Quantum Chemical Calculation of Molecular Properties

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Outline

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Introduction

- Purpose: Establish a connection between quantum calculations and experimental results by computing measurable quantities.
- Challenges:
  - The energy and wavefunctions alone are insufficient to characterize systems.
- Classification of Properties:
  - **Type a:** Energy differences (e.g., reaction energies, dissociation energies).
  - **Type b:** Properties specific to electronic states (e.g., Dipole moment).
  - **Type c:** Transition properties (e.g., excitation energies).

Definitions

- **Molecular Properties:** Quantities characterizing atomic/molecular systems (e.g., dipole moments, polarizabilities).
  - **Dipole moment** (μ): The dipole moment measures how a molecule's charge distribution changes in the presence of an external electric field.
  - **Polarizability** (α) : Polarizability quantifies how a molecule's electronic cloud distorts (polarizes) under an external electric field.
  - **NMR Chemical Shift** : This is the difference in the NMR (nuclear magnetic resonance) signal between a nucleus in a molecule and a reference compound.

Definitions

Table: List of Molecular Properties Computed as Derivatives of Energy

Derivative	**Observable**
$\frac{dE}{d\varepsilon_i}$	Dipole moment; electric field gradients, etc.
$\frac{d^2E}{d\varepsilon_\alpha d\varepsilon_\beta}$	Polarizability
$\frac{d^3E}{d\varepsilon_\alpha d\varepsilon_\beta d\varepsilon_\gamma}$	(First) hyperpolarizability
$\frac{d^2E}{dB_\alpha dB_\beta}$	Magnetizability
$\frac{d^2E}{dm_{K_j} dB_i}$	Nuclear magnetic shielding tensor; relative NMR shifts
$\frac{d^2E}{dI_{K_i} dI_{L_j}}$	Indirect spin-spin coupling constant

Molecular Properties as Analytical Derivatives

- Molecular properties describe the **response** of a system to an external perturbation.
- Example: A molecule in an external electric field ϵ.
- Energy can be expanded as:

$$E(\epsilon) = E(0) + \left.\frac{dE}{d\epsilon}\right|_{\epsilon=0} \epsilon + \frac{1}{2} \left.\frac{d^2E}{d\epsilon^2}\right|_{\epsilon=0} \epsilon^2 + \cdots$$

where

$$\mu = -\left.\frac{dE}{d\epsilon}\right|_{\epsilon=0}, \quad \alpha = -\left.\frac{d^2E}{d\epsilon^2}\right|_{\epsilon=0}, \quad \beta = -\left.\frac{d^3E}{d\epsilon^3}\right|_{\epsilon=0}.$$

Computational Expressions

- **Hellmann-Feynman Theorem**: It provides a way to connect a derivative to expectation value. Spacifically states that

  $$\frac{dE}{dx} = \langle \Psi | \frac{\partial H}{\partial x} | \Psi \rangle$$

  where
  - H is the Hamiltonian operator
  - Ψ is the exact wavefunction of the system.
- Derivative expressions are often preferred over expectation value methods due to better accuracy with approximate wavefunctions.

Numerical vs. Analytical Differentiation

- **Numerical Differentiation:**
  - Approximates derivatives using finite-difference formulas:

$$\frac{dE}{dx} \approx \frac{E(\Delta x) - E(-\Delta x)}{2\Delta x}.$$

  - Simple but suffers from:
    - Limited accuracy (higher-order errors).
    - High computational cost for multiple derivatives.
- **Analytical Differentiation:**
  - Derivatives are computed directly from the energy expression.

$$\frac{dE}{dx} = \frac{\partial E}{\partial x} + \frac{\partial E}{\partial c}\frac{\partial c}{\partial x}.$$

  - Key benefits:
    - High accuracy (avoids finite-difference errors).
    - Scales efficiently with system size.
  - Challenge: Complex implementation.

Analytical Derivatives

- Energy depends on external perturbations (x) and wavefunction parameters (c):

$$E = E(x, c(x)).$$

- Wavefunction parameters (c) satisfy equations of the form:

$$g(x, c(x)) = 0.$$

- Total derivative of energy:

$$\frac{dE}{dx} = \frac{\partial E}{\partial x} + \frac{\partial E}{\partial c}\frac{\partial c}{\partial x}.$$

- Challenge: Derivatives of c with respect to x, $(\frac{\partial c}{\partial x})$ are not directly available.

