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
  \[ \varepsilon(\mu) = \varepsilon^{(0)} + \varepsilon^{(1)} \mu + \frac{1}{2} \varepsilon^{(2)} \mu^2 + \cdots \]

- 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
  \[ \varepsilon^{(1)} = \frac{d\varepsilon}{d\mu} \bigg|_{\mu=0} \]
  \[ \varepsilon^{(2)} = \frac{d^2\varepsilon}{d\mu^2} \bigg|_{\mu=0} \]

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:

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

• The derivatives of this surface are therefore important:

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

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

• The geometrical derivatives are

  – used for locating and characterizing critical points
  – related to spectroscopic constants, vibrational frequencies, and intensities

• Usually, only a few terms are needed in the expansions, but in some cases low-order expansions are inadequate or useless.
Example: Interaction with an external electric field

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

\[ \varepsilon_{\text{int}} = qV - p\overline{E} - \frac{1}{2}Q\overline{F} - \cdots \]

where

- \( V \) potential
- \( q = \frac{d\varepsilon}{dV} \) charge
- \( \overline{E} \) field
- \( p = -\frac{d\varepsilon}{dE} \) dipole moment
- \( \overline{F} \) field gradient
- \( Q = -2\frac{d\varepsilon}{dF} \) quadrupole moment

- The permanent and induced moments are given by

\[ p(\overline{E}) = \underbrace{p_0}_{\text{permanent moment}} + \underbrace{\alpha\overline{E}}_{\text{induced moment}} + \cdots \]

where

- \( p_0 = -\left. \frac{d\varepsilon}{dE} \right|_{\overline{E}=0} \) permanent dipole moment
- \( \alpha = \left. \frac{dp}{dE} \right|_{\overline{E}=0} = -\left. \frac{d^2\varepsilon}{dE^2} \right|_{\overline{E}=0} \) dipole polarizability
Example: Magnetic resonance parameters

- The energy in the presence of nuclear magnetic moments $m$ and an external magnetic field $B$:

\[ \varepsilon(m, B) = \varepsilon_0 + \varepsilon^{(10)} m + \varepsilon^{(01)} B + \frac{1}{2} \varepsilon^{(20)} m^2 + \varepsilon^{(11)} B m + \frac{1}{2} \varepsilon^{(02)} B^2 + \cdots \]

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

\[ \varepsilon^{(11)} = \frac{d^2 \varepsilon}{dmdB} \]

  - 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:

\[ \varepsilon^{(11)}_{\text{mol}} = -I + \sigma \quad \leftarrow \text{shielding constant} \]

- 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)
  - \( \lambda \): 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 $\lambda$ for each value of $x$:

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

Note: The optimization is not necessarily variational!

- Our task is to calculate derivatives of $\varepsilon(x)$ with respect to $x$:

$$\frac{d\varepsilon(x)}{dx} = \left. \frac{\partial E(x, \lambda^*)}{\partial x} \right|_{\lambda^*} + \left. \frac{\partial E(x, \lambda)}{\partial \lambda} \right|_{\lambda=\lambda^*} \frac{\partial \lambda}{\partial x} \bigg|_{\lambda=\lambda^*}$$

- 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 \( \lambda \) the electronic parameters.

- The stationary condition determines \( \lambda \) 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:

\[ \frac{d\varepsilon}{dx} = \frac{\partial E}{\partial x} = \langle \lambda^* | \frac{\partial H}{\partial x} | \lambda^* \rangle \]

- The theorem was originally stated for geometrical distortions:

\[ \frac{d\varepsilon}{dR_K} = -\left\langle \lambda^* \left[ \sum_i \frac{Z_K r_{iK}}{r_{IK}^3} \right] \lambda^* \right\rangle + \sum_{I \neq K} \frac{Z_I Z_K R_{IK}}{R_{IK}^3} \]

- 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:

\[
\frac{\partial^2 E}{\partial \lambda^2} \frac{\partial \lambda}{\partial x} = -\frac{\partial^2 E}{\partial x \partial \lambda}
\]

- electronic Hessian
- 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:

- 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:

\[
kx = -F
\]

