

Energy Derivatives and Molecular Properties

ESQC 05

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- Geometrical derivatives
 - 3/2 lecture
- Magnetic properties
 - 3/2 lecture
- Geometry optimization
 - 1 lecture

Geometrical derivatives

- Examples of derivatives (geometrical and other)
- Energy functions
- Derivatives for variational wave functions
 - molecular gradients and Hessians
 - response equations
 - the $2n + 1$ rule
- Derivatives for nonvariational wave functions
 - Lagrange's method and the $2n + 2$ rule
- Derivatives of electronic Hamiltonian
- Molecular gradients in detail
- Uses of geometrical derivatives
 - molecular equilibrium structures
 - vibrational 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 states. 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 referred to as **time independent**.

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:

$$\begin{aligned} \varepsilon^{(1)} &= \frac{d\varepsilon}{dx} \leftarrow \text{molecular gradient} \\ \varepsilon^{(2)} &= \frac{d^2\varepsilon}{dx^2} \leftarrow \text{molecular Hessian} \end{aligned}$$

- 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

$$p_0 = -\left.\frac{d\varepsilon}{d\bar{E}}\right|_{\bar{E}=0} \quad \text{permanent dipole moment}$$

$$\alpha = \left.\frac{dp}{d\bar{E}}\right|_{\bar{E}=0} = -\left.\frac{d^2\varepsilon}{d\bar{E}^2}\right|_{\bar{E}=0} \quad \text{dipole polarizability}$$

Example: Magnetic resonance parameters

- The energy in the presence of nuclear magnetic moments m and an 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
- Responses to external electric fields
 - permanent and induced moments
 - vibrational intensities
- Responses to nuclear quadrupole moments
 - nuclear field gradients, quadrupole coupling constants
- Responses to external magnetic fields and nuclear magnetic moments
 - NMR and ESR parameters
 - magnetizabilities
 - optical activity
- Responses to molecular rotation
 - spin–rotation constants and molecular g values

Numerical vs. analytical differentiation

- Numerical procedures (finite differences and polynomial fitting)
 - often simple to implement (at least for real singlet perturbations)
 - difficulties related to numerical accuracy and computational efficiency
- Analytical techniques (i.e., the direct calculation of derivatives 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 to some extent for second-order properties (e.g., polarizabilities and molecular Hessians)

Overview: Calculation of derivatives

- General discussion of derivatives
 - variational wave functions
 - the $2n + 1$ rule
 - nonvariational wave functions
 - Lagrange's method of undetermined multipliers
- Hamiltonian derivatives in second quantization
 - perturbation-dependent basis sets
- Derivatives in more detail
 - molecular gradients

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

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

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 λ 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 :

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

- We must take into account both the explicit and the implicit dependence of the energy on the perturbation.
- $\partial\lambda/\partial x$ is the **wave-function response**: it tells us how the wave function changes because of the perturbation.

Variational wave functions

- For variational wave functions, the optimized energy fulfils the **variational (stationary) 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 lowest state of a given symmetry,

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

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 (and Kohn–Sham) energies are variational:

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

- The MCSCF energy is variational:

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

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

- We here assume that the energy has been parametrized in an unconstrained (e.g., exponential) manner.

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 MCSCF (or Hartree–Fock) 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 always represents an upper bound to the exact ground-state energy.
- Other examples: coupled-cluster wave functions and perturbation theory

Molecular gradients

- The total derivative of the energy is given by

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

where the first term accounts for the explicit dependence and the last 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: molecular gradients for Hartree–Fock and MCSCF wave functions

The Hellmann–Feynman theorem

- Assume that the energy may be written as an expectation value:

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

The gradient is then given by the expression:

$$\frac{d\varepsilon}{dx} = \frac{\partial E}{\partial x} = \left\langle \lambda^* \left| \frac{\partial H}{\partial x} \right| \lambda^* \right\rangle$$

- 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
- Relationship to first-order perturbation theory:

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

Molecular Hessians

- Differentiating the molecular gradient, we obtain:

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

- We need only determine the **first-order wave-function response** $\partial\lambda/\partial x$ to calculate the second-order energy $d^2\varepsilon/dx^2$.
- 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:

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

- Response equations:

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

- The electronic Hessian is independent of the perturbation.
- Its dimensions are usually large and it therefore 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 that is proportional to the perturbation.