Simplification

- **For variational parameters** (e.g., molecular orbital coefficients in Hartree-Fock):

  $$\frac{\partial E}{\partial c} = 0 \quad \text{(from variational principle)}.$$

  Total energy derivative simplifies to:

  $$\frac{dE}{dx} = \frac{\partial E}{\partial x}.$$

- **For non-variational parameters** (e.g., coupled-cluster amplitudes):

  $$\frac{\partial E}{\partial c} \neq 0.$$

Simplification

- Use an augmented energy functional with Lagrange multipliers (λ):

$$\tilde{E}(x, c(x), \lambda(x)) = E(x, c(x)) + \lambda(x) g(x, c(x)).$$

- Stationarity conditions:

$$\frac{\partial \tilde{E}}{\partial c} = 0, \quad \frac{\partial \tilde{E}}{\partial \lambda} = 0.$$

- Total derivative simplifies to:

$$\begin{aligned} \frac{d\tilde{E}}{dx} &= \left(\frac{\partial \tilde{E}}{\partial x} \right) \\ &= \left(\frac{\partial E}{\partial x} \right) + \lambda \left(\frac{\partial g}{\partial x} \right) \end{aligned}$$

Second Derivatives

- **Second derivative for variational case**:

$$\frac{d^2E}{dxdy} = \frac{\partial^2 E}{\partial x \partial y} + \frac{\partial^2 E}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 E}{\partial y \partial c}\frac{\partial c}{\partial x} + \frac{\partial^2 E}{\partial c^2}\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}.$$

- **Second derivative for Non-variational case**:

$$\frac{d^2\tilde{E}}{dxdy} = \frac{\partial^2 \tilde{E}}{\partial x \partial y} + \frac{\partial^2 \tilde{E}}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 \tilde{E}}{\partial y \partial c}\frac{\partial c}{\partial x} + \frac{\partial^2 \tilde{E}}{\partial c^2}\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}.$$

Contributions involving higher derivatives of c and λ vanish due to the stationarity conditions and the contribution due to $\frac{\partial \lambda}{\partial x}$ and $\frac{\partial \lambda}{\partial y}$ vanish, because

$$\frac{dg(x, c(x))}{dx} = 0.$$

Higher-Order Derivatives

- Higher derivatives can be obtained by differentiating gradient expressions.
- Simplification rules:
    - $2n+1$ Rule: n-th derivative of c suffices to compute $(2n+1)$-th derivative of energy.
    - $2n+2$ Rule: n-th derivative of λ suffices to compute $(2n+2)$-th derivative of energy.
- Example for third derivative:

$$\frac{d^3 E}{dxdydz} = \frac{\partial^3 \tilde{E}}{\partial x \partial y \partial z} + \cdots$$

Example: Hartree-Fock SCF Gradients

- Energy expression for closed-shell HF-SCF:

$$E = \sum_{\mu\nu} P_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} P_{\mu\nu} P_{\sigma\rho} \left(\langle \mu\nu | \sigma\rho \rangle - \frac{1}{2} \langle \mu\nu | \rho\sigma \rangle \right) ,$$

with

$$P_{\mu\nu} = 2 \sum_{i} c^{*}_{\mu i} c_{\nu i}$$

As the orthonormality of the MOs needs to be considered as additional constraint, energy functional will be

$$\tilde{E} = \sum_{\mu\nu} P_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} P_{\mu\nu} P_{\sigma\rho} \left(\langle \mu\sigma \mid \nu\rho \rangle - \frac{1}{2} \langle \mu\sigma \mid \rho\nu \rangle \right)$$

$$- 2 \sum_{ij} \varepsilon_{ij} \left(\sum_{\mu\nu} c^{*}_{\mu i} S_{\mu\nu} c_{\nu j} - \delta_{ij} \right)$$

First Derivatives: Hartree-Fock SCF Gradients

- Based on the discussion in the previous section, the following gradient expression:

$$\frac{dE}{dx} = \sum_{\mu\nu} P_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial x} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} P_{\mu\nu} P_{\sigma\rho} \frac{\partial}{\partial x} \left(\langle \mu\nu | \sigma\rho \rangle - \frac{1}{2} \langle \mu\nu | \rho\sigma \rangle \right) - \sum_{\mu\nu} W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial x}.$$

- Energy-weighted density matrix:

$$W_{\mu\nu} = 2 \sum_i c^*_{\mu i} \varepsilon_i c_{\nu i},$$

where ε_i are orbital energies.