- The wave function relaxes by an amount that is proportional to the perturbation.
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
\[
\frac{\partial^2 E}{\partial x \partial \lambda_n} = 2 \left\langle 0 \middle| H^{(1)} \middle| n \right\rangle
\]
\[
\frac{\partial^2 E}{\partial \lambda_m \partial \lambda_n} = 2\delta_{mn}(E_n - E_0) \leftarrow \text{diagonal representation}
\]

This gives us the following expression for the FCI molecular Hessian (compare with second-order perturbation theory):
\[
\varepsilon^{(2)} = \left\langle 0 \middle| H^{(2)} \middle| 0 \right\rangle - 2 \sum_n \frac{\left\langle 0 \middle| H^{(1)} \middle| n \right\rangle \left\langle n \middle| H^{(1)} \middle| 0 \right\rangle}{E_n - E_0}
\]
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:

<table>
<thead>
<tr>
<th>energy</th>
<th>$\varepsilon^{(0)}$</th>
<th>$\varepsilon^{(1)}$</th>
<th>$\varepsilon^{(2)}$</th>
<th>$\varepsilon^{(3)}$</th>
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<td>wave function</td>
<td>$\lambda^{(0)}$</td>
<td>$\lambda^{(0)}$</td>
<td>$\lambda^{(0)}, \lambda^{(1)}$</td>
<td>$\lambda^{(0)}, \lambda^{(1)}$</td>
<td>$\lambda^{(0)}, \lambda^{(1)}, \lambda^{(2)}$</td>
</tr>
</tbody>
</table>
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:

    \[ E_{\text{CI}}(x, P, \kappa) \leftarrow \text{state-transfer parameters } P \]
    \[ \text{orbital-rotation parameters } \kappa \]

  – 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:

\[
\frac{d\varepsilon_{CI}}{dx} = \frac{\partial E_{CI}}{\partial x} + \frac{\partial E_{CI}}{\partial P} \frac{\partial P}{\partial x} + \frac{\partial E_{CI}}{\partial \kappa} \frac{\partial \kappa}{\partial x}
\]

\[
= \frac{\partial E_{CI}}{\partial x} + \frac{\partial E_{CI}}{\partial \kappa} \frac{\partial \kappa}{\partial x} \quad \leftarrow \kappa\text{-contribution does not vanish}
\]

- It looks as if we need the first-order response of the orbitals.

- The (Hartree–Fock) orbitals fulfil the condition

\[
\frac{\partial E_{SCF}}{\partial \kappa} = 0
\]

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

\[
\frac{\partial^2 E_{SCF}}{\partial \kappa^2} \frac{\partial \kappa}{\partial x} = -\frac{\partial^2 E_{SCF}}{\partial x \partial \kappa}
\]

- 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 $\kappa$:

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

• Use Lagrange’s method of undetermined multipliers. Construct the Lagrangian

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

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

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

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

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

• Note the duality between $\kappa$ and $\bar{\kappa}$. 
The CI Lagrangian is given by

\[ L_{\text{CI}} = E_{\text{CI}} + \kappa \frac{\partial E_{\text{SCF}}}{\partial \kappa} \]

Since the Lagrangian is variational, we may invoke the \(2n + 1\) rule:

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

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

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:

$$L(x, \lambda, \overline{\lambda}) = E(x, \lambda) + \overline{\lambda} (e(x, \lambda) - 0)$$

  Lagrangian energy function constraints

- The stationary (variational) conditions:

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

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

Note the duality between $\lambda$ and $\overline{\lambda}$.

- The Lagrangian reduces to the Hylleraas functional when applied to a perturbation expression.

- The Lagrangian technique may be generalized to time-dependent properties.
• 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:

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

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

• 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:
  \[ \lambda^{(n)} \text{ determines the energy to order } 2n + 1. \]

- 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:
  \[ \overline{\lambda}^{(n)} \text{ determines the energy to order } 2n + 2. \]

- Responses required to order 10:

<table>
<thead>
<tr>
<th>$\varepsilon^{(n)}$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tbody>
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<td>3</td>
<td>3</td>
<td>4</td>
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<td>5</td>
</tr>
<tr>
<td>$\overline{\lambda}^{(k)}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
For variational wave functions, the wave function to order $n$ determines the energy to order $2n + 1$ (the $2n + 1$ rule):

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

← Hellmann–Feynman

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

$$L(x, \lambda, \bar{\lambda}) = E(x, \lambda) + \bar{\lambda}e(x, \lambda)$$

← Lagrangian

$$e(x, \lambda) = 0 \text{ (all } x)$$

← constraints

The molecular gradient may then be calculated as

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

← zero-order multiplier needed

$$\frac{\partial E}{\partial \lambda} + \bar{\lambda} \frac{\partial e}{\partial \lambda} = 0$$

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

- Its construction requires an orthonormal MO basis \( \phi_p \).