Hessian for full CI

- 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:

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

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

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

CI gradients the straightforward way

- Straightforward differentiation 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 (Hartree–Fock) orbitals fulfil the condition

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

at all geometries. We obtain a set of equations for the orbital responses by differentiating this expression:

$$\frac{\partial^2 E_{\text{SCF}}}{\partial \kappa^2} \frac{\partial \kappa}{\partial x} = - \frac{\partial^2 E_{\text{SCF}}}{\partial x \partial \kappa}$$

- One such set of equations must be solved for **each** perturbation.

Lagrange's method

- To calculate the CI energy, we minimize E_{CI} with respect to P and κ :

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

- Use Lagrange's method of undetermined multipliers. Construct the Lagrangian

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

- Adjust the multipliers $\bar{\kappa}$ such that the Lagrangian becomes variational:

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

← 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 $\bar{\kappa}$

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

← SCF conditions

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

CI gradients the easy way

- The CI Lagrangian is given by

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

- Since the Lagrangian is variational, 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 should be contrasted with the 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 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 (variational) conditions:

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

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

Note the duality between λ and $\bar{\lambda}$.

- The Lagrangian reduces to the Hylleraas functional when applied to a perturbation expression.
- The Lagrangian method may be generalized to time-dependent properties.
- It constitutes a generalization of the Handy–Schaefer method.

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, we still have the $2n + 1$ rule **provided** the energy is expressed as a Lagrangian.
- For the new variables—the multipliers—we have the stronger $2n + 2$ rule:
 $\bar{\lambda}^{(n)}$ 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):

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

- 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 the calculation of 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 must now learn to take derivatives $H^{(1)}$ of the Hamiltonian.
- A trivial matter?
 - No, complications arise whenever the AO basis set depends on the geometry.

Second-quantization Hamiltonian

- Hamiltonian operator in second quantization:

$$H = \sum_{pq} h_{pq} \sum_{\sigma} a_{p\sigma}^{\dagger} a_{q\sigma} + \frac{1}{2} \sum_{pqrs} g_{pqrs} \sum_{\sigma\tau} a_{p\sigma}^{\dagger} a_{r\tau}^{\dagger} a_{s\tau} a_{q\sigma} + h_{\text{nuc}}$$

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

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

- Its construction requires an **orthonormal MO basis** ϕ_p .
- 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 requirement 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 useless for constructing 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 construct the Hamiltonian.

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,

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

Molecular gradients I

- 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:

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

- The gradient may 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:

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

Molecular gradients II

- Molecular gradient in MO basis:

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

- Calculation carried out in AO basis:

$$\begin{aligned} \sum_{pq} D_{pq} h_{pq}^{(1)} &= \sum_{pq} D_{pq} \sum_{\mu\nu} C_{p\mu}^{(0)} C_{q\nu}^{(0)} h_{\mu\nu}^{(1)} \\ &= \sum_{\mu\nu} h_{\mu\nu}^{(1)} \sum_{pq} D_{pq} C_{p\mu}^{(0)} C_{q\nu}^{(0)} = \sum_{\mu\nu} D_{\mu\nu} h_{\mu\nu}^{(1)} \end{aligned}$$

