Coupled Perturbed Hartree-Fock (CPHF)

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- Perturbation theory applied to the Hartree-Fock equations.
- It is used in many contexts, here we will focus on the calculation of response properties to an external perturbation (electromagnetic field).
- Density Matrix formalism. AO based method mainly developed by R. McWeeny in the '60.

References

- R. McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960)
- R. McWeeny, *Phys. Rev.* **126**, 1028 (1962)
- G. Diercksen and R. McWeeny, *J. Chem. Phys.* **44**, 3554 (1966).
- R. McWeeny, "*Methods of Molecular Quantum Mechanics*", Second Edition (Academic Press, London 1992)
- R. Ditchfield, *Mol. Phys.* **27**, 789 (1974)
- K. Wolinski, J.F. Hinton and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990)

Introduction: review of HF theory

- Electronic Hamiltonian

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i<j} \frac{1}{r_{ij}} + V_{NN}$$

- Fock operator

$$f(\boldsymbol{x}_1) = h(\boldsymbol{x}_1) + \sum_j J_j(\boldsymbol{x}_1) - K_j(\boldsymbol{x}_1)$$

- Kohn-Sham operator (CPHF theory can be directly applied to KS DFT)

$$f^{KS}(\boldsymbol{x}_1) = h(\boldsymbol{x}_1) + \int \frac{\rho(\boldsymbol{x}_2)}{r_{12}} + V_{XC}(\boldsymbol{x}_1)$$

- Hartree-Fock equations

$$f(\boldsymbol{x}_1)\chi_i(\boldsymbol{x}_1)=\varepsilon_i\chi_i(\boldsymbol{x}_1)$$

- Atomic basis set: LCAO MO matrix equations

$$\chi_i=\sum_{\mu=1}^{K} C_{\mu i}\tilde{\chi}_\mu$$

$$\boldsymbol{FC}=\boldsymbol{SC}\,\boldsymbol{\varepsilon}$$

- Density Matrix

$$\boldsymbol{C} = \overbrace{\boldsymbol{c}_1 \boldsymbol{c}_2 \cdots \boldsymbol{c}_n}$$

$$\boldsymbol{R} = \sum_{i=1}^{n} \boldsymbol{c}_i \boldsymbol{c}_i^{\boldsymbol{T}}$$

- Fock Matrix. One- and two-electron part

$$\boldsymbol{F} = \boldsymbol{h} + \boldsymbol{G}(\boldsymbol{R})$$

$$h_{pq} = \langle p|h|q \rangle$$

$$G_{pq} = \sum_{rs} R_{rs} (\langle pr|qs \rangle - \langle pr|sq \rangle)$$

- Building **G** is the most computationally demanding step of an HF calculation

- HF energy

$$E = 2\,Tr\left(\boldsymbol{F}'\boldsymbol{R}\right)$$

$$\boldsymbol{F}' = \boldsymbol{h} + \frac{1}{2}\boldsymbol{G}\left(\boldsymbol{R}\right)$$

- Commutation relation between **F** and **R** and idem potency of **R**

$$\boldsymbol{FRS} - \boldsymbol{SRF} = 0$$

$$\boldsymbol{RSR} = \boldsymbol{R}$$

- Löwdin orthogonalization

$$\chi \rightarrow \chi S^{-1/2}$$

$$c_i \rightarrow S^{1/2} c_i$$

$$R \rightarrow S^{1/2} R S^{1/2}$$

$$F \rightarrow S^{-1/2} F S^{-1/2}$$

- Density matrix as a projection operator

$$\boldsymbol{p}_i = \boldsymbol{c}_i \boldsymbol{c}_i^T \qquad \boldsymbol{p}_i^2 = \boldsymbol{p}_i \qquad \sum_i \boldsymbol{p}_i = \mathbf{1}$$

- Occupied and virtual subspace projectors

$$\boldsymbol{R}_1 \equiv \boldsymbol{R} = \sum_{i=occ} \boldsymbol{c}_i \boldsymbol{c}_i^T \qquad \boldsymbol{R}_2 \equiv \mathbf{1} - \boldsymbol{R}_1 = \sum_{j=vir} \boldsymbol{c}_j \boldsymbol{c}_j^T$$