- 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:

\[ \phi(x_0) = C^{(0)} \chi(x_0) \]
\[ S(x_0) = \langle \phi(x_0) \big| \phi^\dagger(x_0) \rangle = I \]

2. Geometrical distortion \( x = x_0 + \Delta x \):

\[ \phi(x) = C^{(0)} \chi(x) \]
\[ S(x) = \langle \phi(x) \big| \phi^\dagger(x) \rangle \neq I \]

This basis is nonorthogonal and useless for constructing the Hamiltonian.

3. Orthonormalize the basis set:

\[ \psi(x) = S^{-1/2}(x) \phi(x) \]
\[ \tilde{S}(x) = S^{-1/2}(x) S(x) S^{-1/2}(x) = I \]

From these orthonormalized MOs (OMOs), we may construct the Hamiltonian.
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:

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

- 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

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

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:

\[ \sum_{pq} D_{pq} h_{pq}^{(1)} = \sum_{pq} D_{pq} \sum_{\mu\nu} C_{\mu}^{(0)} C_{\nu}^{(0)} h_{\mu\nu}^{(1)} = \sum_{\mu\nu} h_{\mu\nu}^{(1)} \sum_{pq} D_{pq} C_{\mu}^{(0)} C_{\nu}^{(0)} = \sum_{\mu\nu} D_{\mu\nu} h_{\mu\nu}^{(1)} \]

- 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):

<table>
<thead>
<tr>
<th></th>
<th>DZ</th>
<th>TZ</th>
<th>QZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>1.94</td>
<td>2.63</td>
<td>2.74</td>
</tr>
<tr>
<td>MP2</td>
<td>1.35</td>
<td>0.56</td>
<td>0.51</td>
</tr>
<tr>
<td>CCSD</td>
<td>1.19</td>
<td>0.64</td>
<td>0.80</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>1.68</td>
<td>0.20</td>
<td>0.16</td>
</tr>
</tbody>
</table>

- Bonds shorten with increasing basis:
  - HF: DZ → TZ 0.8 pm; TZ → QZ 0.1 pm
  - corr.: DZ → TZ 1.6 pm; TZ → 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:
  - best | CISD & MP3 | CCSD(T) & MP4
  - worst | CCSD(T) & MP4 | CISD & MP3
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):

<table>
<thead>
<tr>
<th></th>
<th>DZ</th>
<th>TZ</th>
<th>QZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$</td>
<td>1.68</td>
<td>0.01</td>
<td>-0.12</td>
</tr>
<tr>
<td>$</td>
<td>\Delta</td>
<td>$</td>
<td>1.68</td>
</tr>
</tbody>
</table>

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

Bond distances are further reduced by
- basis-set extension QZ → 6Z: $\approx -0.10$ pm
- triples relaxation CCSD(T) → CCSDT: $\approx -0.02$ pm

