Time-independent molecular properties

Trygve Helgaker

Hylleraas Centre, Department of Chemistry, University of Oslo, Norway

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Sections

Section 1

Introduction

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Time-Independent Molecular Properties

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

$$\mathcal{E}(\mu) = \mathcal{E}^{(0)} + \mathcal{E}^{(1)}\mu + \tfrac{1}{2}\mathcal{E}^{(2)}\mu^2 + \cdots$$

- 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

$$\mathcal{E}^{(1)} = \left.\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}\mu}\right|_{\mu=0}$$
$$\mathcal{E}^{(2)} = \left.\frac{\mathrm{d}^2\mathcal{E}}{\mathrm{d}\mu^2}\right|_{\mu=0}$$

  - such properties are said to be time independent
- We do not here consider time-dependent molecular properties
  - if periodic, these can be calculated in similar way using the quasi-energy

Examples of Derivatives

- Responses to geometrical perturbations
  - forces and force constants
  - spectroscopic constants
- Responses to external electromagnetic fields
  - permanent and induced moments
  - polarizabilities and magnetizabilities
  - optical activity
- Responses to external magnetic fields and nuclear magnetic moments
  - NMR shielding and indirect spin–spin coupling constants
  - EPR hyperfine coupling constants and g values
- Responses to nuclear quadrupole moments
  - nuclear field gradients, quadrupole coupling constants
- Responses to molecular rotation
  - spin–rotation constants and molecular g values

Numerical vs. analytical differentiation

- Numerical differentiation (finite differences and polynomial fitting)
  - often simple to implement (at least for real singlet perturbations)
  - difficulties related to numerical accuracy and computational efficiency
- Analytical differentiation (derivatives calculated from analytical expressions)
  - considerable programming effort required
  - greater speed, precision, and convenience
- Implementations of analytical techniques
  - first-order properties (dipole moments and gradients)
  - second-order properties (polarizabilities and Hessians, NMR parameters)

Section 2

Energy Functions

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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 (here in second quantization)

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

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 $\lambda(x)$.

Electronic Energy and its Derivatives

- The electronic energy $\mathcal{E}(x)$ is obtained by optimizing the energy function $E(x, \lambda)$ with respect to λ for each value of x:

$$\mathcal{E}(x) = E(x, \lambda^*)$$

  - note: the optimization is not necessarily a variational minimization
- Our task is to calculate derivatives of $\mathcal{E}(x)$ with respect to x:

$$\frac{\mathrm{d}\mathcal{E}(x)}{\mathrm{d}x} = \underbrace{\frac{\partial E(x, \lambda^*)}{\partial x}}_{\text{explicit dependence}} + \underbrace{\left.\frac{\partial E(x, \lambda)}{\partial \lambda}\right|_{\lambda=\lambda^*} \left.\frac{\partial \lambda}{\partial x}\right|_{\lambda=\lambda^*}}_{\text{implicit dependence}}$$

  - the implicit as well as explicit dependence must be accounted for
- The quantity $\partial\lambda/\partial x$ is the wave-function response
  - it tells us how the electronic structure changes when the system is perturbed
- To proceed, we need to make a distinction between
  - variationally determined wave functions
  - nonvariationally determined wave functions

Variational and Nonvariational Wave Functions

Variational wave functions

- the optimized energy fulfils the stationary (variational) condition:

$$\frac{\partial E(x,\lambda)}{\partial \lambda} = 0 \quad \text{(for all } x\text{)}$$

- the Hartree–Fock energy in an unconstrained exponential parameterization

$$|\mathrm{HF}\rangle = \exp(-\kappa)|0\rangle, \quad \kappa^{\dagger} = -\kappa$$

- the energy of the full CI (FCI) wave function $|\mathrm{FCI}\rangle = \sum_i c_i |i\rangle$ as an expectation value:

$$\frac{\partial E_{\mathrm{FCI}}(x,c)}{\partial c} = 0$$

Nonvariational wave functions

- the optimized energy does not fulfil the stationary (variational) condition:

$$\frac{\partial E(x,\lambda)}{\partial \lambda} \neq 0$$

- the Hartree–Fock and Kohn–Sham energies in a constrained LCAO parameterization (orthonormality)

$$|\mathrm{HF}\rangle = \frac{1}{\sqrt{N!}}\det|\phi_1, \phi_2, \ldots \phi_N|, \quad \phi_p(\mathbf{r};\mathbf{x}) = \sum\nolimits_{\mu} C_{\mu p}\chi_\mu(\mathbf{r};\mathbf{x}), \quad \langle \phi_p|\phi_q\rangle = \delta_{pq}$$

