

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
 - response equations
 - the $2n + 1$ rule
- Derivatives for nonvariational wave functions
 - Lagrange's method and the $2n + 2$ rule
- Hamiltonian derivatives
- Molecular gradients in detail
- 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 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

$p_0 = -\left.\frac{d\varepsilon}{d\bar{E}}\right _{\bar{E}=0}$	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

- 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 :

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

- 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) energy is 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 in Hartree–Fock and MCSCF theories

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 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

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

- 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:

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

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

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 technique 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):

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

- 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

- 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** 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 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,

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

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:

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

- 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:

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

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:

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

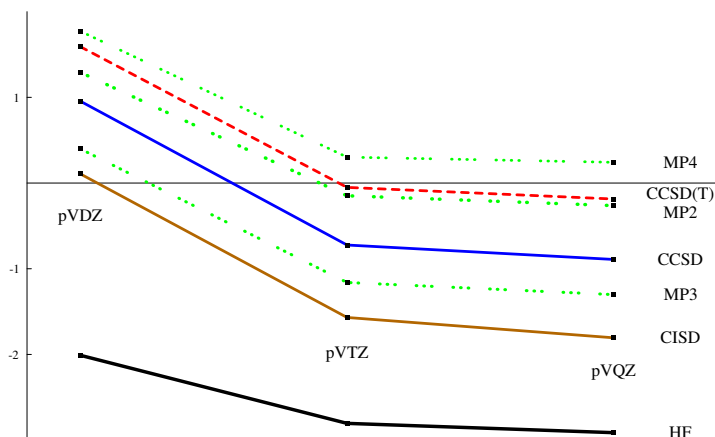
- integrals are multiplied by densities on the fly and not written to disk
- very efficient procedure—no optimization, no linear equations involved
- Gradients of CI and other nonvariational methods may be cast in a similar form using modified densities involving the Lagrange multipliers.

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 abs. errors for 28 distances at the all-el. 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:

- singles < doubles < triples < ...

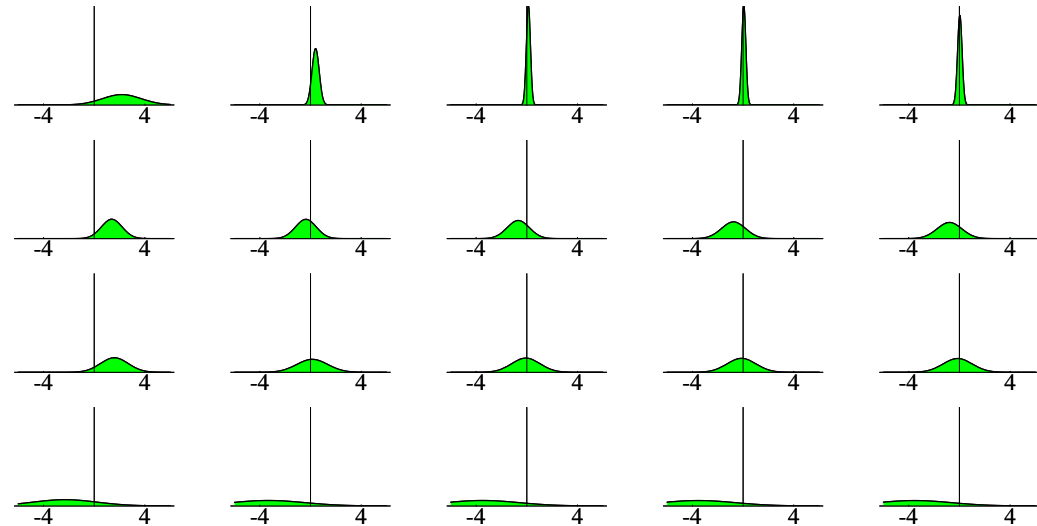
- There is considerable scope for error cancellation: **CISD/DZ, MP3/DZ**

- DZ/TZ inversion:

	DZ	TZ & QZ
best	CISD & MP3	CCSD(T) & MP4
worst	CCSD(T) & MP4	CISD & MP3

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: ≈ -0.10 pm
 - triples relaxation CCSD(T) \rightarrow CCSDT: ≈ -0.02 pm
- Intrinsic error of the CCSDT model: ≈ -0.2 pm