Intrinsic error of the CCSDT model: $\approx -0.2$ pm
## Bond distances III

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>emp.</th>
<th>eks.</th>
</tr>
</thead>
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<td>91.7</td>
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<td>95.4</td>
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<td>95.7</td>
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<tr>
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<td>96.6</td>
<td>96.2</td>
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<td>96.6</td>
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<td>106.2</td>
<td>106.2</td>
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<td>107.9</td>
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<td>108.1</td>
<td>108.1</td>
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<td>108.5</td>
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<td>108.6</td>
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<td>109.8</td>
<td>109.9</td>
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<td>110.1</td>
<td>110.1</td>
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<td>110.6</td>
<td>110.7</td>
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<td>115.4</td>
<td>115.3</td>
<td>115.3</td>
</tr>
<tr>
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<td>116.4</td>
<td>115.3</td>
<td>116.0</td>
<td>116.0</td>
<td>116.0</td>
</tr>
<tr>
<td>HNC</td>
<td>114.4</td>
<td>117.0</td>
<td>116.2</td>
<td>116.9</td>
<td>116.9</td>
<td>116.9</td>
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<tr>
<td>C₂H₂</td>
<td>117.9</td>
<td>120.5</td>
<td>119.7</td>
<td>120.4</td>
<td>120.4</td>
<td>120.3</td>
</tr>
<tr>
<td>CH₂O</td>
<td>117.6</td>
<td>120.6</td>
<td>119.7</td>
<td>120.4</td>
<td>120.5</td>
<td>120.3</td>
</tr>
<tr>
<td>N₂H₂</td>
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<td>123.6</td>
<td>124.7</td>
<td>124.6</td>
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<td>C₂H₄</td>
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<td>132.6</td>
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<td>133.1</td>
<td>133.1</td>
<td>133.1</td>
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<tr>
<td>F₂</td>
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<td>138.8</td>
<td>141.1</td>
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</tr>
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<td>HOF</td>
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<td>142.0</td>
<td>141.2</td>
<td>143.3</td>
<td>143.4</td>
<td>143.4</td>
</tr>
</tbody>
</table>
Calculation of harmonic frequencies

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

\[ V(x) = \frac{1}{2} G x^2 \]

• 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, N$_2$, and F$_2$ at optimized geometry (cm$^{-1}$):

<table>
<thead>
<tr>
<th>$\bar{\Delta}$</th>
<th>HF</th>
<th>MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm$^{-1}$</td>
<td>287</td>
<td>71</td>
<td>72</td>
<td>10</td>
</tr>
</tbody>
</table>

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

\[
|\Delta|_{\text{val.}} \quad \text{DZ} \quad \text{TZ} \quad \text{QZ} \quad 5Z \quad 6Z
\]

\[
\begin{array}{c|cccccc}
\bar{\Delta} & -38 & -0.4 & 2.6 & 2.6 & 2.2 \\
\text{all} & -36 & 5.7 & 9.4 & 9.8 \\
|\Delta| & 43 & 17 & 8.8 & 7.0 & 6.4 \\
\text{all} & 42 & 14 & 9.4 & 9.8 \\
\end{array}
\]

- 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:
Harmonic frequencies $\omega_e$ of diatoms (cm$^{-1}$)

- Wave-function convergence

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>CCSDT</th>
<th>CCSDTQ</th>
<th>exp.</th>
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<tr>
<td>BH</td>
<td>2489</td>
<td>2448</td>
<td>2382</td>
<td>2370</td>
<td></td>
<td></td>
<td>2367</td>
</tr>
<tr>
<td>HF</td>
<td>4474</td>
<td>4151</td>
<td>4181</td>
<td>4147</td>
<td>4146</td>
<td>4142</td>
<td>4138</td>
</tr>
<tr>
<td>CO</td>
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<td>2139</td>
<td>2247</td>
<td>2175</td>
<td></td>
<td></td>
<td>2170</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2731</td>
<td>2222</td>
<td>2452</td>
<td>2371</td>
<td>2381</td>
<td>2362</td>
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<td>F$_2$</td>
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<td>1010</td>
<td>1023</td>
<td>928</td>
<td>934</td>
<td>918</td>
<td>917</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>CVDZ</th>
<th>CVTZ</th>
<th>CVQZ</th>
<th>CV5Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH</td>
<td>2342</td>
<td>2357</td>
<td>2369</td>
<td>2370</td>
</tr>
<tr>
<td>HF</td>
<td>4152</td>
<td>4178</td>
<td>4166</td>
<td>4155</td>
</tr>
<tr>
<td>CO</td>
<td>2147</td>
<td>2163</td>
<td>2174</td>
<td>2175</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2341</td>
<td>2355</td>
<td>2366</td>
<td>2370</td>
</tr>
<tr>
<td>F$_2$</td>
<td>786</td>
<td>925</td>
<td>922</td>
<td>928</td>
</tr>
</tbody>
</table>
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:
  \[ E(n) = V_0 + \sum_k \hbar \omega_k (n_k + \frac{1}{2}) + \sum_{k \leq l} x_{kl} (n_k + \frac{1}{2})(n_l + \frac{1}{2}) \]