- the truncated CI energy with respect to orbital rotations:

$$\frac{\partial E_{\mathrm{CI}}(x,c,\kappa)}{\partial c} = 0, \quad \frac{\partial E_{\mathrm{CI}}(x,c,\kappa)}{\partial \kappa} \neq 0$$

Section 3

Derivatives for Variational Wave Functions

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Molecular Gradients for Variational Wave Functions

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

$$\frac{\mathrm{d}\mathcal{E}(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x} + \frac{\partial E(x,\lambda)}{\partial \lambda}\frac{\partial \lambda}{\partial x}$$

  - the first term accounts for the explicit dependence on x
  - the last term accounts for the implicit dependence on x
- We now invoke the stationary condition:

$$\frac{\partial E(x,\lambda)}{\partial \lambda} = 0 \qquad \text{(zero electronic gradient for all } x\text{)}$$

- The molecular gradient then simplifies to

$$\frac{\mathrm{d}\mathcal{E}(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x}$$

  - examples: HF/KS and MCSCF molecular gradients (exponential parameterization)

For variational wave functions, we do not need the response of the wave function $\partial\lambda/\partial x$ to calculate the molecular gradient $\mathrm{d}\mathcal{E}/\mathrm{d}x$.

Hellmann–Feynman Theorem

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

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

- The gradient is then given by the expectation-value expression:

$$\frac{\mathrm{d}\mathcal{E}(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x} = \left\langle \lambda \left| \frac{\partial H}{\partial x} \right| \lambda \right\rangle \qquad \leftarrow \text{the Hellmann–Feynman theorem}$$

- Relationship to first-order perturbation theory:

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

- The Hellmann–Feynman theorem was originally stated for geometrical distortions:

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

- Classical interpretation: integration over the force operator

Molecular Hessians for Variational Wave Functions

- Differentiating the molecular gradient, we obtain the molecular Hessian:

$$\frac{\mathrm{d}^2\mathcal{E}(x)}{\mathrm{d}x^2} = \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial E(x,\lambda)}{\partial x} = \left(\frac{\partial}{\partial x} + \frac{\partial \lambda}{\partial x}\frac{\partial}{\partial \lambda}\right)\frac{\partial E(x,\lambda)}{\partial x}$$
$$= \frac{\partial^2 E(x,\lambda)}{\partial x^2} + \frac{\partial^2 E(x,\lambda)}{\partial x \partial \lambda}\frac{\partial \lambda}{\partial x}$$

  - we need the first-order response $\partial\lambda/\partial x$ to calculate the Hessian
  - but we do not need the second-order response $\partial^2\lambda/\partial x^2$ for stationary energies

- To determine the response, we differentiate the stationary condition:

$$\frac{\partial E(x,\lambda)}{\partial \lambda} = 0 \quad \text{(all } x\text{)} \implies \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial E(x,\lambda)}{\partial \lambda} = 0$$
$$\implies \frac{\partial^2 E(x,\lambda)}{\partial x \partial \lambda} + \frac{\partial^2 E(x,\lambda)}{\partial \lambda^2}\frac{\partial \lambda}{\partial x} = 0$$

- 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

- The molecular Hessian for stationary energies:

$$\frac{\mathrm{d}^2\mathcal{E}}{\mathrm{d}x^2} = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial x \partial \lambda}\frac{\partial \lambda}{\partial x}$$

- The response equations:

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

    - the electronic Hessian is a Hermitian matrix, independent of the perturbation
    - its dimensions are usually large and it cannot be constructed explicitly
    - the response equations are typically solved by iterative techniques
    - key step: multiplication of the Hessian with a trial vector
- Analogy with Hooke's law:

$$\text{force constant} \rightarrow \quad kx = -F \quad \leftarrow \text{force}$$

    - the wave function relaxes by an amount proportional to the perturbation

$2n + 1$ Rule

- For molecular gradients and Hessians, we have the expressions

$$\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}x} = \frac{\partial E}{\partial x} \qquad \leftarrow \text{zero-order response needed}$$

$$\frac{\mathrm{d}^2\mathcal{E}}{\mathrm{d}x^2} = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial x \partial \lambda}\frac{\partial \lambda}{\partial x} \qquad \leftarrow \text{first-order response needed}$$

- In general, we have the $2n + 1$ rule:

For variational wave functions, the derivatives of the wave function to order n determine the derivatives of the energy to order $2n + 1$.

