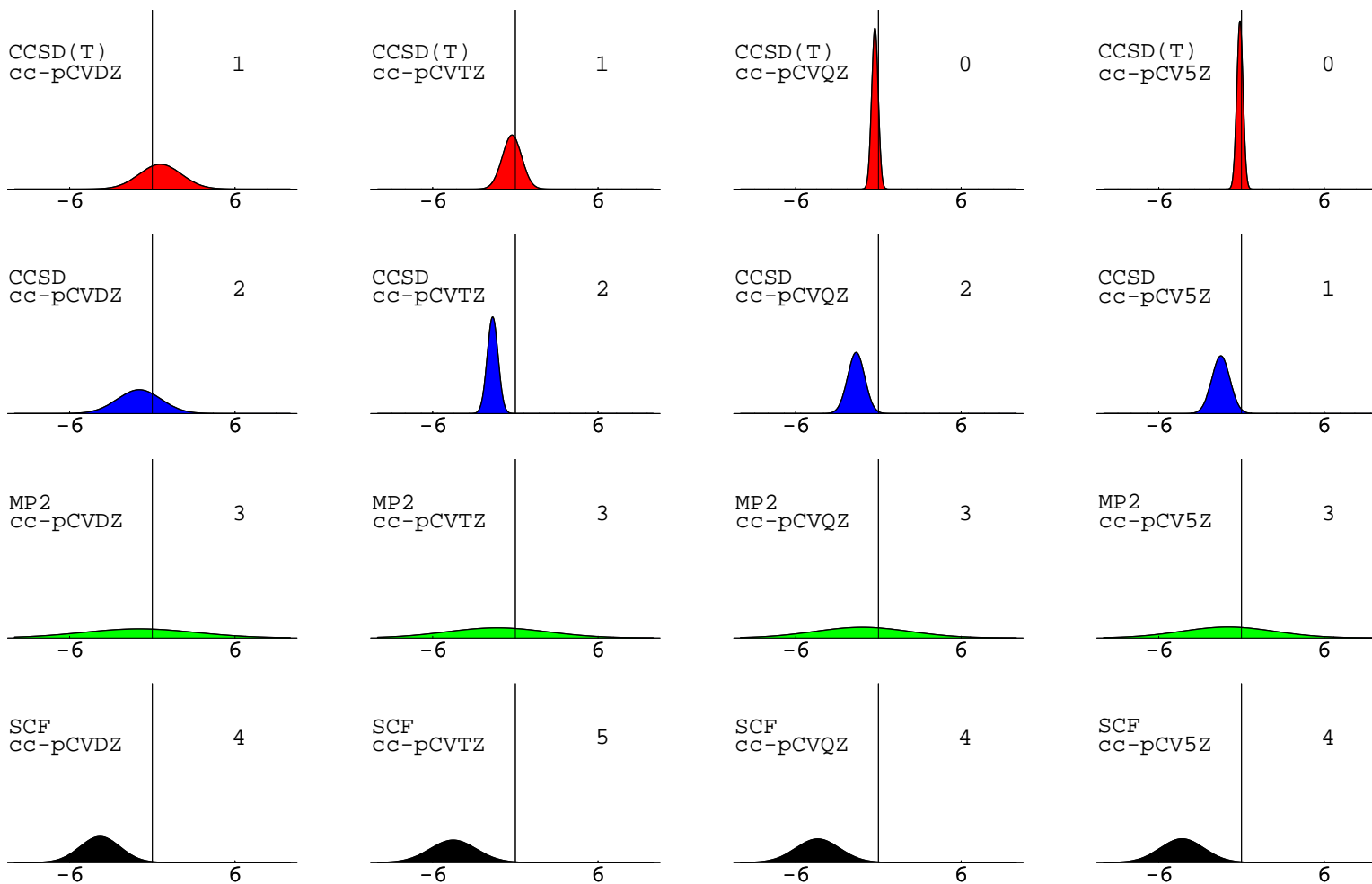
- Off-diagonal anharmonic constants (asymmetric top):