Bond distances III

		HF	MP2	CCSD	CCSD(T)	emp.	eks.
H ₂	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 ₂ 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 ₃	R_{NH}	99.8	100.8	100.9	101.1	101.1	101.1
N ₂ H ₂	R_{NH}	101.1	102.6	102.5	102.8	102.9	102.9
C ₂ H ₂	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 ₂ H ₄	R_{CH}	107.4	107.8	107.9	108.1	108.1	108.1
CH ₄	R_{CH}	108.2	108.3	108.5	108.6	108.6	108.6
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
N ₂ H ₂	R_{NN}	120.8	124.9	123.6	124.7	124.6	124.7
C ₂ H ₄	R_{CC}	131.3	132.6	132.5	133.1	133.1	133.1
F ₂	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 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, 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

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

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

- Mass-weighted Hessian:

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

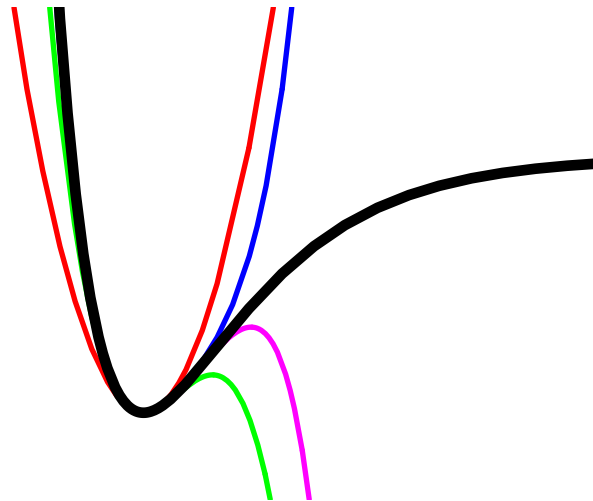
- Diagonalize mass-weighted Hessian to obtain normal coordinates and harmonic frequencies:

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

- 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 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

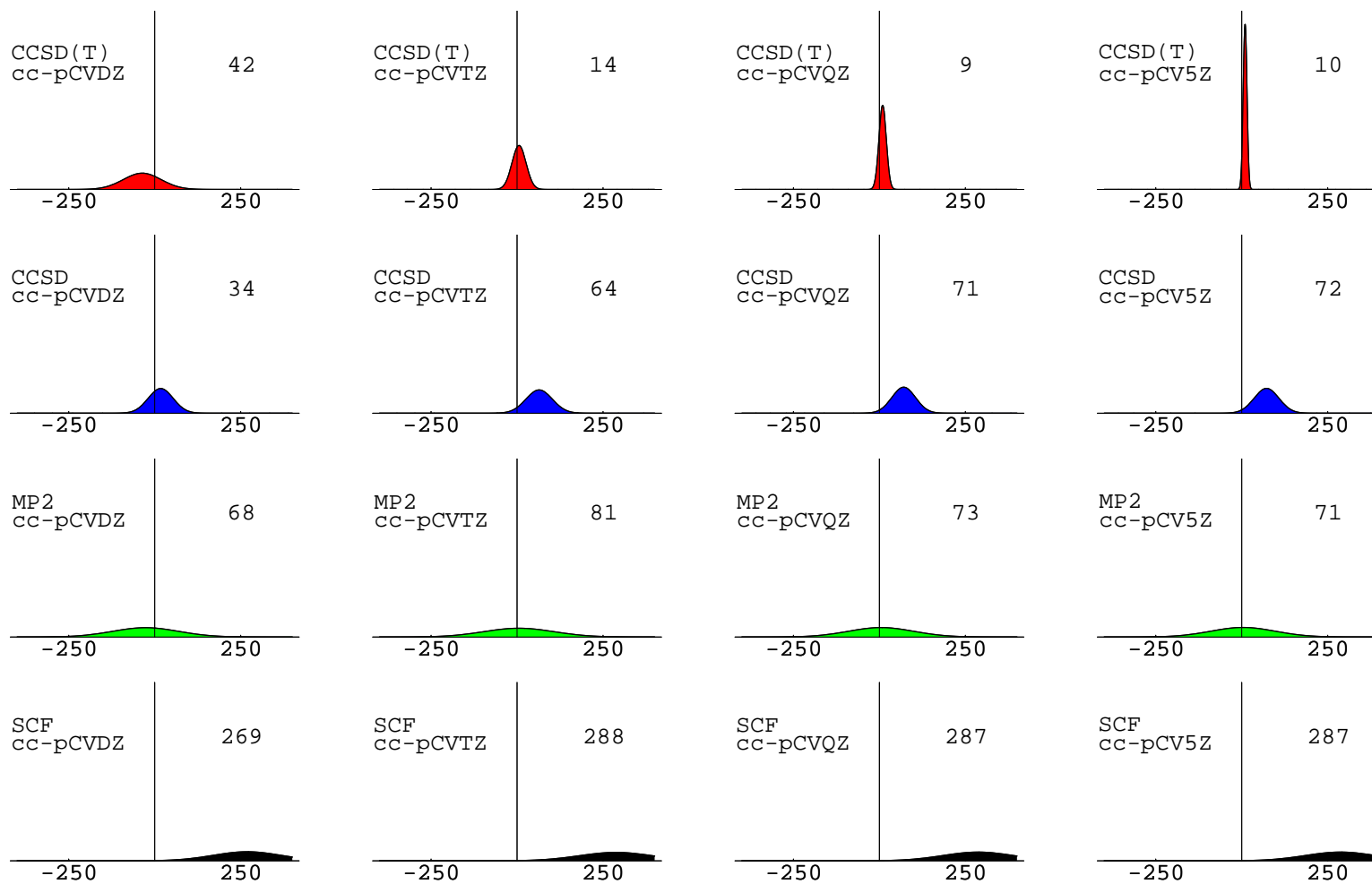
- Diagonal anharmonic constants (asymmetric top):