- Examples: wave-function responses needed to fourth order:

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

Section 4

Derivatives for Nonvariational Wave Functions

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Nonvariational Wave Functions

- The $2n+1$ rule simplifies property evaluation for variational wave functions
- What about the nonvariational wave functions?
  - any energy may be made stationary by Lagrange's method of undetermined multipliers
  - the $2n+1$ rule is therefore of general interest
- Example: the CI energy
  - the CI energy function is given by:

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

  - it is nonstationary with respect to the orbital-rotation parameters:

$$\frac{\partial E_{\mathrm{CI}}(x, c, \kappa)}{\partial c} = 0 \leftarrow \text{stationary}$$

$$\frac{\partial E_{\mathrm{CI}}(x, c, \kappa)}{\partial \kappa} \neq 0 \leftarrow \text{nonstationary}$$

- We shall now consider its molecular gradient:
  1. by differentiation of the CI energy
  2. by differentiation of the CI Lagrangian
- In coupled-cluster theory, all parameters are nonvariationally determined

CI Molecular Gradients the Straightforward Way

- Straightforward differentiation of $E_{\mathrm{CI}}(x, c, \kappa)$ gives the expression

$$\begin{aligned}\frac{\mathrm{d}\mathcal{E}_{\mathrm{CI}}}{\mathrm{d}x} &= \frac{\partial E_{\mathrm{CI}}}{\partial x} + \frac{\partial E_{\mathrm{CI}}}{\partial c}\frac{\partial c}{\partial x} + \frac{\partial E_{\mathrm{CI}}}{\partial \kappa}\frac{\partial \kappa}{\partial x} \\ &= \frac{\partial E_{\mathrm{CI}}}{\partial x} + \frac{\partial E_{\mathrm{CI}}}{\partial \kappa}\frac{\partial \kappa}{\partial x} \quad \leftarrow \kappa \text{ contribution does not vanish}\end{aligned}$$

  - it appears that we need the first-order response of the orbitals

- The HF orbitals used in CI theory fulfil the following conditions at all geometries:

$$\frac{\partial E_{\mathrm{HF}}}{\partial \kappa} = 0 \qquad \leftarrow \text{HF stationary conditions}$$

  - we obtain the orbital responses by differentiating this equation with respect to x:

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

  - one such set of equations must be solved for each perturbation

- Calculated in this manner, the CI gradient becomes expensive

Lagrange's Method of Undetermined Multipliers

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

$$\min_{c,\kappa} E_{\mathrm{CI}}(x,c,\kappa) \quad \text{subject to the constraints} \quad \frac{\partial E_{\mathrm{HF}}(x,\kappa)}{\partial \kappa} = 0$$

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

$$L_{\mathrm{CI}}(x,c,\kappa,\overline{\kappa}) = E_{\mathrm{CI}}(x,c,\kappa) + \overline{\kappa}\left(\frac{\partial E_{\mathrm{HF}}(x,\kappa)}{\partial \kappa} - 0\right)$$

  - adjust the Lagrange multipliers $\overline{\kappa}$ such that the Lagrangian becomes stationary:

$$\frac{\partial L_{\mathrm{CI}}}{\partial c} = 0 \implies \frac{\partial E_{\mathrm{CI}}}{\partial c} = 0 \qquad \leftarrow \text{CI conditions}$$

$$\frac{\partial L_{\mathrm{CI}}}{\partial \kappa} = 0 \implies \frac{\partial E_{\mathrm{CI}}}{\partial \kappa} + \overline{\kappa}\,\frac{\partial^2 E_{\mathrm{HF}}}{\partial \kappa^2} = 0 \qquad \leftarrow \text{linear set of equations for } \overline{\kappa}$$

$$\frac{\partial L_{\mathrm{CI}}}{\partial \overline{\kappa}} = 0 \implies \frac{\partial E_{\mathrm{HF}}}{\partial \kappa} = 0 \qquad \leftarrow \text{HF conditions}$$

  - note the duality between κ and $\overline{\kappa}$
- Note that $E_{\mathrm{CI}} = L_{\mathrm{CI}}$ when the Lagrangian is stationary
  - we now have a stationary CI energy expression L_{CI}