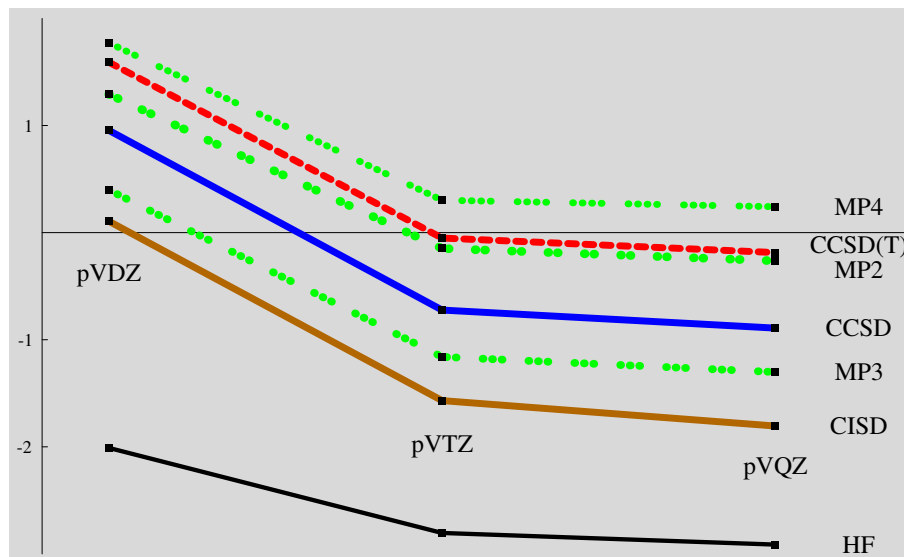
- Integrals are multiplied by densities on the fly and not written to disk.
- Very efficient procedure—no optimization, no linear equations are involved.
- CI and gradients of other nonvariational methods may be cast in a similar form using modified densities involving the Lagrange multipliers.

Uses of geometrical derivatives

- To explore molecular potential-energy surfaces ($3N - 6$ dimensions)
 - localization and characterization of stationary points (minima and saddle points)
 - localization of avoided crossings and conical intersections
 - calculation of minimum energy paths, 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

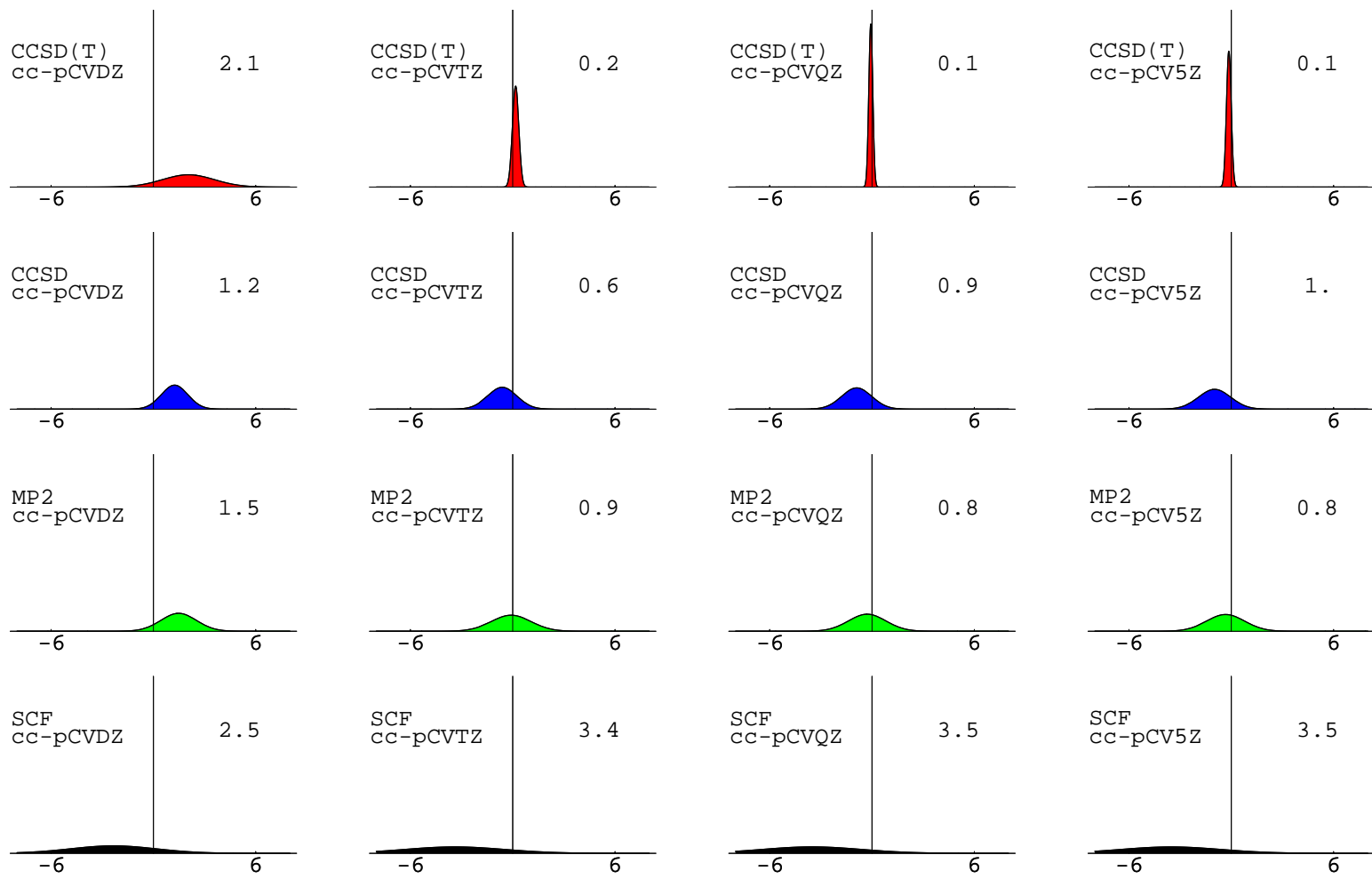
- Mean and mean absolute errors for 28 distances at the all-electron cc-pVXZ level (pm):