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

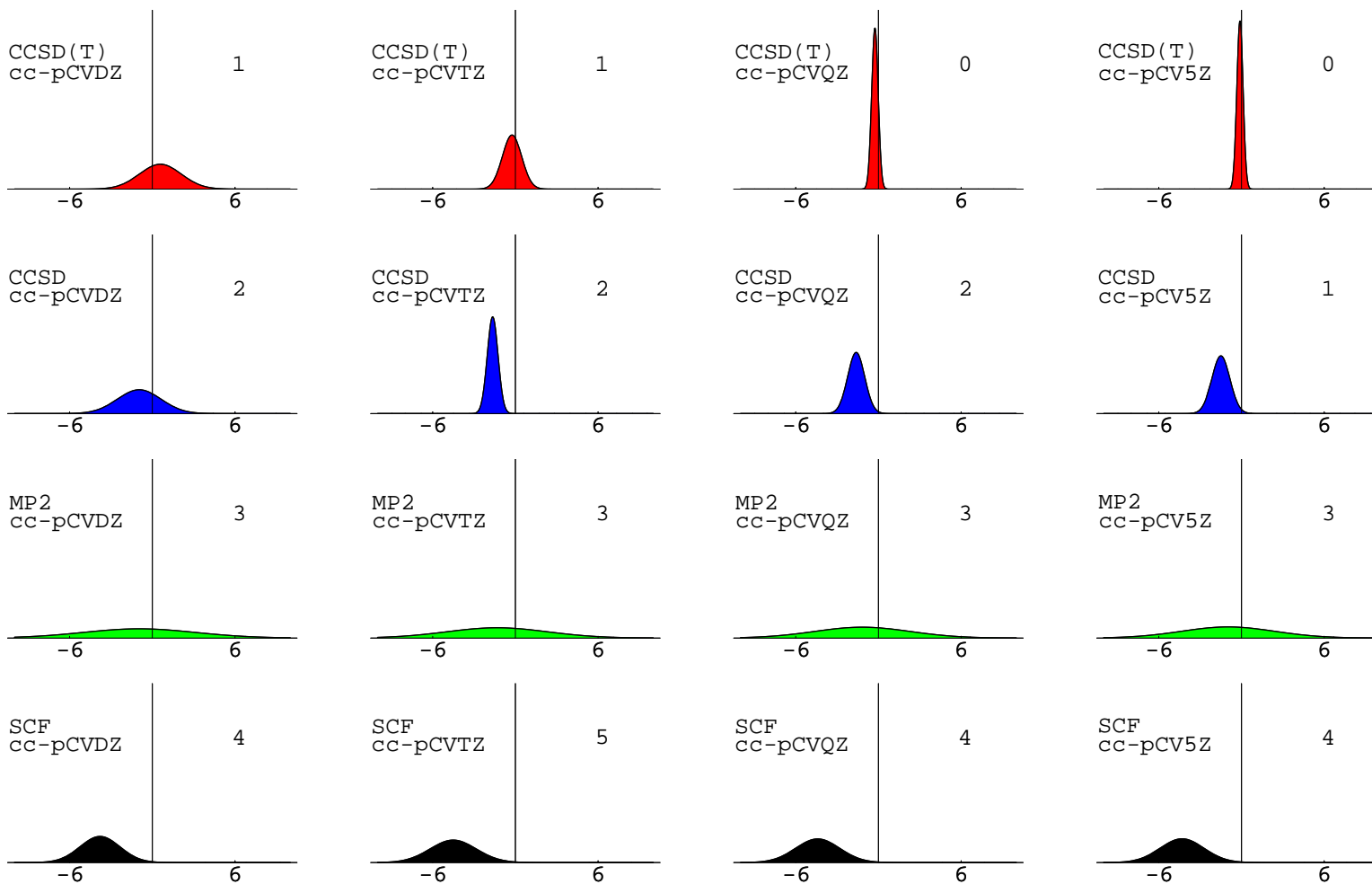
- Off-diagonal anharmonic constants (asymmetric top):