CI Molecular Gradients the Easy Way

- The CI Lagrangian is given by

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

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

$$\frac{\mathrm{d}E_{\mathrm{CI}}}{\mathrm{d}x} = \frac{\mathrm{d}L_{\mathrm{CI}}}{\mathrm{d}x} = \frac{\partial L_{\mathrm{CI}}}{\partial x} = \frac{\partial E_{\mathrm{CI}}}{\partial x} + \bar{\kappa}\frac{\partial^2 E_{\mathrm{HF}}}{\partial \kappa \partial x}$$

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

- This result should be contrasted with the original expression

$$\frac{\mathrm{d}E_{\mathrm{CI}}}{\mathrm{d}x} = \frac{\partial E_{\mathrm{CI}}}{\partial x} + \frac{\partial E_{\mathrm{CI}}}{\partial \kappa}\,\frac{\partial \kappa}{\partial x}$$

$$\text{first-order response equations} \rightarrow \quad \frac{\partial^2 E_{\mathrm{HF}}}{\partial \kappa^2}\,\frac{\partial \kappa}{\partial x} = -\frac{\partial^2 E_{\mathrm{HF}}}{\partial \kappa \partial x}$$

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

Lagrange's Method Summarized

- (1) Establish the energy function $E(x,\lambda)$ and identify conditions on the variables

$$e(x,\lambda)=0$$

- (2) Set up the Lagrangian energy function:

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

- (3) Satisfy the stationary conditions for the variables and their multipliers:

$$\begin{aligned}\frac{\partial L}{\partial \bar{\lambda}} &= e(x,\lambda)=0 && \leftarrow \text{condition for } \bar{\lambda} \text{ determines } \lambda\\ \frac{\partial L}{\partial \lambda} &= \frac{\partial E}{\partial \lambda}+\bar{\lambda}\,\frac{\partial e}{\partial \lambda}=0 && \leftarrow \text{condition for } \lambda \text{ determines } \bar{\lambda}\end{aligned}$$

  - note the duality between λ and $\bar{\lambda}$!
- (4) Calculate derivatives from the stationary Lagrangian
- The Lagrangian approach is generally applicable:
  - it gives the Hylleraas functional when applied to a perturbation expression
  - it may be generalized to time-dependent properties

$2n + 1$ and $2n + 2$ Rules

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

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

- The Lagrangian technique extends this rule to nonvariational wave functions
- 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:

$\mathcal{E}^{(n)}$	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

Section 5

Examples of derivatives

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Hartree–Fock Energy

- The MOs are expanded in atom-fixed AOs

$$\phi_p(\mathbf{r};\mathbf{x}) = \sum\nolimits_\mu C_{\mu p}\chi_\mu(\mathbf{r};\mathbf{x})$$

- The HF energy may be written in the general form

$$E_{\mathrm{HF}} = \sum\nolimits_{pq} D_{pq}h_{pq} + \tfrac{1}{2}\sum\nolimits_{pqrs} d_{pqrs}g_{pqrs} + \sum\nolimits_{K>L}\frac{Z_K Z_L}{R_{KL}}$$

  where the one- and two-electron integrals are given by

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

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

  - note: all integrals depend explicitly on the geometry

- In closed-shell restricted HF (RHF) theory, the energy is given by

$$E_{\mathrm{RHF}} = 2\sum\nolimits_i h_{ii} + \sum\nolimits_{ij}\left(2g_{iijj} - g_{ijji}\right) + \sum\nolimits_{K>L}\frac{Z_K Z_L}{R_{KL}}$$

  - summations over doubly occupied orbitals

Hartree–Fock Equations

- The HF energy is minimized subject to orthonormality constraints

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

- We therefore introduce the HF Lagrangian:

$$\begin{aligned} L_{\mathrm{HF}} &= E_{\mathrm{HF}} - \sum\nolimits_{ij} \varepsilon_{ij} \left(S_{ij} - \delta_{ij} \right) \\ &= \sum\nolimits_{ij} D_{ij} h_{ij} + \tfrac{1}{2} \sum\nolimits_{ijkl} d_{ijkl} g_{ijkl} - \sum\nolimits_{ij} \varepsilon_{ij} \left(S_{ij} - \delta_{ij} \right) + \sum\nolimits_{K>L} \frac{Z_K Z_L}{R_{KL}} \end{aligned}$$