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

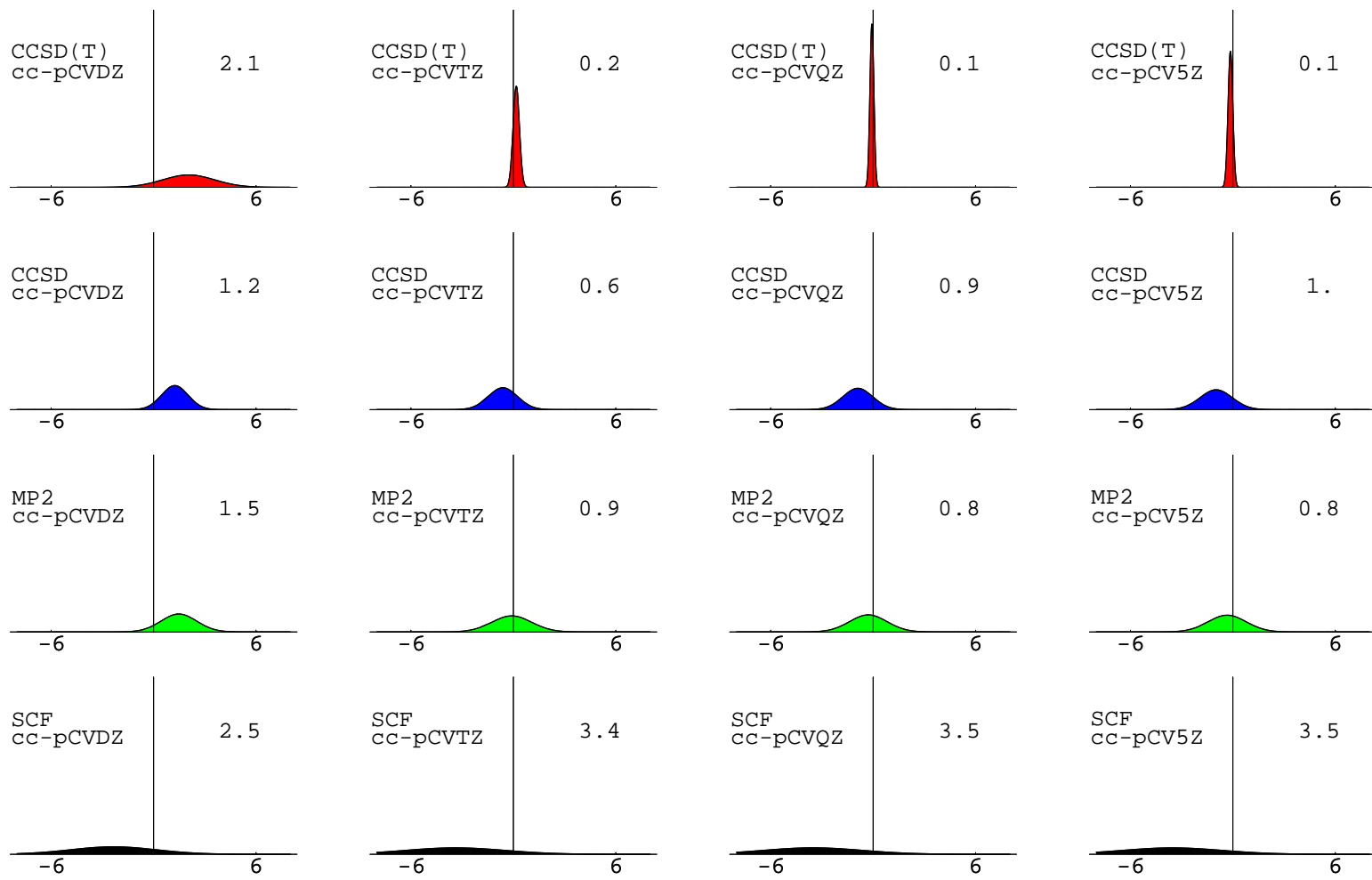
# Harmonic constants $\omega_e$ of BH, CO, N<sub>2</sub>, HF, and F<sub>2</sub> (cm<sup>-1</sup>)



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



# Bond distances $R_e$ of BH, CO, N<sub>2</sub>, HF, and F<sub>2</sub> (cm<sup>-1</sup>)



## Difficulties with harmonic constants

- Harmonic constants  $\omega_e$  are difficult; anharmonic constants  $\omega_e x_e$  are easy:

$ \overline{\Delta} $ (cm <sup>-1</sup> )	RHF	MP2	CCSD	CCSD(T)	judgment
$\omega_e$	287	71	72	10	DIFFICULT!
$\omega_e x_e$	4	3	1	0	EASY!