- A generic matrix associated with an operator on the full space can be separated in projection components

$$\boldsymbol{M} = \boldsymbol{M}_{11} + \boldsymbol{M}_{12} + \boldsymbol{M}_{21} + \boldsymbol{M}_{22}$$

$$\boldsymbol{M}_{ab} = \boldsymbol{R}_a \boldsymbol{M} \boldsymbol{R}_b$$

- Spectral resolution of the Fock matrix

$$\boldsymbol{F} = \sum_{i=1}^{m} \varepsilon_i \boldsymbol{c}_i \boldsymbol{c}_i^T \qquad \boldsymbol{F}^{-1} = \sum_{i=1}^{m} \varepsilon_i^{-1} \boldsymbol{c}_i \boldsymbol{c}_i^T$$

- Perturbation expansions

$$\boldsymbol{F} = \boldsymbol{F}^{(0)} + \lambda\, \boldsymbol{F}^{(1)} + \lambda^2\, \boldsymbol{F}^{(2)} + \ldots$$

$$\boldsymbol{F}^{(n)} = \boldsymbol{h}^{(n)} + \boldsymbol{G}\left(\boldsymbol{R}^{(n)} \right)$$

$$\boldsymbol{R} = \boldsymbol{R}^{(0)} + \lambda\, \boldsymbol{R}^{(1)} + \lambda^2\, \boldsymbol{R}^{(2)} + \ldots$$

$$FR - RF = 0$$

$$RR = R$$

$$F^{(0)} R^{(0)} - R^{(0)} F^{(0)} = 0$$

$$R^{(0)} R^{(0)} = R^{(0)}$$

$$F^{(0)} R^{(1)} - R^{(1)} F^{(0)} + F^{(1)} R^{(0)} - R^{(0)} F^{(1)} = 0$$

$$R^{(0)} R^{(1)} + R^{(1)} R^{(0)} = R^{(1)}$$

- First order density matrix

$$\boldsymbol{R}^{(1)} = \sum_{i=occ} \left(\boldsymbol{c}_i^{(0)} \boldsymbol{c}_i^{(1)T} + \boldsymbol{c}_i^{(1)} \boldsymbol{c}_i^{(0)T} \right)$$

$$\boldsymbol{R}^{(1)} = \boldsymbol{R}_{12} + \boldsymbol{R}_{21} = \boldsymbol{X} + \boldsymbol{X}^T$$

- (1,2) projection of the first order commutator

$$\boldsymbol{F}^{(0)} \boldsymbol{X} - \boldsymbol{X} \boldsymbol{F}^{(0)} - \boldsymbol{F}_{12}^{(1)} = 0$$

- Solution of the first order equation

$$\boldsymbol{X} = \left(\boldsymbol{F}^{(0)}\right)^{-1}\left(\boldsymbol{X}\,\boldsymbol{F}^{(0)} + \boldsymbol{F}_{12}^{(1)}\right)$$

- Iteration starting with **X**=0

$$\boldsymbol{X} = \sum_{n=0}^{\infty}\left(\boldsymbol{F}^{(0)}\right)^{-(n+1)}\boldsymbol{F}_{12}^{(1)}\left(\boldsymbol{F}^{(0)}\right)^{n}$$

- substituting the spectral resolution of $\mathbf{F}^{(0)}$ and $\mathbf{F}^{(0)\text{-}1}$

$$\boldsymbol{X} = \sum_{j=occ}\sum_{k=vir}\frac{1}{\varepsilon_j - \varepsilon_k}\boldsymbol{c}_j^{T}\boldsymbol{F}^{(1)}\boldsymbol{c}_k\,\boldsymbol{c}_j\,\boldsymbol{c}_k^{T}$$

- Expansion of the energy

$$E = 2\,Tr\left(\boldsymbol{F}'\,\boldsymbol{R}\right)$$

$$\boldsymbol{F}' = \boldsymbol{h} + \frac{1}{2}\boldsymbol{G}\left(\boldsymbol{R}\right)$$

- First order energy

$$E^{(1)} = 2\,Tr\left(\boldsymbol{F}^{(0)\prime}\,\boldsymbol{R}^{(1)} + \boldsymbol{F}^{(1)\prime}\,\boldsymbol{R}^{(0)}\right)$$

$$Tr\,\boldsymbol{A}\boldsymbol{G}\left(\boldsymbol{B}\right) = Tr\,\boldsymbol{B}\boldsymbol{G}\left(\boldsymbol{A}\right)$$

$$E^{(1)} = 2\,Tr\left(\boldsymbol{F}^{(0)}\,\boldsymbol{R}^{(1)} + \boldsymbol{h}^{(1)}\,\boldsymbol{R}^{(0)}\right) = 2\,Tr\,\boldsymbol{h}^{(1)}\,\boldsymbol{R}^{(0)}$$