- The stationary conditions on the Lagrangian become:

$$\begin{aligned} \frac{\partial L_{\mathrm{HF}}}{\partial \varepsilon_{ij}} &= S_{ij} - \delta_{ij} = 0 \\ \frac{\partial L_{\mathrm{HF}}}{\partial C_{\mu i}} &= \frac{\partial E_{\mathrm{HF}}}{\partial C_{\mu i}} - \sum\nolimits_{kl} \varepsilon_{kl} \frac{\partial S_{kl}}{\partial C_{\mu i}} = 0 \end{aligned}$$

- Note:
  - the multiplier conditions are the orthonormality constraints
  - the MO stationary conditions are the Roothaan–Hall equations

$$\frac{\partial E_{\mathrm{HF}}}{\partial C_{\mu i}} = \sum\nolimits_{kl} \varepsilon_{kl} \frac{\partial S_{kl}}{\partial C_{\mu i}} \quad \Longrightarrow \quad \mathbf{F}^{\mathrm{AO}} \mathbf{C} = \mathbf{S}^{\mathrm{AO}} \mathbf{C} \boldsymbol{\varepsilon}$$

Hartree–Fock Molecular Gradient

- From the $2n + 1$ rule, we obtain the RHF molecular gradient:

$$\frac{\mathrm{d}E_{\mathrm{HF}}}{\mathrm{d}\mathbf{x}} = \frac{\mathrm{d}L_{\mathrm{HF}}}{\mathrm{d}\mathbf{x}} = \frac{\partial L_{\mathrm{HF}}}{\partial \mathbf{x}} = \frac{\partial E_{\mathrm{HF}}}{\partial \mathbf{x}} - \sum_{ij} \varepsilon_{ij} \frac{\partial S_{ij}}{\partial \mathbf{x}}$$

- In terms of MO integrals and density-matrix elements, we obtain the expression

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

- We then express the gradient in terms of AO integrals:

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

  - density matrices transformed to AO basis
  - derivative integrals added directly to gradient elements

- Important points:

  - the gradient does not involve MO differentiation because of the $2n + 1$ rule
  - the time-consuming step is integral differentiation

FCI Energy

- Consider a normalized CI wave function:

$$|\mathbf{c}\rangle = \sum\nolimits_{n=0}^{\infty} c_n |n\rangle, \quad \mathbf{c}^{\mathrm{T}}\mathbf{c} = 1, \quad \langle m|n\rangle = \delta_{mn}$$

- The basis functions $|n\rangle$ are the normalized CI eigenstates of the unperturbed problem:

$$\langle m|H|n\rangle = \delta_{mn} E_n, \quad E_0 \leq E_1 \leq E_2 \cdots$$

- We assume that the ground-state energy function depends on two external parameters:

$$\langle \mathbf{c}|H(x,y)|\mathbf{c}\rangle = \sum\nolimits_{mn} c_m \langle m|H(x,y)|n\rangle c_n, \quad \sum_n c_n^2 = 1$$

- We construct a variational CI Lagrangian:

$$L(x,y,\mathbf{c},\mu) = \sum_{mn} c_m \langle m|H(x,y)|n\rangle c_n - \mu\Big(\sum_n c_n^2 - 1\Big)$$

- The stationary conditions are given by

$$\begin{aligned} \frac{\partial L(x,y,\mathbf{c},\mu)}{\partial c_n} = 0 \quad &\Longrightarrow \quad 2\langle n|H(x,y)|\mathbf{c}\rangle - 2\mu c_n = 0 \quad &&\Longrightarrow \quad \mathbf{H}(x,y)\mathbf{c} = E_0(x,y)\mathbf{c} \\ \frac{\partial L(x,y,\mathbf{c},\mu)}{\partial \mu} = 0 \quad &\Longrightarrow \quad \sum_n c_n^2 - 1 = 0 \quad &&\Longrightarrow \quad \mathbf{c}^{\mathrm{T}}\mathbf{c} = 1 \end{aligned}$$

  - the first condition is the CI eigenvalue problem with ground-state energy $E_0(x,y) = \mu$
  - the second condition is the CI normalization condition

FCI Molecular Gradient and Hessian

- Using the CI Lagrangian, we calculate CI energy derivative in the usual way:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\partial L}{\partial x}, \quad \frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x \partial y} + \sum_n \frac{\partial^2 L}{\partial x \partial c_n}\frac{\partial c_n}{\partial x}, \quad \sum_n \frac{\partial^2 L}{\partial c_m \partial c_n}\frac{\partial c_n}{\partial x} = -\frac{\partial^2 L}{\partial x \partial c_m}$$