- The anharmonic constants \( x_{kl} \) may be obtained from:
  - the harmonic constants \( \omega_k \)
  - the cubic and quartic force constants
    \[ f_{klm} = \frac{d^3V}{dQ_k dQ_l dQ_m}, \quad f_{klmn} = \frac{d^4V}{dQ_k dQ_l dQ_m dQ_n} \]
    where \( Q_k \) are the normal coordinates
  - the rotational constants \( B_\alpha \) and the Coriolis-coupling constants \( \zeta_{kl}^\alpha \).

- The fundamentals are then given by
  \[ \nu_k = \omega_k + \frac{2}{\hbar} x_{kk} + \frac{1}{2\hbar} \sum_{l \neq k} x_{kl} \]
Anharmonic constants

- Diagonal anharmonic constants (asymmetric top):
  \[
x_{kk} = \frac{\hbar^2}{16\omega_k^2} \left[ f_{kkkk} - \sum_l \frac{f_{kkl}^2(8\omega_k^2 - 3\omega_l^2)}{\omega_l^2(4\omega_k^2 - \omega_l^2)} \right]
  \]

- Off-diagonal anharmonic constants (asymmetric top):
  \[
x_{kl} = \frac{\hbar^2}{4\omega_k\omega_l} \left[ f_{kkl} - \sum_m \frac{f_{kkm}f_{llm}}{\omega_m^2} \right. \\
  \quad + \sum_m \frac{2f_{klm}^2(\omega_k^2 + \omega_l^2 - \omega_m^2)}{[(\omega_k + \omega_l)^2 - \omega_m^2][(\omega_k - \omega_l)^2 - \omega_m^2]} \\
  \quad + \left( \frac{\omega_k}{\omega_l} + \frac{\omega_l}{\omega_k} \right) \sum_\alpha B_\alpha \left( \zeta_{kl}^\alpha \right)^2 \right]
  \]
Anharmonic constants \((\omega_e x_e = -x_{11})\) of diatoms (\(\text{cm}^{-1}\))

- Wave-function convergence

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH</td>
<td>43</td>
<td>44</td>
<td>48</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>HF</td>
<td>85</td>
<td>87</td>
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<td>90</td>
</tr>
<tr>
<td>CO</td>
<td>11</td>
<td>13</td>
<td>12</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>(N_2)</td>
<td>11</td>
<td>19</td>
<td>13</td>
<td>14</td>
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<tr>
<td>(F_2)</td>
<td>7</td>
<td>9</td>
<td>9</td>
<td>12</td>
<td>11</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>CVDZ</th>
<th>CVTZ</th>
<th>CVQZ</th>
<th>CV5Z</th>
</tr>
</thead>
<tbody>
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<td>BH</td>
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<td>49</td>
<td>49</td>
<td>49</td>
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<tr>
<td>HF</td>
<td>93</td>
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<td>90</td>
<td>90</td>
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<td>CO</td>
<td>13</td>
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<td>13</td>
</tr>
<tr>
<td>(N_2)</td>
<td>15</td>
<td>14</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>(F_2)</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>
### Anharmonicities of triatoms (cm$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th>exp.</th>
</tr>
</thead>
<tbody>
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<tr>
<td></td>
<td>def</td>
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<tr>
<td></td>
<td>$B_2$</td>
<td>str</td>
<td>-178</td>
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<tr>
<td><strong>NH$_3$</strong></td>
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<tr>
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<td>$E$</td>
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Errors in fundamental frequencies

- SCF
  - cc-pVDZ
- SCF
  - cc-pVTZ
- SCF
  - cc-pVQZ
- MP2
  - cc-pVDZ
- MP2
  - cc-pVTZ
- MP2
  - cc-pVQZ
- CCD
  - cc-pVDZ
- CCD
  - cc-pVTZ
- CCD
  - cc-pVQZ
- CCSDH1
  - cc-pVDZ
- CCSDH1
  - cc-pVTZ
- CCSDH1
  - cc-pVQZ