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

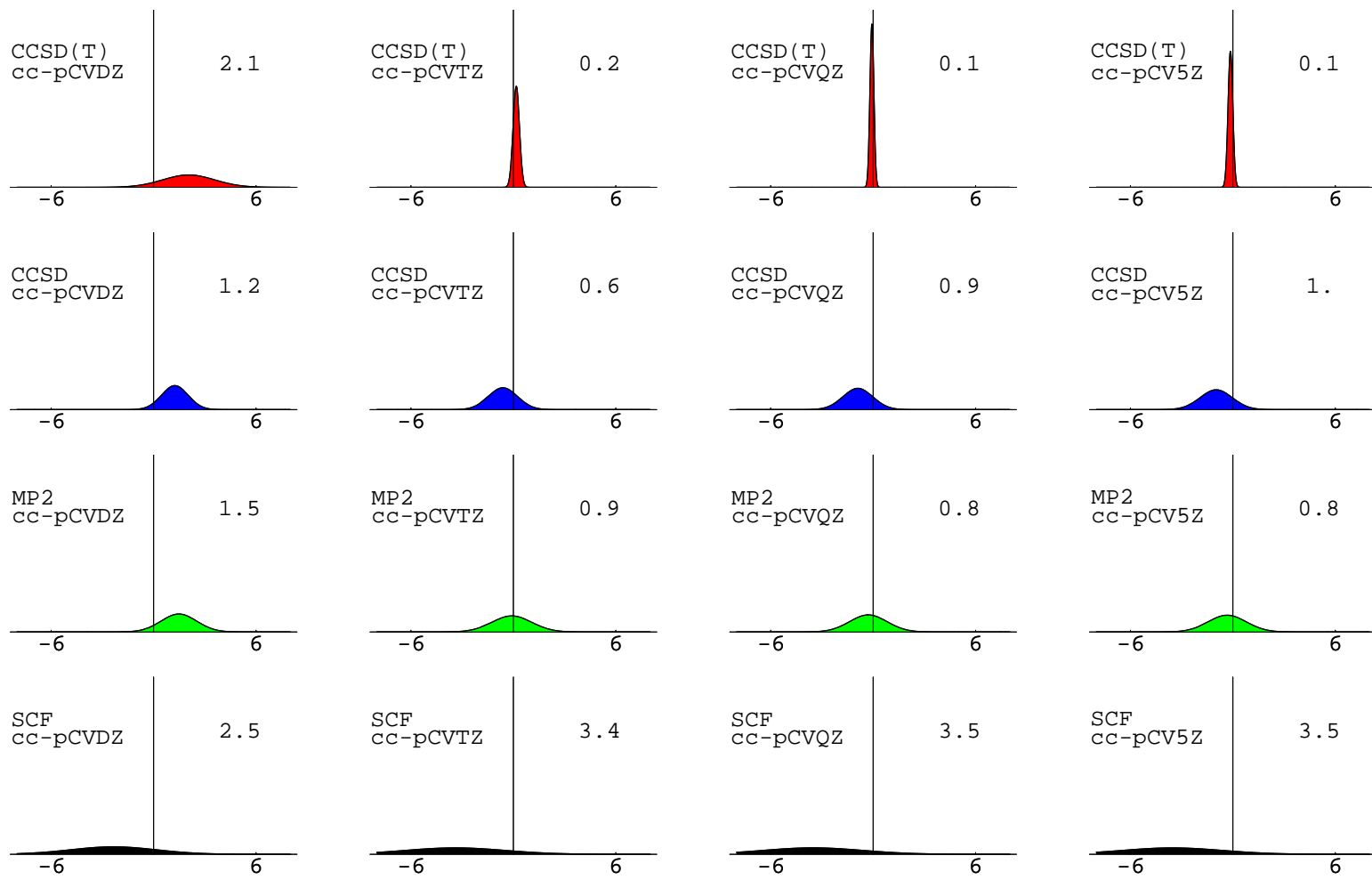
Harmonic constants ω_e of BH, CO, N₂, HF, and F₂ (cm⁻¹)