- By inverting the electronic Hessian, we obtain the more compact expression:

$$\frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x \partial y} - \sum_{mn} \frac{\partial^2 L}{\partial x \partial c_m}\left[\frac{\partial^2 L}{\partial c_m \partial c_n}\right]^{-1}\frac{\partial^2 L}{\partial c_n \partial y}$$

- We next evaluate the various partial derivatives at $x = y = 0$ where $|\mathbf{c}\rangle = |0\rangle$:

$$\frac{\partial L}{\partial x} = \left\langle 0 \left| \frac{\partial H}{\partial x} \right| 0 \right\rangle, \quad \frac{\partial^2 L}{\partial x \partial y} = \left\langle 0 \left| \frac{\partial^2 H}{\partial x \partial y} \right| 0 \right\rangle, \quad \frac{\partial^2 L}{\partial x \partial c_n} = 2\left\langle n \left| \frac{\partial H}{\partial x} \right| 0 \right\rangle$$

$$\frac{\partial^2 L}{\partial c_m \partial c_n} = 2\left\langle m \left| H - E_0 \right| n \right\rangle = 2(E_n - E_0)\delta_{mn}$$

- Inserted above, we recover Rayleigh–Schrödinger perturbation theory to second order:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \left\langle 0 \left| \frac{\partial H}{\partial x} \right| 0 \right\rangle, \quad \frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \left\langle 0 \left| \frac{\partial^2 H}{\partial x \partial y} \right| 0 \right\rangle - 2\sum_n \frac{\left\langle 0 \left| \frac{\partial H}{\partial x} \right| n \right\rangle \left\langle n \left| \frac{\partial H}{\partial y} \right| 0 \right\rangle}{E_n - E_0}$$

Section 6

Derivatives in second quantization

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Second-Quantization Hamiltonian

- In second quantization, the Hamiltonian operator is given by:

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

- Its construction assumes an orthonormal basis of MOs 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 often depend explicitly on the perturbation
  - such basis sets are said to be perturbation-dependent:

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

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

MOs and Hamiltonian at Distorted geometries

1. Orthonormal MOs at the reference geometry:

$$\boldsymbol{\phi}(x_0) = \mathbf{C}^{(0)}\boldsymbol{\chi}(x_0)$$
$$\mathbf{S}(x_0) = \left\langle \boldsymbol{\phi}(x_0) \,\middle|\, \boldsymbol{\phi}^\dagger(x_0)\right\rangle = \mathbf{I}$$

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

$$\boldsymbol{\phi}(x) = \mathbf{C}^{(0)}\boldsymbol{\chi}(x)$$
$$\mathbf{S}(x) = \left\langle \boldsymbol{\phi}(x) \,\middle|\, \boldsymbol{\phi}^\dagger(x)\right\rangle \neq \mathbf{I}$$

note: this basis is nonorthogonal and not useful for setting up the Hamiltonian.

3. Orthonormalize the basis set (e.g., by Löwdin orthonormalization):

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

4. From these orthonormalized MOs (OMOs) ψ_p, construct Hamiltonian in the usual manner

$$H = \sum\nolimits_{pq} \tilde{h}_{pq} a_p^\dagger a_q + \sum\nolimits_{pqrs} \tilde{g}_{pqrs} a_p^\dagger a_r^\dagger a_s a_q + h_{\text{nuc}}$$
$$\tilde{h}_{pq} = \langle \psi_p^*(\mathbf{r}) | h(\mathbf{r}) | \psi_q(\mathbf{r})\rangle$$
$$\tilde{g}_{pqrs} = \langle \psi_p^*(\mathbf{r}_1)\psi_r^*(\mathbf{r}_2) | r_{12}^{-1} | \psi_q(\mathbf{r}_1)\psi_s(\mathbf{r}_2)\rangle$$

Hamiltonian at all Geometries

- The Hamiltonian is now well defined at all geometries:

$$H(x) = \sum_{pq} \tilde{h}_{pq}(x) E_{pq}(x) + \tfrac{1}{2} \sum_{pqrs} \tilde{g}_{pqrs}(x) e_{pqrs}(x) + h_{\text{nuc}}(x)$$

- The OMO integrals are given by

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

  in terms of the usual MO integrals

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

  and similarly for the two-electron integrals.