$ \bar{\Delta} $	DZ	TZ	QZ
HF	1.94	2.63	2.74
MP2	1.35	0.56	0.51
CCSD	1.19	0.64	0.80
CCSD(T)	1.68	0.20	0.16

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

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



Bond distances: empirical and experimental bond distances

		HF	MP2	CCSD	CCSD(T)	emp.	exp.
H ₂ O	R_{OH}	94.0	95.7	95.4	95.7	95.8	95.7
NH ₃	R_{NH}	99.8	100.8	100.9	101.1	101.1	101.1
C ₂ H ₂	R_{CH}	105.4	106.0	106.0	106.2	106.2	106.2
C ₂ H ₄	R_{CH}	107.4	107.8	107.9	108.1	108.1	108.1
N ₂	R_{NN}	106.6	110.8	109.1	109.8	109.8	109.8
CH ₂ O	R_{CH}	109.3	109.8	109.9	110.1	110.1	110.1
CH ₂	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 ₂	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 ₂ H ₂	R_{CC}	117.9	120.5	119.7	120.4	120.4	120.3
CH ₂ O	R_{CO}	117.6	120.6	119.7	120.4	120.5	120.3
C ₂ H ₄	R_{CC}	131.3	132.6	132.5	133.1	133.1	133.1

Error cancellation CCSD(T)

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

	DZ	TZ	QZ
$\bar{\Delta}$	1.68	0.01	-0.12
$ \bar{\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: ≈ -0.10 pm
 - triples relaxation CCSD(T) \rightarrow CCSDT: ≈ -0.02 pm
- Intrinsic error of the CCSDT model: ≈ -0.2 pm
- The error in the approximate treatment of the triples in CCSD(T) is in part cancelled by the neglect of higher excitations.

Coupled-cluster 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

- 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 pm, quadruples up to 0.4 pm, 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

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

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

- Mass-weighted Hessian:

