Theoretical Chemistry

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Summary

- The Hartree-Fock-Roothaan method
- Pople and Dunning basis sets
- Semiempirical models
- Configuration interaction
- **Möller-Plesset perturbation theory**
- Density functional theory
- Time-dependent DFT

Many-Body Perturbation Theory

Perturbed Hamiltonian

$$\hat{H} = \hat{H}^0 + \lambda \hat{V}$$

Reference (non-perturbed) Hamiltonian

Perturbation
λ = perturbation parameter; determine the strength of the perturbation ($0 \leq \lambda \leq 1$).

Expanding the eigenfunctions and the respective eigenvalues as Taylor series in λ:

$$\Psi_i = \Psi_i^{(0)} + \lambda \frac{\partial \Psi_i}{\partial \lambda}\bigg|_{\lambda=0} + \frac{1}{2!}\lambda^2 \frac{\partial^2 \Psi_i}{\partial \lambda^2}\bigg|_{\lambda=0} + \frac{1}{3!}\lambda^3 \frac{\partial^3 \Psi_i}{\partial \lambda^3}\bigg|_{\lambda=0} + \cdots$$

$$= \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} + \lambda^3 \Psi_i^{(3)} + \ldots$$

$\Psi_i^{(n)}$ = *n*-th order correction to $\Psi_i^{(0)}$

$$E_i = E_i^{(0)} + \lambda \frac{\partial E_i}{\partial \lambda}\bigg|_{\lambda=0} + \frac{1}{2!}\lambda^2 \frac{\partial^2 E_i}{\partial \lambda^2}\bigg|_{\lambda=0} + \frac{1}{3!}\lambda^3 \frac{\partial^3 E_i}{\partial \lambda^3}\bigg|_{\lambda=0} + \cdots$$

$$= E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \lambda^3 E_i^{(3)} + \ldots$$

Many-Body Perturbation Theory

Schrödinger equation for the ground-state Ψ_0

$$\left(\hat{H}^0 + \lambda\hat{V}\right)\Psi_0 = E_0\Psi_0$$

$$\left(\hat{H}^0 + \lambda\hat{V}\right)\left|\Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \ldots\right\rangle$$

$$= \left(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \ldots\right)\left|\Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \ldots\right\rangle$$

Equating terms in the same power of λ

$$H^0\left|\Psi_0^{(0)}\right\rangle = E_0^{(0)}\left|\Psi_0^{(0)}\right\rangle$$ **Order 0**

$$H^0\left|\Psi_0^{(1)}\right\rangle + \hat{V}\left|\Psi_0^{(0)}\right\rangle = E_0^{(0)}\left|\Psi_0^{(1)}\right\rangle + E_0^{(1)}\left|\Psi_0^{(0)}\right\rangle$$ **Order 1**

$$H^0\left|\Psi_0^{(2)}\right\rangle + \hat{V}\left|\Psi_0^{(1)}\right\rangle = E_0^{(0)}\left|\Psi_0^{(2)}\right\rangle + E_0^{(1)}\left|\Psi_0^{(1)}\right\rangle + E_0^{(2)}\left|\Psi_0^{(0)}\right\rangle$$ **Order 2**

Many-Body Perturbation Theory

Schrödinger equation for the ground-state Ψ_0

$$H^0\left|\Psi_0^{(0)}\right\rangle = E_0^{(0)}\left|\Psi_0^{(0)}\right\rangle$$

$$H^0\left|\Psi_0^{(1)}\right\rangle + \hat{V}\left|\Psi_0^{(0)}\right\rangle = E_0^{(0)}\left|\Psi_0^{(1)}\right\rangle + E_0^{(1)}\left|\Psi_0^{(0)}\right\rangle$$

$$H^0\left|\Psi_0^{(2)}\right\rangle + \hat{V}\left|\Psi_0^{(1)}\right\rangle = E_0^{(0)}\left|\Psi_0^{(2)}\right\rangle + E_0^{(1)}\left|\Psi_0^{(1)}\right\rangle + E_0^{(2)}\left|\Psi_0^{(0)}\right\rangle$$

Multiplying from the left by $\langle\Psi_i^{(0)}|$

Taking advantage of the relations:

$$\left\langle\Psi_0^{(0)}\middle|\Psi_0^{(n)}\right\rangle = \delta_{0n} \qquad \left\langle\Psi_0^{(0)}\middle|H^0\middle|\Psi_0^{(n)}\right\rangle = \left\langle\Psi_0^{(n)}\middle|H^0\middle|\Psi_0^{(0)}\right\rangle^*$$

$$\begin{cases} E_0^{(0)} = \left\langle\Psi_0^{(0)}\middle|H^0\middle|\Psi_0^{(0)}\right\rangle \\ E_0^{(1)} = \left\langle\Psi_0^{(0)}\middle|\hat{V}\middle|\Psi_0^{(0)}\right\rangle \\ E_0^{(2)} = \left\langle\Psi_0^{(0)}\middle|\hat{V}\middle|\Psi_0^{(1)}\right\rangle \end{cases}$$

Many-Body Perturbation Theory

Second-order correction of the energy

$$E_0^{(2)} = \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_0^{(1)} \right\rangle$$

$\Psi_0^{(1)}$ can be expressed as a linear combination of the complete set of eigenfunctions of H^0

$$\left| \Psi_0^{(1)} \right\rangle = \sum_i C_i^{(1)} \left| \Psi_i^{(0)} \right\rangle \quad \xrightarrow{\left\langle \Psi_k^{(0)} \middle| \Psi_0^{(1)} \right\rangle = C_k^{(1)}} \quad \left| \Psi_0^{(1)} \right\rangle = \sum_{i \neq 0} \left\langle \Psi_i^{(0)} \middle| \Psi_0^{(1)} \right\rangle \left| \Psi_i^{(0)} \right\rangle$$