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)



Difficulties with harmonic constants

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

$ \overline{\Delta} $ (cm ⁻¹)	RHF	MP2	CCSD	CCSD(T)	judgment
ω_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 N₂:

cm ⁻¹	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)

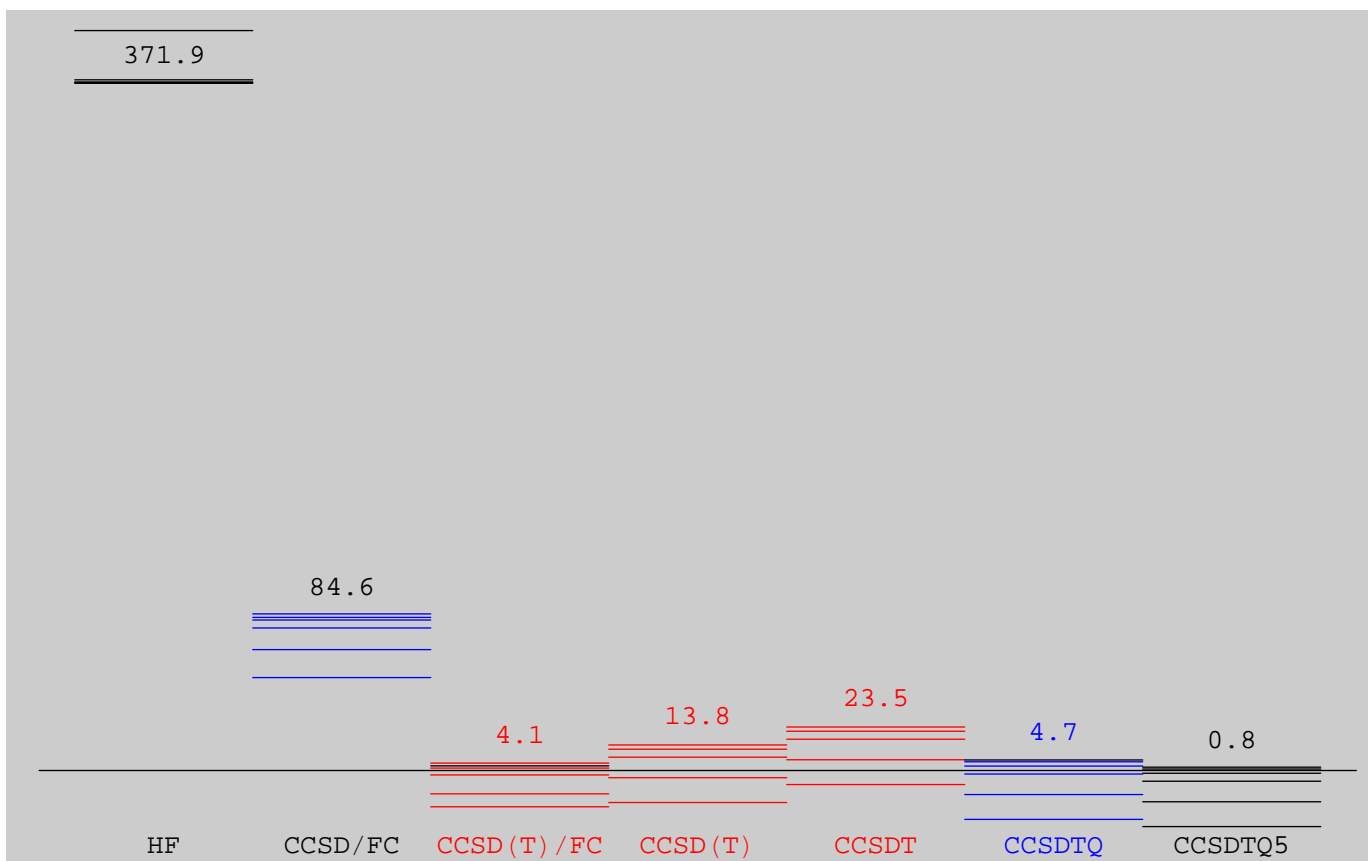
Contributions to harmonic frequencies ω_e (cm^{-1})