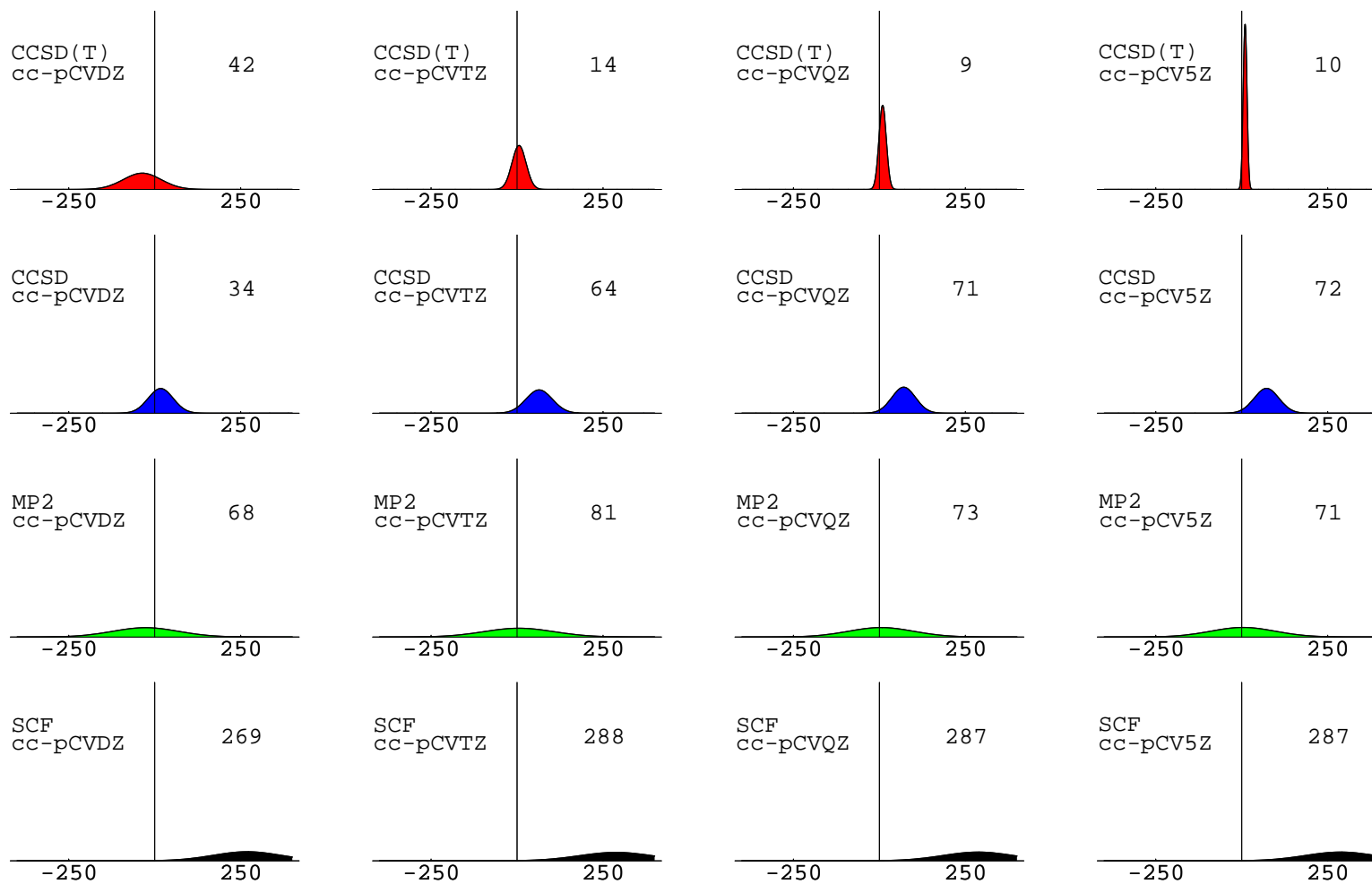
$$H_{ij} = \frac{G_{ij}}{\sqrt{m_i m_j}}$$

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

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

- For small molecules, harmonic constants have been determined experimentally.
- Harmonic frequencies can be used as first-order approximation to fundamental frequencies.
 - too high but qualitatively useful