- Higher order energies

$$E^{(2)} = 2\,Tr\left(\frac{1}{2}\boldsymbol{h}^{(1)}\boldsymbol{R}^{(1)} + \boldsymbol{h}^{(2)}\boldsymbol{R}^{(0)}\right)$$

$$E^{(3)} = 2\,Tr\left(\boldsymbol{F}^{(1)}\left(\boldsymbol{R}_{11}^{(2)} + \boldsymbol{R}_{22}^{(2)}\right) + \boldsymbol{h}^{(2)}\boldsymbol{R}^{(1)} + \boldsymbol{h}^{(3)}\boldsymbol{R}^{(0)}\right)$$

- *2n+1* theorem of perturbation theory

- Electric properties: polarizabilities

$$\hat{H} = \hat{H^{(0)}} + \hat{H^{(1)}} = \hat{H^{(0)}} + \hat{\mu}$$

$$W = W^{(0)} - \mu_a E_a - \frac{1}{2}\alpha_{ab} E_a E_b - \frac{1}{6}\beta_{abc} E_a E_b E_c$$

$$- \frac{1}{24}\gamma_{abcd} E_a E_b E_c E_d$$

- Magnetic properties: nuclear magnetic shieldings

$$\sigma_N^{ab} = Tr\left(\boldsymbol{h}_N^{\mathbf{0b}}\,\boldsymbol{R}^{\boldsymbol{a0}} + \boldsymbol{h}_N^{\boldsymbol{ab}}\,\boldsymbol{R}^{\mathbf{00}}\right)$$

$$h_N^{ab} = \frac{1}{2\mathrm{c}^2}\,\frac{\left[\boldsymbol{r}\cdot(\boldsymbol{r}-\boldsymbol{R}) - \boldsymbol{r}_{\boldsymbol{a}}(\boldsymbol{r}-\boldsymbol{R})_b\right]}{|\boldsymbol{r}-\boldsymbol{R}|^3}$$

$$h_N^{0\mathrm{b}} = \frac{-i}{c}\,\frac{\left[(\boldsymbol{r}-\boldsymbol{R})\times\nabla\right]_b}{|\boldsymbol{r}-\boldsymbol{R}|^3}$$

$$h^a = \frac{-i}{c}\left[\boldsymbol{r}\times\nabla\right]_a$$

- Perturbation dependent basis set: Gauge Including Atomic Orbitals (GIAO)

$$\chi_p = \exp\left[\frac{-i}{2c}(\boldsymbol{H}\times\boldsymbol{R}_p)\cdot\boldsymbol{r}\right]\chi_p^{(0)}$$

$$\boldsymbol{F}^{(1)}\boldsymbol{R}^{(0)}\boldsymbol{S}^{(0)}+\boldsymbol{F}^{(0)}\boldsymbol{R}^{(1)}\boldsymbol{S}^{0}+\boldsymbol{F}^{(0)}\boldsymbol{R}^{(0)}\boldsymbol{S}^{(1)}$$

$$-\boldsymbol{S}^{(1)}\boldsymbol{R}^{(0)}\boldsymbol{F}^{(0)}-\boldsymbol{S}^{(0)}\boldsymbol{R}^{(1)}\boldsymbol{F}^{(0)}-\boldsymbol{S}^{(0)}\boldsymbol{R}^{(0)}\boldsymbol{F}^{(1)}=0$$

$$\boldsymbol{F}^{(\mathbf{1})} = \boldsymbol{h}^{(\mathbf{1})} + \boldsymbol{G}\left(\boldsymbol{R}^{(\mathbf{1})}, g^{(0)}\right) + \boldsymbol{G}\left(\boldsymbol{R}^{(\mathbf{0})}, g^{(1)}\right)$$

$$\boldsymbol{h}^{(\mathbf{1})}_{\boldsymbol{pq}} = \langle p^{(1)} | \boldsymbol{h} | q \rangle + \langle p | \boldsymbol{h}^{(\mathbf{1})} | q \rangle + \langle p | \boldsymbol{h} | q^{(1)} \rangle$$