- There are two main problems with harmonic constants:
  - basis-set incompleteness
  - lack of high-order connected excitations
- Basis-set incompleteness treated by extrapolation or explicitly corr. methods
  - valence-electron CCSD/cc-pVXZ calculations on N<sub>2</sub>:

cm <sup>-1</sup>	D	T	Q	5	6	R12
raw	2408.8	2423.9	2435.6	2439.9	2441.3	2443.2
extrapolated		2440.2	2445.6	2443.9	2443.1	

- extrapolation does improve results but not as consistently as for AEs
- Higher excitations require special CC code (or another approach)



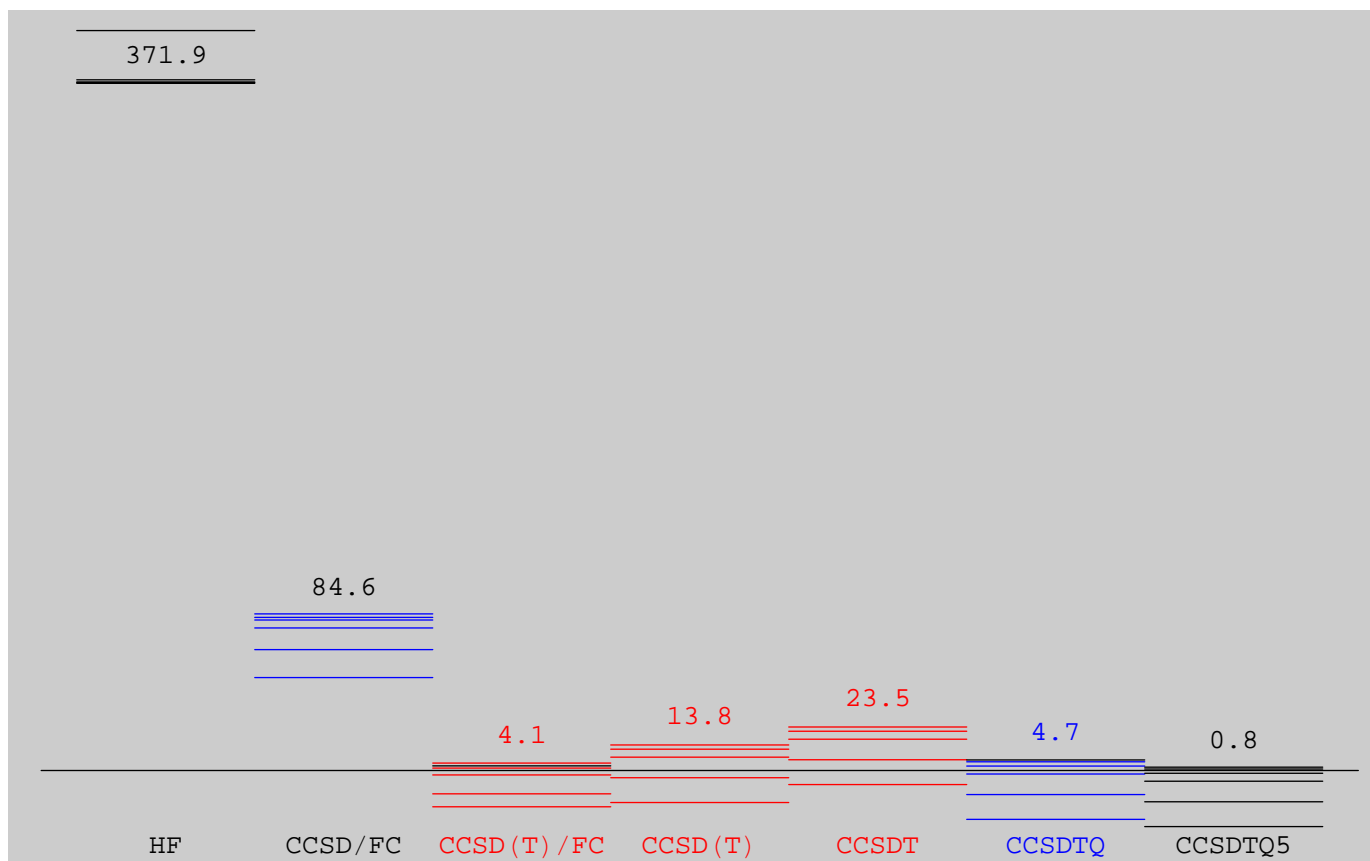
## Contributions to harmonic frequencies $\omega_e$ ( $\text{cm}^{-1}$ )