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

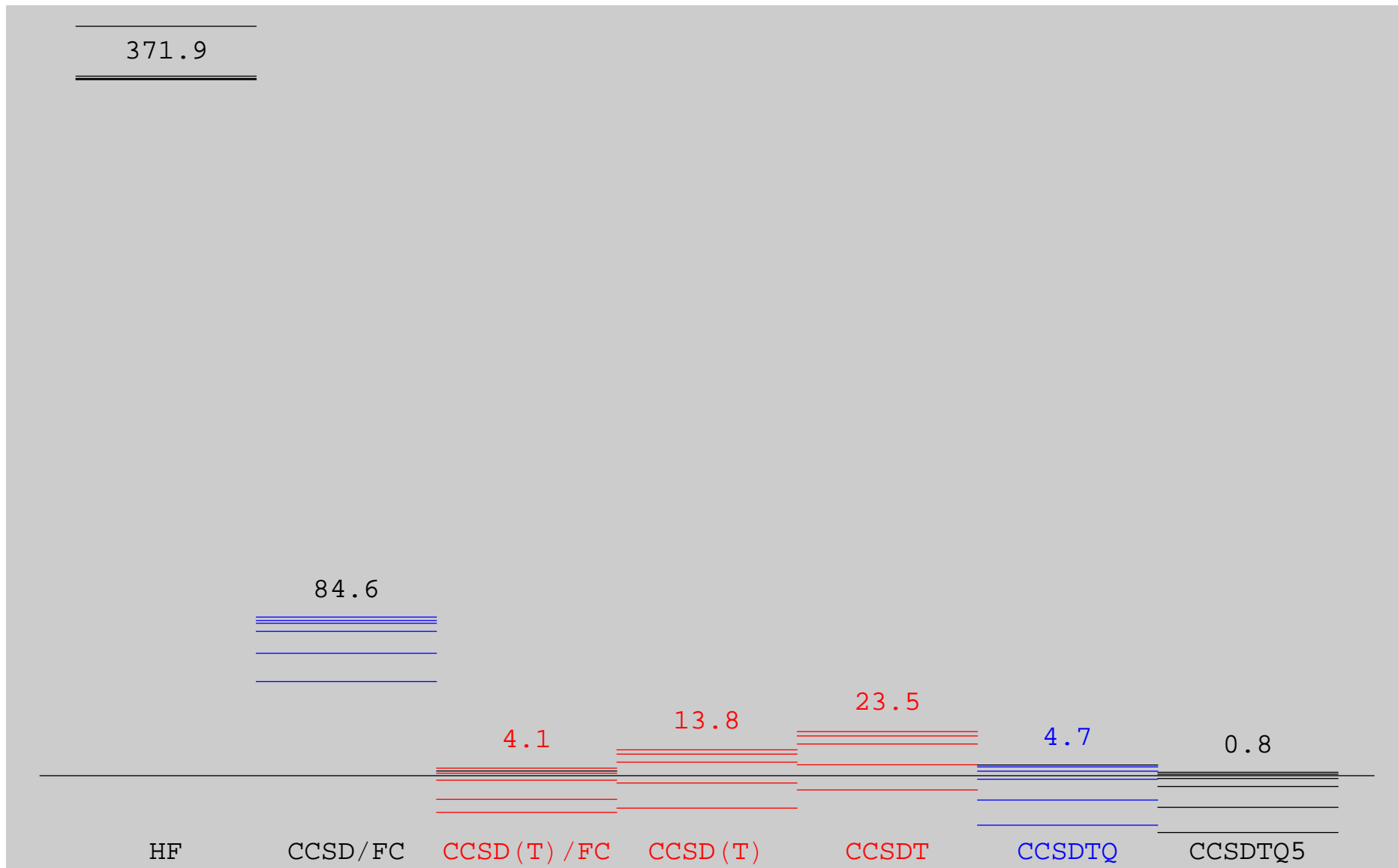


Contributions to harmonic frequencies ω_e (cm^{-1})

