

Energy Derivatives and Molecular Properties

- 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
- Hamiltonian derivatives
- 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

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

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

- 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:

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

- 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:

$$\begin{aligned} \frac{\partial L_{\text{CI}}}{\partial P} &= \frac{\partial E_{\text{CI}}}{\partial P} = 0 && \leftarrow \text{CI conditions} \\ \frac{\partial L_{\text{CI}}}{\partial \kappa} &= \frac{\partial E_{\text{CI}}}{\partial \kappa} + \bar{\kappa} \frac{\partial^2 E_{\text{SCF}}}{\partial \kappa^2} = 0 && \leftarrow \text{linear set of equations for } \bar{\kappa} \\ \frac{\partial L_{\text{CI}}}{\partial \bar{\kappa}} &= \frac{\partial E_{\text{SCF}}}{\partial \kappa} = 0 && \leftarrow \text{SCF conditions} \end{aligned}$$

- 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:

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

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

- This should be contrasted with the expression

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

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

- 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, 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

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

The molecular gradient may then be calculated as

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

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:

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q + h_{\text{nuc}}$$
$$h_{pq} = \langle \phi_p^*(\mathbf{r}) | h(\mathbf{r}) | \phi_q(\mathbf{r}) \rangle$$
$$g_{pqrs} = \langle \phi_p^*(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) | r_{12}^{-1} | \phi_q(\mathbf{r}_1) \phi_s(\mathbf{r}_2) \rangle$$

- Its construction 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:

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

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

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

This basis is nonorthogonal and useless for constructing the Hamiltonian.

3. Orthonormalize the basis set:

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

From these orthonormalized MOs (OMOs), we may 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:

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

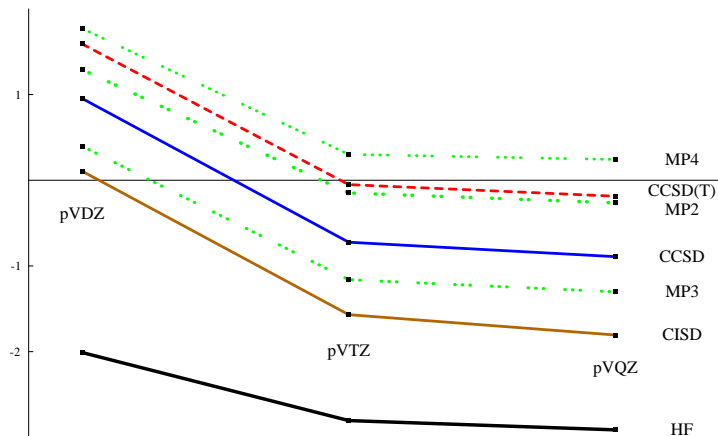
- Integrals are multiplied by densities on the fly and not written to disk.
- Very efficient procedure—no optimization, no linear equations are involved.
- CI and gradients of other nonvariational methods may be cast in a similar form using modified densities involving the Lagrange multipliers.

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):



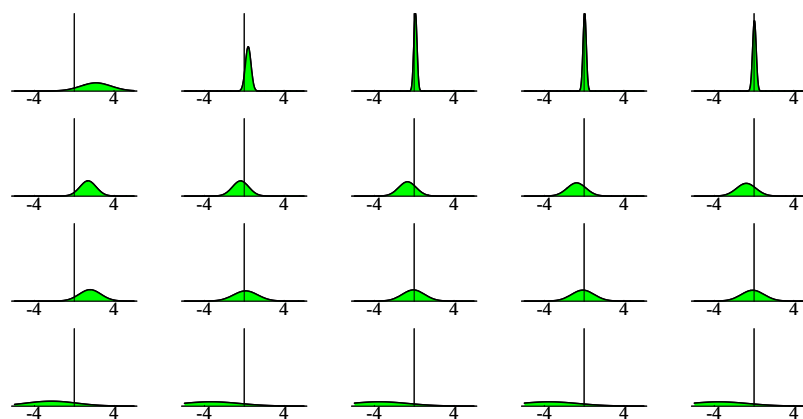
$ \bar{\Delta} $	DZ	TZ	QZ
HF	1.94	2.63	2.74
MP2	1.35	0.56	0.51
CCSD	1.19	0.64	0.80
CCSD(T)	1.68	0.20	0.16

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

		DZ	TZ & QZ
• DZ/TZ inversion:	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 experiment (pm):

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

- However, the high accuracy arises in part because of error cancellation.
- 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

Calculation of harmonic frequencies

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

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

- Mass-weighted Hessian:

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

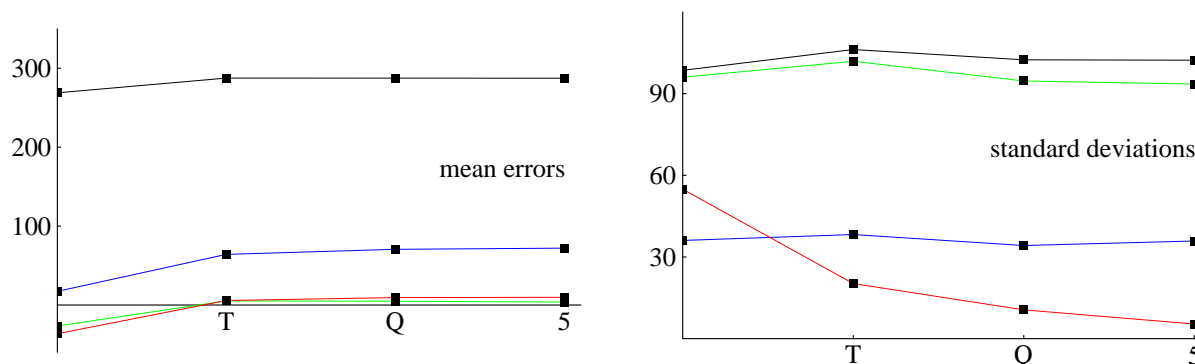
- Diagonalize mass-weighted Hessian to obtain normal coordinates and harmonic frequencies:

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

- Harmonic frequencies are too high but often qualitatively useful.