- What about the geometry dependence of the excitation operators?
  - this may be neglected when calculating derivatives since, for all geometries,

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

HF Molecular Gradients in Second Quantization

- The molecular gradient now follows from the Hellmann–Feynman theorem:

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

- We need the derivatives of the OMO integrals:

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

- The gradient may therefore be written in the form

$$E^{(1)} = \sum_{pq} D_{pq}h^{(1)}_{pq} + \tfrac{1}{2}\sum_{pqrs} d_{pqrs}g^{(1)}_{pqrs} - \sum_{pq} F_{pq}S^{(1)}_{pq} + h^{(1)}_{\text{nuc}},$$

  where the generalized Fock matrix is given by:

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

- For RHF theory, this result is equivalent to that derived in first quantization

Section 7

Geometrical Properties

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Geometrical Derivatives

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

$$\mathcal{E}(x) = \mathcal{E}_0 + \mathcal{E}^{(1)}\Delta x + \tfrac{1}{2}\mathcal{E}^{(2)}\Delta x^2 + \cdots \leftarrow \text{expansion around the reference geometry}$$

- The derivatives of this surface are therefore important:

$$\mathcal{E}^{(1)} = \frac{\mathrm{d}\mathcal{E}}{\mathrm{d}x} \qquad \leftarrow \text{molecular gradient}$$

$$\mathcal{E}^{(2)} = \frac{\mathrm{d}^2\mathcal{E}}{\mathrm{d}x^2} \qquad \leftarrow \text{molecular Hessian}$$

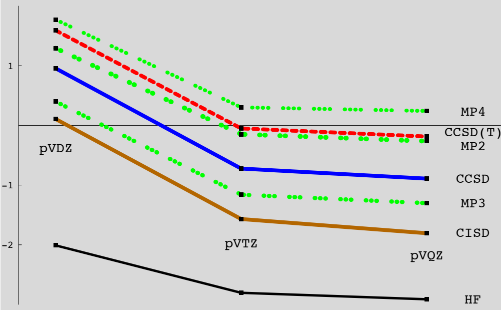
- The geometrical derivatives are
  - used for locating and characterizing critical points
  - related to spectroscopic constants, vibrational frequencies, and intensities
- Usually, only a few terms are needed in the expansions
  - in some cases low-order expansions are inadequate or useless

Uses of Geometrical Derivatives

- To explore molecular potential-energy surfaces ($3N - 6$ dimensions)
  - localization and characterization of stationary points
  - localization of avoided crossings and conical intersections
  - calculation of reaction paths and reaction-path Hamiltonians
  - application to direct dynamics
- To calculate spectroscopic constants
  - molecular structure
  - 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

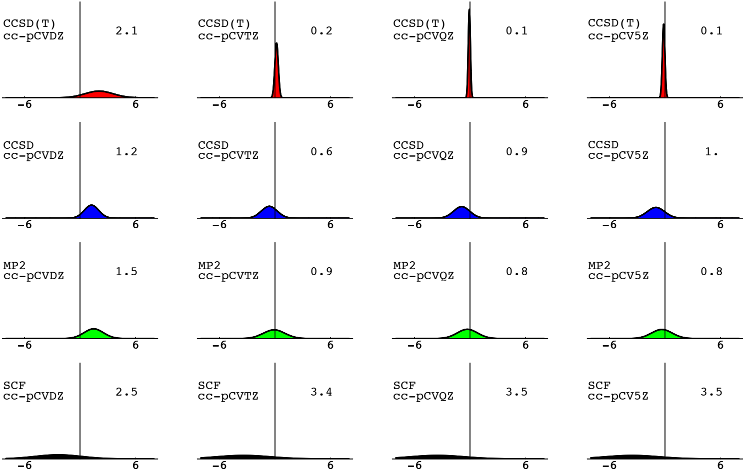
- Mean and mean abs. errors for 28 distances at the all-el. cc-pVXZ level (pm):



$\lvert\overline{\Delta}\rvert$	DZ	TZ	QZ
CCSD	1.2	0.6	0.8
CCSD(T)	1.7	0.2	0.2

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

Bond Distances R_e of BH, CO, N_2, HF, and F_2 (pm)