	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

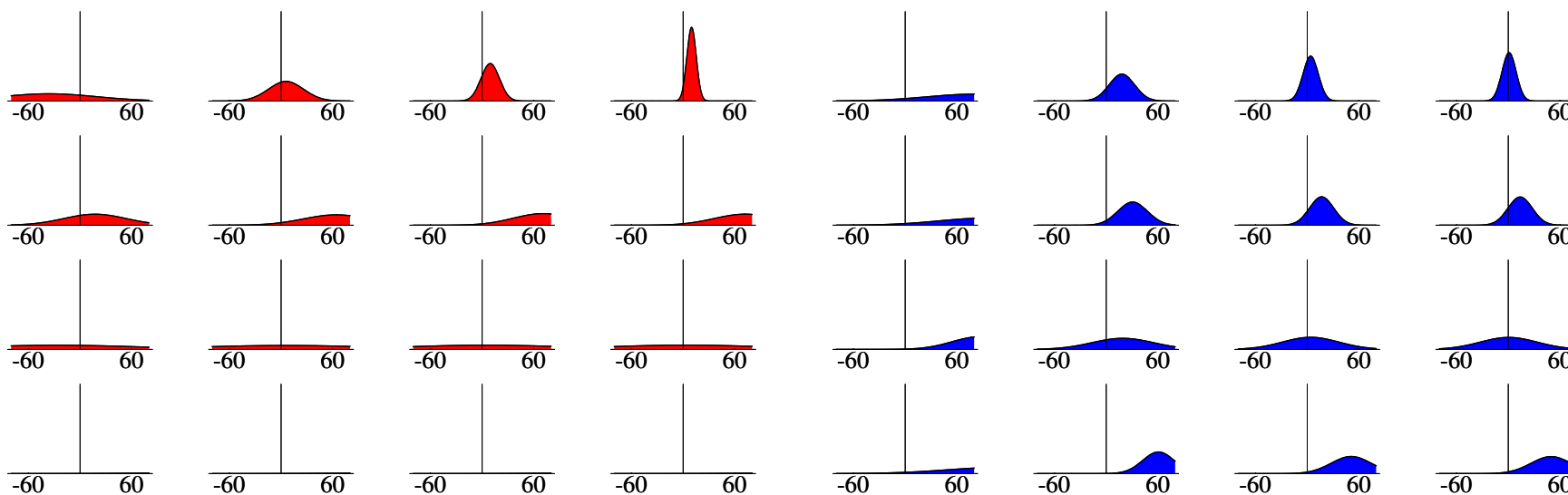
- agreement with experiment to within 1 cm^{-1} except for F₂
- Hartree–Fock theory overestimates harmonic frequencies by up to 38% (in F₂).
- all correlation contributions are large and negative
 - triples contribute up to 95 cm^{-1} , quadruples 20 cm^{-1} , and quintuples 4 cm^{-1}
 - sextuples are sometimes needed for convergence to within 1 cm^{-1}
- relativistic corrections are of the order of 1 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 ω_e in N_2



Choice of reference geometry

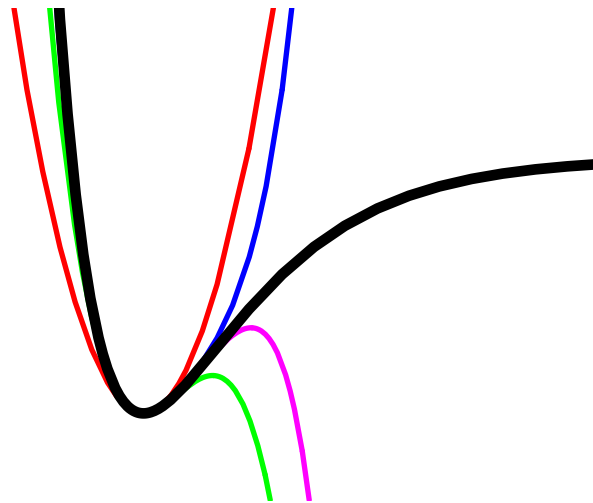
- Harmonic frequencies are significantly improved by carrying out the calculations at the experimental geometry.
- This approach is equivalent to the addition of an empirical linear term to the force field.



- It is particularly useful for simple models such as HF and MP2.

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



- odd-order expansions are unbounded from below

Fundamental frequencies

- Vibrational energy levels of an asymmetric top:

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

- The **anharmonic constants** x_{kl} may be obtained from
 - the harmonic constants ω_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_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