	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

- 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}

Harmonic frequencies of HF, N₂, F₂, and CO

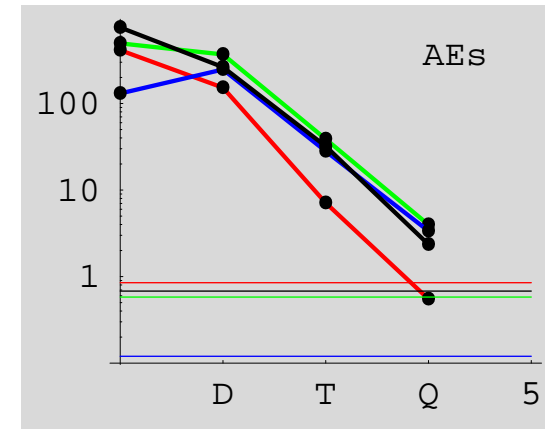
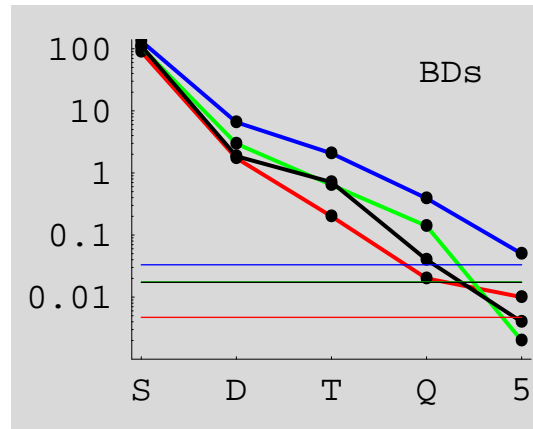
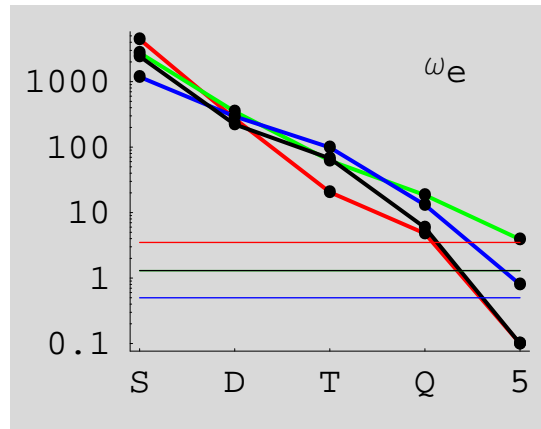
- Contributions to harmonic constants (cm⁻¹):