Second Derivatives: Hartree-Fock SCF

- Second derivative expression:

$$\frac{d^2E}{dxdy} = \sum_{\mu\nu} P_{\mu\nu}\frac{\partial^2 h_{\mu\nu}}{\partial x\partial y} + \frac{1}{2}\sum_{\mu\nu\rho\sigma} P_{\mu\nu}P_{\sigma\rho}\frac{\partial^2}{\partial x\partial y}\Bigg(\langle\mu\nu|\sigma\rho\rangle - \frac{1}{2}\langle\mu\nu|\rho\sigma\rangle\Bigg)$$

$$-\sum_{\mu\nu} W_{\mu\nu}\frac{\partial^2 S_{\mu\nu}}{\partial x\partial y} + \sum_{\mu\nu}\frac{\partial P_{\mu\nu}}{\partial y}\Bigg(\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} P_{\sigma\rho}\frac{\partial}{\partial x}\bigg(\langle\mu\nu|\sigma\rho\rangle - \frac{1}{2}\langle\mu\nu$$

$$-\sum_{\mu\nu}\frac{\partial W_{\mu\nu}}{\partial y}\frac{\partial S_{\mu\nu}}{\partial x}.$$

- Derivatives of $P_{\mu\nu}$ and $W_{\mu\nu}$:

$$\frac{\partial P_{\mu\nu}}{\partial x} = 2\sum_{i}\left(\frac{\partial c^*_{\mu i}}{\partial x}c_{\nu i} + c^*_{\mu i}\frac{\partial c_{\nu i}}{\partial x}\right),$$

$$\frac{\partial W_{\mu\nu}}{\partial x} = 2\sum_{i}\left(\frac{\partial c^*_{\mu i}}{\partial x}\varepsilon_i c_{\nu i} + c^*_{\mu i}\varepsilon_i\frac{\partial c_{\nu i}}{\partial x}\right) + \sum_{ij} c^*_{\mu i}\frac{\partial \varepsilon_{ij}}{\partial x}c_{\nu j}.$$

Availability of Analytical Derivatives

- First introduced by Pulay in 1969 for Hartree-Fock gradients.
- Milestones in development:
  - 1979: Pople et al. implemented MP2 gradients and HF second derivatives.
  - 1985: Handy and Bartlett developed MP2 second derivatives.
  - 1987: Schaefer et al. implemented CCSD gradients.
- Broad adoption in quantum chemistry:
  - Most standard quantum chemical methods (e.g., HF, DFT, MP2, CCSD) support analytical gradients.
  - Some advanced methods (e.g., CCSDTQ) still lack implementations due to complexity.
- Advances in integral derivative packages have facilitated widespread use.

Introduction to Magnetic Properties

- Magnetic properties describe molecular interactions with magnetic fields, crucial for understanding:
  - NMR chemical shifts.
  - Indirect spin-spin coupling constants.
- Quantum chemical calculations are essential for:
  - Assigning experimental NMR spectra.
  - Deriving molecular structure and bonding information.
- Analytical derivative theory enables efficient computation of:
  - Magnetizabilities.
  - Nuclear magnetic shielding tensors (NMR shifts).
  - Spin-spin coupling constants.

Qualitative Understanding of Magnetic Shielding

- External magnetic field (B) interacts with the nuclear magnetic moment ($\mu_K = \gamma_K I_K$):

  $$\Delta E = -\mu_K \cdot B.$$

- **Induced Magnetic Field:**
  - B generates electronic currents in the molecule.
  - These currents create an induced magnetic field (B_{ind}).
- Relationship between induced and external fields:

  $$B_{\text{ind}} = -\sigma_K B,$$

  where σ_K is the chemical shielding tensor.
- Total magnetic field at the nucleus:

  $$B_{\text{local}} = B + B_{\text{ind}}.$$

- Energy correction with shielding effect:

  $$\Delta E = -\mu_K \cdot B_{\text{local}} = -\mu_K \cdot (1 - \sigma_K)B.$$

Taylor Expansion of Energy

- Total molecular energy expanded as:

$$E(B, m_K) = E(0) + \sum_j \sum_i \left. \frac{\partial^2 E}{\partial B_j \, \partial m_{Ki}} \right|_{B, m_K = 0} B_j m_{Ki} + \cdots$$

- Quadratic term provides shielding tensor:

$$\sigma_{K,ij} = \frac{\partial^2 E}{\partial B_j \, \partial m_{Ki}}.$$

- Shielding tensors quantify the interaction between:
  - External magnetic field (B).
  - Nuclear magnetic moments (m_K).