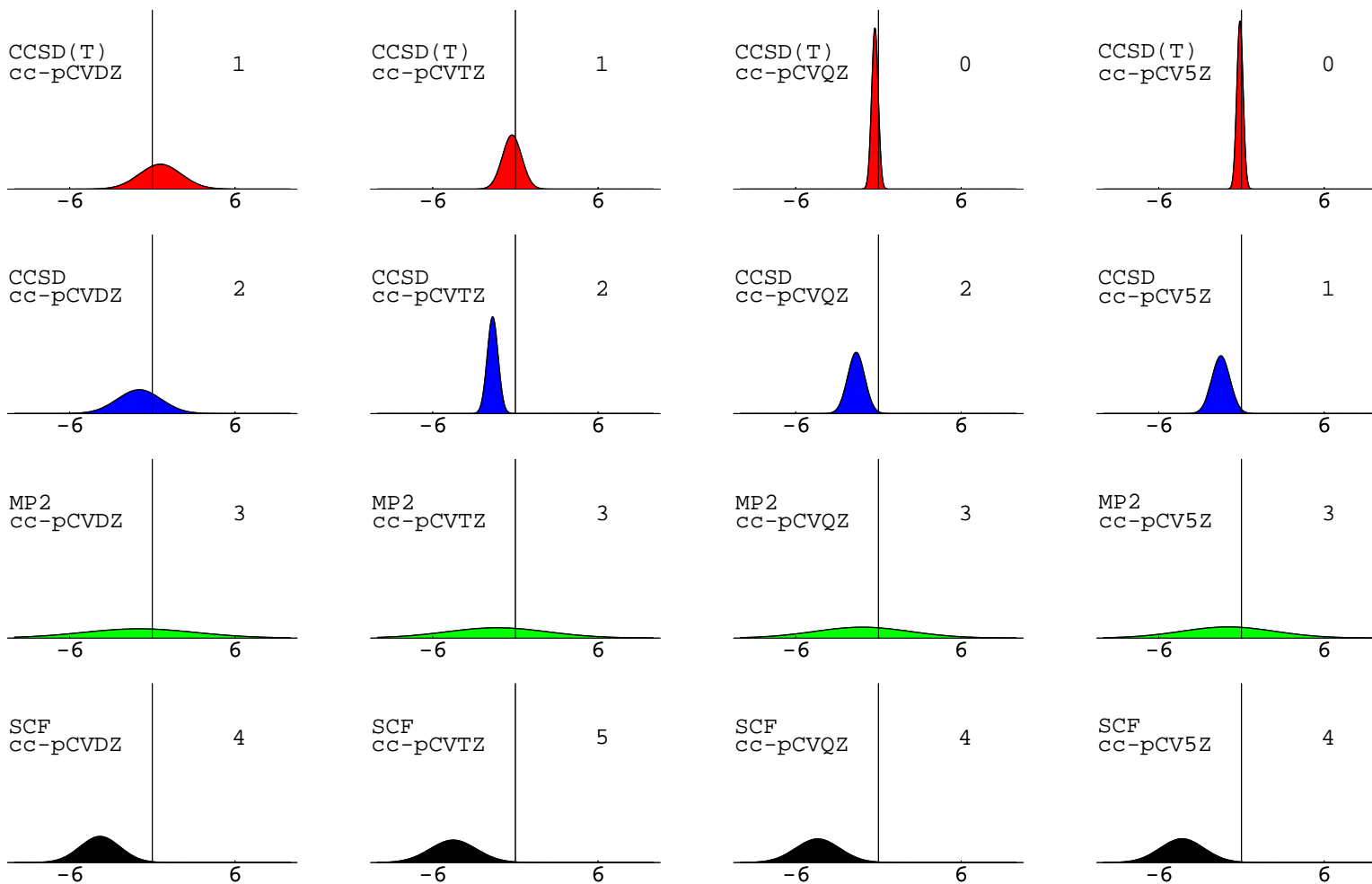
- Diagonal anharmonic constants (asymmetric top):

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

- Off-diagonal anharmonic constants (asymmetric top):

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

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



Anharmonic constants ($\omega_e x_e = -x_{11}$) of diatoms (cm^{-1})

- Wave-function convergence

	HF	MP2	CCSD	CCSD(T)	exp.
BH	43	44	48	49	49
HF	85	87	88	90	90
CO	11	13	12	13	14
N ₂	11	19	13	14	14
F ₂	7	9	9	12	11

- Basis-set convergence for all-electron CCSD(T)

	CVDZ	CVTZ	CVQZ	CV5Z
BH	49	49	49	49
HF	93	89	90	90
CO	13	13	13	13
N ₂	15	14	14	14
F ₂	12	12	12	12

Anharmonicities of triatoms (cm^{-1})

			HF	exp.
H ₂ O	<i>A</i> ₁	str	-167	-175
		def	-57	-54
	<i>B</i> ₂	str	-178	-187
NH ₃	<i>A</i> ₁	str	-124	-170
		inv	-98	-72
	<i>E</i>	str	-155	-133
		def	-47	-65
CH ₄	<i>A</i> ₁	str	-103	-105
		<i>E</i>	def	-39
	<i>T</i> ₂	str	-129	-134
		def	-36	-59