	HF	N ₂	F ₂	CO
CCSD-R12	4191.0	2443.2	1026.5	2238.5
CCSD(T)–CCSD aug-cc-pV6Z/FC	–48.4	–80.6	–95.7	–71.5
CCSDTQ–CCSD(T) cc-pVTZ/FC	–4.5	–9.1	–12.2	–6.5
CCSDTQ5–CCSDTQ cc-pVDZ/FC	–0.1	–3.9	–0.8	0.0
CCSD(T) core correlation aug-cc-pCV5Z	4.0	9.8	1.6	9.9
relativistic correction	–3.5	–1.4	–0.5	–1.3
adiabatic correction	0.4	0.0	0.0	0.0
theory	4138.9	2358.0	918.9	2169.1
experiment	4138.3	2358.6	916.6	2169.8
error	0.1	–0.6	2.3	0.7

- it does not seem possible yet to obtain harmonic frequencies to within 1 cm⁻¹
- error in F₂ may be explained by a too short bond distance (141.19 vs. 141.27 pm)

Excitation-level convergence

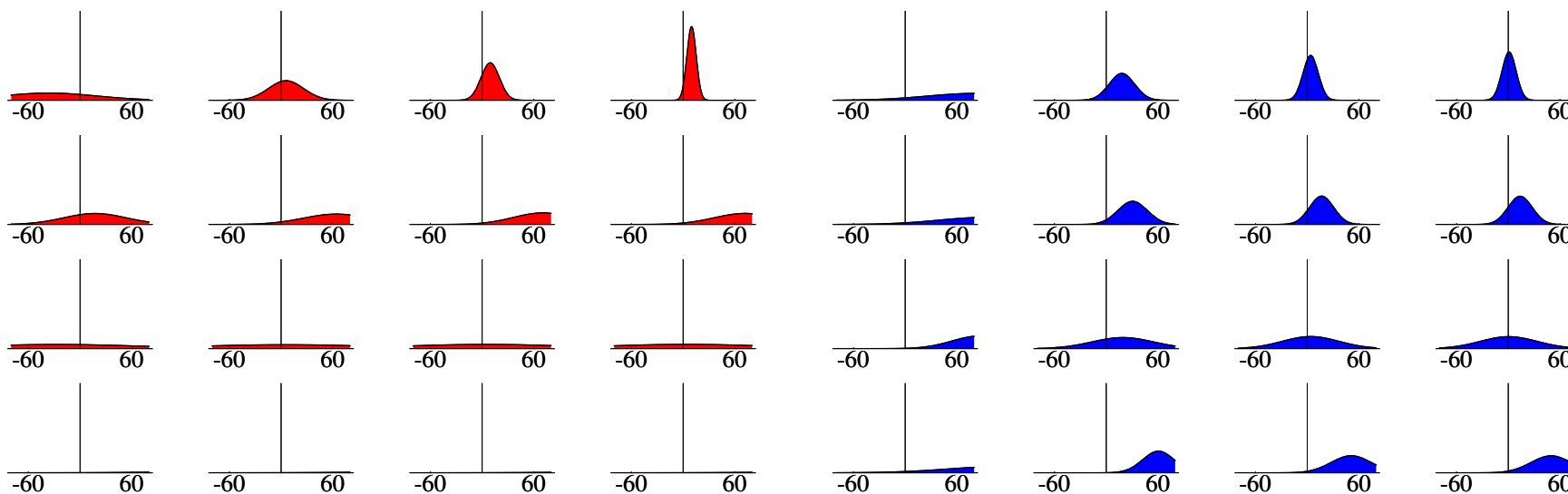
- Log plots of contributions to harmonic frequencies, bond lengths, and atomization energies:



- color code: HF (red), N₂ (green), F₂ (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}

Harmonic frequencies at experimental geometry

- Harmonic frequencies are significantly improved by carrying out the calculations at the experimental geometry.
- Pulay *et al.* (1983), Allen and Császár (1993)
- 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 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
		def	-39	-50
	<i>T</i> ₂	str	-129	-134
		def	-36	-59