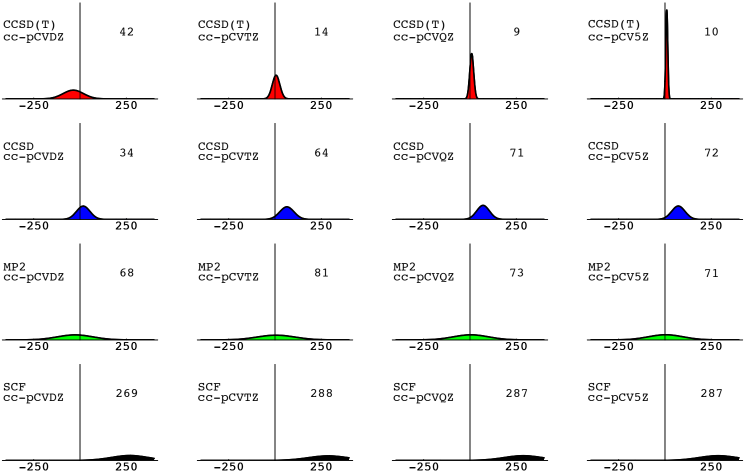


Contributions to Equilibrium Bond Distances (pm)

	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

- We have agreement with experiment to within 0.01 pm except for F_2
- Hartree–Fock theory underestimates bond distances by up to 8.6 pm (for F_2)
- All correlation contributions are positive
  - approximately linear convergence, slowest for F_2
  - triples contribute up to 2.0, quadruples up to 0.4, and quintuples 0.03 pm
  - sextuples are needed for convergence to within 0.01 pm
- Relativistic corrections are small except for F_2 (0.05 pm)
  - of the same magnitude and direction as the quintuples

Harmonic Constants ω_e of BH, CO, N_2, HF, and F_2 (cm^{-1})



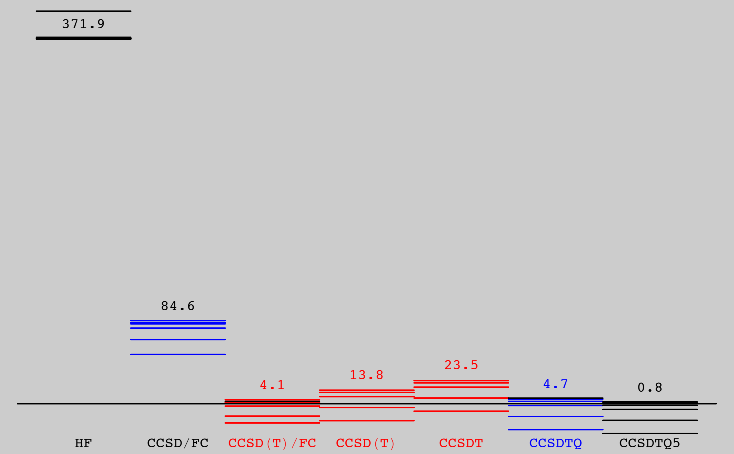
Contributions to Harmonic Frequencies ω_e (cm^{-1})

	RHF	SD	T	Q	5	rel.	adia.	theory	exp.	err.
HF	4473.8	−277.4	−50.2	−4.1	−0.1	−3.5	0.4	4138.9	4138.3	0.1
N_2	2730.3	−275.8	−72.4	−18.8	−3.9	−1.4	0.0	2358.0	2358.6	−0.6
F_2	1266.9	−236.1	−95.3	−15.3	−0.8	−0.5	0.0	918.9	916.6	2.3
CO	2426.7	−177.4	−71.7	−7.2	0.0	−1.3	0.0	2169.1	2169.8	0.7

- We have agreement with experiment to within $1\,\text{cm}^{-1}$ except for F_2
- Hartree–Fock theory overestimates harmonic frequencies by up to 38% (in F_2).
- All correlation contributions are large and negative
    - triples contribute up to $95\,\text{cm}^{-1}$, quadruples $20\,\text{cm}^{-1}$, and quintuples $4\,\text{cm}^{-1}$
    - sextuples are sometimes needed for convergence to within $1\,\text{cm}^{-1}$
- The relativistic corrections are of the order of $1\,\text{cm}^{-1}$
    - of the same magnitude and direction as the quadruples or quintuples

Higher-Order Connected Contributions to ω_e in N_2 (cm^{-1})

- 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}

Anharmonic Constants $\omega_e x_e$ of BH, CO, N_2, HF, and F_2 (cm^{-1})