- **Unperturbed Hamiltonian** The standard molecular Hamiltonian without a magnetic field is:

$$H = \frac{\vec{p}^2}{2m} + V(\vec{r}),$$

  where:
  - $\vec{p}$ is the momentum operator.
  - $V(\vec{r})$ is the potential energy function.
- **Including the Magnetic Field** In the presence of a magnetic field $\vec{B}$, the momentum operator $\vec{p}$ is replaced by the mechanical momentum $\vec{\pi}$:

$$\pi = \vec{p} + \frac{e}{c}\vec{A}(\vec{r}),$$

  where:
  - $\vec{A}$ is the vector potential.

Modified Hamiltonian

Substituting π, and Expanding terms, we get:

$$H = \frac{\mathbf{p}^2}{2m} + \frac{e}{mc}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2mc^2}\mathbf{A}^2 + V(\mathbf{r})$$

where $\mathbf{p}$ is given by $-i\hbar\boldsymbol{\nabla}$ and $\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{r}$. As the vector potential satisfies the (Coulomb gauge) condition

$$\boldsymbol{\nabla}\cdot\mathbf{A} = 0$$

Hamiltonian takes the form

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{ie\hbar}{2mc}\mathbf{B}\cdot(\mathbf{r}\times\boldsymbol{\nabla}) + \frac{e^2}{8mc^2}[(\mathbf{B}\cdot\mathbf{B})(\mathbf{r}\cdot\mathbf{r}) - (\mathbf{B}\cdot\mathbf{r})(\mathbf{B}\cdot\mathbf{r})] + V(\mathbf{r})$$

Derivatives of the Hamiltonian

First derivative with respect to the magnetic field:

$$\frac{\partial H}{\partial B_i} = -\frac{ie\hbar}{2mc}(\vec{r} \times \nabla)_i .$$

Second derivative with respect to the magnetic field:

$$\frac{\partial^2 H}{\partial B_i \partial B_j} = \frac{e^2}{4mc^2}\left[(r.r)\delta_{ij} - r_i r_j\right].$$

Considering in addition the vector potential due to the magnetic moments

$$\mathbf{A}' = \frac{\mathbf{m}_K \times (\mathbf{r} - \mathbf{R}_K)}{|\mathbf{r} - \mathbf{R}_K|^3}$$

Derivatives of the Hamiltonian

the corresponding derivative of H with respect to m_K is

$$\frac{\partial h}{\partial m_{Kj}} = -\frac{ie\hbar}{mc} \frac{[(\mathbf{r} - \mathbf{R}_K) \times \nabla]_j}{|\mathbf{r} - \mathbf{R}_K|^3}$$

Mixed derivative with respect to $\vec{B}$ and nuclear magnetic moment $\vec{m}_K$:

$$\frac{\partial^2 H}{\partial B_i \partial m_{Kj}} = \frac{e^2}{2mc^2} \frac{r \cdot (\vec{r} - \vec{R}_K)\delta_{ij} - r_j(\vec{r} - \vec{R}_K)_i}{|\vec{r} - \vec{R}_K|^3}.$$

- Matrix elements of $\frac{\partial H}{\partial B_i}$ are imaginary:

$$\langle \mu | \frac{\partial H}{\partial B_i} | \nu \rangle = -\langle \nu | \frac{\partial H}{\partial B_i} | \mu \rangle.$$

- Matrices for magnetic field interactions are antisymmetric, contrasting with the symmetric matrices for electric field interactions.