By multiplying the first-order equation from the left by $<\Psi_i^{(0)}|$

$$\left| \Psi_0^{(1)} \right\rangle = \sum_{i \neq 0} \frac{\left\langle \Psi_i^{(0)} \middle| \hat{V} \middle| \Psi_0^{(0)} \right\rangle}{E_0^{(0)} - E_i^{(0)}} \left| \Psi_i^{(0)} \right\rangle$$

Substituting in the second-order correction of the energy

$$E_0^{(2)} = \sum_{i \neq 0} \frac{\left| \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_i^{(0)} \right\rangle \right|^2}{E_0^{(0)} - E_i^{(0)}}$$

MÖLLER-PLESSET PERTURBATION THEORY

Perturbed Hamiltonian

$$\hat{H} = \hat{H}^0 + \hat{V}$$

Reference = sum of the N one-electron Fock operators

$$\hat{H}^0 = \hat{H}^{HF} = \sum_{i=1}^{Nocc} \hat{F}(i) = \sum_{i}^{N} \hat{h}(i) + \sum_{i}^{N} \hat{V}^{HF}(i) = \sum_{i}^{N} \hat{h}(i) + \sum_{i}^{N} \left(\hat{J}(i) - \hat{K}(i) \right)$$

Perturbation = difference between the exact electron repulsion operator, and how it is computed in the HF method

$$\hat{V} = \hat{V}_{exact} - \hat{V}_{HF} = \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i}^{N} \hat{V}^{HF}(i) = \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i}^{N} \left(\hat{J}(i) - \hat{K}(i) \right)$$

MÖLLER-PLESSET PERTURBATION THEORY

Eigenstates

$$\Psi_0^{(0)} = \Phi_{HF}$$

$$\Psi_i^{(0)} = \text{excited configurations (Slater determinants)}$$

Zeroth-order term

$$E_0^{(0)} = \left\langle \Psi_0^{(0)} \middle| H^0 \middle| \Psi_0^{(0)} \right\rangle$$

$$E_0^{(0)} = \sum_{i=1}^{Nocc} \left\langle \Psi_0^{(0)} \middle| \hat{F}(i) \middle| \Psi_0^{(0)} \right\rangle = \sum_{i=1}^{Nocc} \varepsilon_i$$

The zeroth-order term corresponds to the sum of the spin-orbitals energies

MÖLLER-PLESSET PERTURBATION THEORY

First-order term

$$E_0^{(1)} = \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_0^{(0)} \right\rangle$$

$$E_0^{(1)} = \left\langle \Psi_0^{(0)} \middle| \hat{V}_{exact} - \hat{V}_{HF} \middle| \Psi_0^{(0)} \right\rangle = \sum_i^N \sum_{j>i}^N \left\langle \Psi_0^{(0)} \middle| \frac{1}{r_{ij}} \middle| \Psi_0^{(0)} \right\rangle - \sum_i^N \left\langle \Psi_0^{(0)} \middle| \hat{J}(i) - \hat{K}(i) \middle| \Psi_0^{(0)} \right\rangle$$

$$\begin{aligned} E_0^{(0)} + E_0^{(1)} &= \left\langle \Psi_0^{(0)} \middle| \hat{H}^{(0)} \middle| \Psi_0^{(0)} \right\rangle + \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_0^{(0)} \right\rangle \\ &= \left\langle \Psi_0^{(0)} \middle| \hat{H}^{(0)} + \hat{V} \middle| \Psi_0^{(0)} \right\rangle \\ &= \left\langle \Psi_0^{(0)} \middle| \hat{H} \middle| \Psi_0^{(0)} \right\rangle = E_{HF} \end{aligned}$$

The sum of the zeroth- and first-order terms corresponds to the total HF energy

MÖLLER-PLESSET PERTURBATION THEORY

Second-order term

first term that contributes to the electron correlation energy

$$E_0^{(2)} = \sum_{i\neq 0} \frac{\left|\left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_i^{(0)} \right\rangle\right|^2}{E_0^{(0)} - E_i^{(0)}} = \sum_{i\neq 0} \frac{\left|\left\langle \Psi_0^{(0)} \middle| \hat{H} \middle| \Psi_i^{(0)} \right\rangle\right|^2}{E_0^{(0)} - E_i^{(0)}} - \underbrace{\sum_{i\neq 0} \frac{\left|\left\langle \Psi_0^{(0)} \middle| \hat{H}^0 \middle| \Psi_i^{(0)} \right\rangle\right|^2}{E_0^{(0)} - E_i^{(0)}}}_{=0}$$

$\left\langle \Psi_0^{(0)} \middle| \hat{H} \middle| \Psi_i^{(0)} \right\rangle$ ***given by the Slater rules***

The only non-zero terms involve the coupling matrix elements between $\boldsymbol{\Psi_0^{(0)}}$ and doubly excited determinants $\Psi_i^{(0)} = \Psi_{mn}^{pq}$

$$E_0^{(2)} = \sum_{m}^{occ} \sum_{n>m}^{occ} \sum_{p}^{unocc} \sum_{q>p}^{unocc} \frac{\left| (mp|nq) - (mq|np) \right|^2}{\varepsilon_m + \varepsilon_n - \varepsilon_p - \varepsilon_q}$$