Convergence of harmonic frequencies

- Errors in the harmonic frequency of BH, HF, CO, N₂, and F₂ at optimized geometry (cm⁻¹):



- Mean absolute errors are quite large—in particular, for HF, MP2, and CCSD:

$ \overline{\Delta} $	HF	MP2	CCSD	CCSD(T)
cm^{-1}	287	71	72	10

– connected triples are important for vibrational frequencies (bond stretching)

- CCSD(T) mean error is quite small at the TZ level but error cancellation often occurs:

		DZ	TZ	QZ	5Z	6Z
$\overline{\Delta}$	val.	-38	-0.4	2.6	2.6	2.2
	all	-36	5.7	9.4	9.8	
$ \overline{\Delta} $	val.	43	17	8.8	7.0	6.4
	all	42	14	9.4	9.8	

Harmonic frequencies ω_e of diatoms (cm^{-1})

- Wave-function convergence

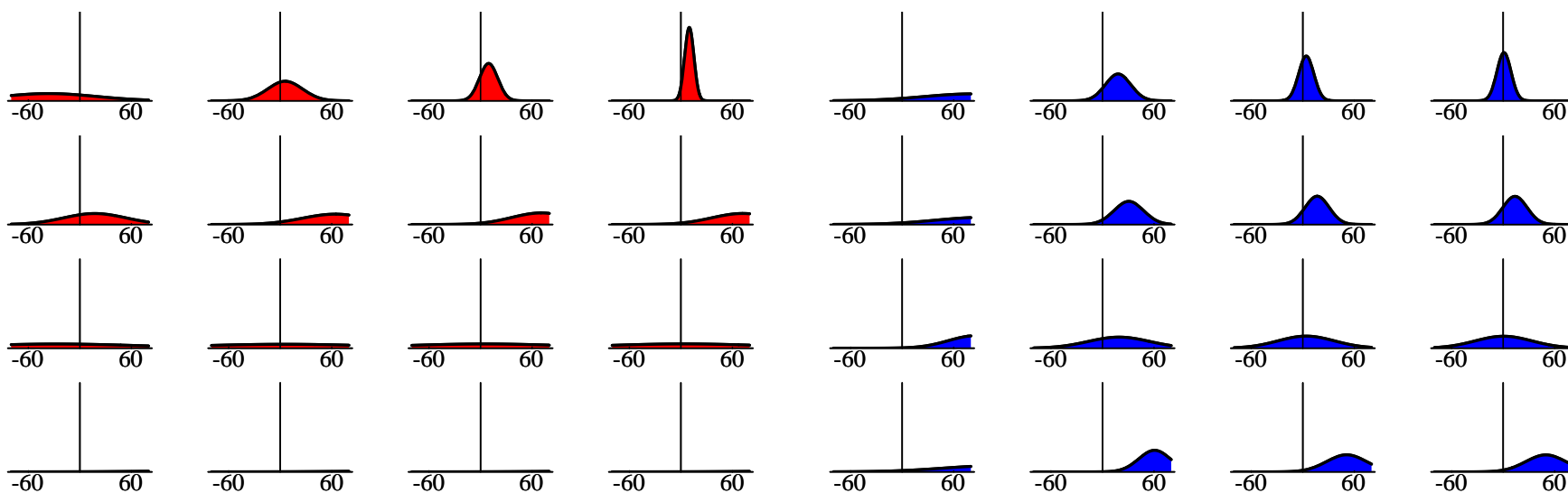
	HF	MP2	CCSD	CCSD(T)	CCSDT	CCSDTQ	exp.
BH	2489	2448	2382	2370			2367
HF	4474	4151	4181	4147	4146	4142	4138
CO	2427	2139	2247	2175			2170
N ₂	2731	2222	2452	2371	2381	2362	2359
F ₂	1267	1010	1023	928	934	918	917

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

	CVDZ	CVTZ	CVQZ	CV5Z
BH	2342	2357	2369	2370
HF	4152	4178	4166	4155
CO	2147	2163	2174	2175
N ₂	2341	2355	2366	2370
F ₂	786	925	922	928

Choice of reference geometry

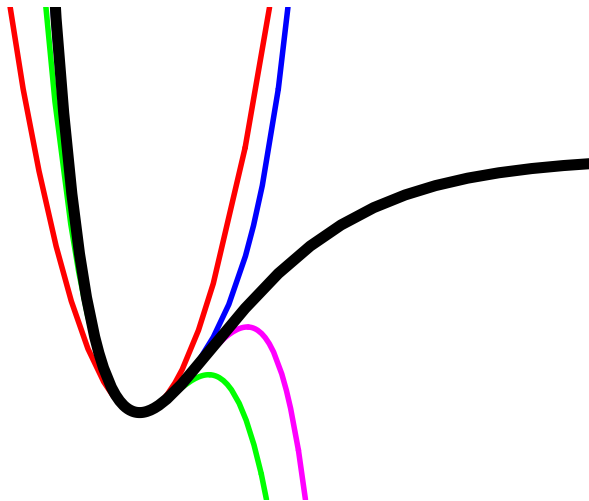
- Harmonic frequencies are significantly improved by carrying out the calculations at the experimental geometry.
- Pulay *et al.* (1983), Allen and Császár (1993)
- This approach is equivalent to the addition of an empirical linear term to the force field.



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

Anharmonic 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 ($\omega_e x_e = -x_{11}$) 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

Errors in fundamental frequencies