Key Concepts in Gauge-Origin Dependence

- The magnetic field $\vec{B}$ is derived from the vector potential $\vec{A}$:

  $$\vec{B} = \nabla \times \vec{A}.$$

- The vector potential $\vec{A}$ is not unique; it can be shifted by a gauge transformation:

  $$\vec{A}' = \vec{A} + \nabla\chi,$$

  where χ is an arbitrary scalar function.
- For a static homogenous field, for example, the vector potential can be chosen in the general form

  $$\mathbf{A} = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{R}_O)$$

  with $\mathbf{R}_O$ as an arbitrary parameter, the so-called gauge origin.

Physical Requirements

- **Gauge-Invariance**: Physically observable quantities like shielding constants or NMR shifts must be independent of gauge origin.
- **Methods to Address Gauge-Origin Dependence**
  - **Gauge-Including Atomic Orbitals (GIAOs)**:
    - Incorporate $\vec{A}$ directly into atomic orbital phases.
  - **Distributed Gauge Origins**:
    - Assign separate gauge origins to different molecular fragments or atoms.
  - Explicit Gauge-Invariant Formulations
    - Formulations of the Hamiltonian and response functions that are explicitly gauge-invariant can also be used.

Introduction to Local Gauge Origin Methods

- Local gauge origin methods assign a specific gauge origin $\vec{R}_A$ for each nucleus A.
- **Local Gauge Origins**:

  $$\vec{A}_A(\vec{r}) = \frac{1}{2}\vec{B} \times (\vec{r} - \vec{R}_A),$$

  where:
  - $\vec{R}_A$: Local gauge origin for nucleus A.
  - $\vec{A}_A$: Local vector potential for nucleus A.
- Magnetic properties are calculated as sums of local contributions:

  $$\sigma = \sum_A \sigma_A,$$

  where σ_A is the contribution from nucleus A with respect to its local gauge origin.

Introduction

- NMR chemical shifts are essential for interpreting NMR spectroscopy data.
- Accurate calculations of shielding constants σ_K are crucial for predicting chemical shifts:

  $$\delta_K = \sigma_{\text{ref}} - \sigma_K,$$

  where:
    - σ_{ref}: Shielding constant for the reference nucleus.
    - σ_K: Shielding constant for the nucleus of interest.
- Various computational methods are available, differing in accuracy, cost, and applicability.

Available Methods and Software for NMR Calculations

- Various methods exist for calculating NMR shielding constants and chemical shifts.
- Trade-offs between accuracy and computational cost determine the method of choice:
  - HF: Fast but less accurate.
  - DFT: Versatile for many systems.
  - MP2: Intermediate in accuracy and cost.
  - CC: Most accurate but computationally expensive.
- GIAOs are critical for gauge-invariant calculations.
- Software like Gaussian, ORCA, and Dalton offer robust implementations for NMR calculations.

Introduction to Indirect Spin-Spin Coupling

- Indirect spin-spin coupling constants (J_{KL}) describe interactions between nuclear spins mediated by bonding electrons.
  The spin-spin coupling constant J_{KL} consists of four components:

$$J_{KL} = J_{KL}^{\text{FC}} + J_{KL}^{\text{SD}} + J_{KL}^{\text{PSO}} + J_{KL}^{\text{DSO}}$$

  - **Fermi Contact (FC)**: Dominates in ^{1}H couplings.
  - **Spin-Dipolar (SD)**: Magnetic dipole interaction sensitive to geometry.
  - **Paramagnetic Spin-Orbit (PSO)**: Due to spin-orbit coupling of bonding electrons.
  - **Diamagnetic Spin-Orbit (DSO)**: Interaction via electrons' orbital motion.

Introduction to Frequency-Dependent Properties

- Frequency-dependent molecular properties are essential for understanding interactions between molecules and electromagnetic fields.
- Examples include:
    - Optical rotation
    - Dispersion forces
- Response theory is the foundation for frequency-dependent properties.
- Involves solving the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = H(t)\Psi(t), \tag{1}$$

Summary

- Quantum chemical calculations are essential for understanding molecular properties.
- Analytic derivative techniques are the cornerstone for accurate property calculations
- Computational strategies now extend to magnetic and frequency-dependent properties, making them accessible for larger systems.

Challenges and Future Directions

- Challenges:
  - Scalability for large systems.
  - Accurate computation of higher-order properties.
- Future Directions:
  - Machine learning integration for faster predictions.
  - Real-time simulations for dynamic molecular interactions.
- These advancements will drive applications in material science, molecular design, and industry.

Thank You!

Questions?