	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 <sub>2</sub>	2730.3	-275.8	-72.4	-18.8	-3.9	-1.4	0.0	2358.0	2358.6	-0.6
F <sub>2</sub>	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

- 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  $95 \text{ cm}^{-1}$ , quadruples  $20 \text{ cm}^{-1}$ , and quintuples  $4 \text{ cm}^{-1}$
  - sextuples are sometimes needed for convergence to within  $1 \text{ cm}^{-1}$
- relativistic corrections are of the order of  $1 \text{ cm}^{-1}$ 
  - of the same magnitude and direction as the quadruples or quintuples
  - two-electron terms may be needed for CCSDTQ5 wave functions

## Higher-order connected contributions to $\omega_e$ in $N_2$

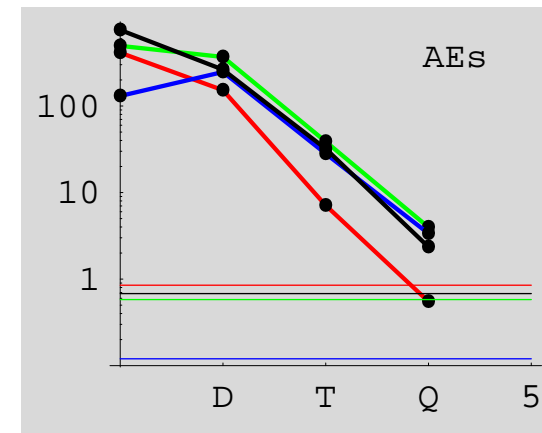
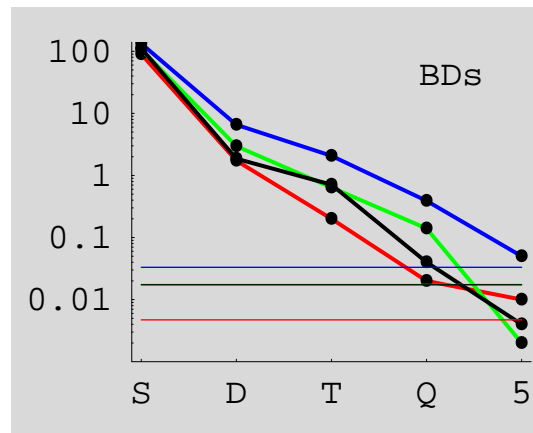
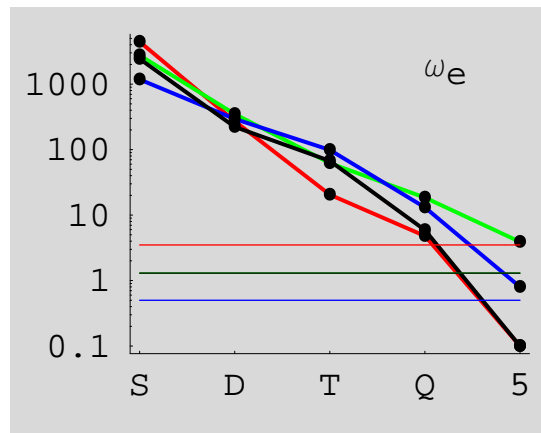
- There are substantial higher-order corrections:



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

## Excitation-level convergence

- Log plots of contributions to harmonic frequencies, bond lengths, and atomization energies:



- color code: HF (red), N<sub>2</sub> (green), F<sub>2</sub> (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:  $X^{-3}$