Targeting excited states at the Hartree-Fock level

The Maximum Overlap Method (MOM)

Antoine Marie

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ENS de Lyon/LCPQ

Laboratoire de Chimie et Physique Quantiques

ENS DE LYON

The Hartree-Fock method

The independent particle model

The HF many-body wavefunction

$$\psi^{\mathrm{HF}}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n) = \begin{bmatrix} \chi_1(\boldsymbol{x}_1) & \chi_2(\boldsymbol{x}_1) & \cdots & \chi_N(\boldsymbol{x}_1) \\ \chi_1(\boldsymbol{x}_2) & \chi_2(\boldsymbol{x}_2) & \cdots & \chi_N(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\boldsymbol{x}_N) & \chi_2(\boldsymbol{x}_N) & \cdots & \chi_N(\boldsymbol{x}_N) \end{bmatrix} \tag{1}$$

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The HF energy

$$E_{\mathrm{HF}} = \sum_{i=1}^{N} h_i + \sum_{i<j}^{N} (\mathcal{J}_{ij} - \mathcal{K}_{ij}) \tag{2}$$

$$\mathcal{J}_i(\boldsymbol{x})\chi_p(\boldsymbol{x}) = \left[\int \mathrm{d}\boldsymbol{x}' \chi_i(\boldsymbol{x}') \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} \chi_i(\boldsymbol{x}') \right] \chi_p(\boldsymbol{x}) \tag{3a}$$

$$\mathcal{K}_i(\boldsymbol{x})\chi_p(\boldsymbol{x}) = \left[\int \mathrm{d}\boldsymbol{x}' \chi_i(\boldsymbol{x}') \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} \chi_p(\boldsymbol{x}') \right] \chi_i(\boldsymbol{x}) \tag{3b}$$

The Fock operator

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The eigenvalue equation

$$f(\boldsymbol{x})\chi_p(\boldsymbol{x}) = [h(\boldsymbol{x}) + v^{\mathrm{HF}}(\boldsymbol{x})]\chi_p(\boldsymbol{x}) = \epsilon_p \chi_p(\boldsymbol{x}), \tag{4}$$

$$h(\boldsymbol{x}) = -\frac{\boldsymbol{\nabla}^2}{2} + \sum_A^N \frac{Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|} \tag{5a}$$

$$v^{\mathrm{HF}}(\boldsymbol{x}) = \sum_i [J_i(\boldsymbol{x}) - K_i(\boldsymbol{x})] \tag{5b}$$

Introduction of a basis

Expansion in a basis

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Matrix elements of the Fock operator

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\langle\mu\nu|\lambda\sigma\rangle - \langle\mu\nu|\lambda\sigma\rangle) \tag{8}$$

The Fock matrix is a $K \times K$ matrix, thus there are K eigenfunctions.

The density matrix

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$$P_{\mu\nu} = \sum_{i}^{N} c_{\mu i} c_{\nu i}^{*} \tag{9}$$

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The density matrix depends on N coefficients

There are $\binom{K}{N}$ possibilities!

How to choose consistently always the same N orbitals?

The Maximum Overlap Method

The papers

The Maximum Overlap Method

13164 *J. Phys. Chem. A* **2008,** *112,* 13164–13171

Self-Consistent Field Calculations of Excited States Using the Maximum Overlap Method (MOM)†

Andrew T. B. Gilbert,*,‡ Nicholas A. Besley,§ and Peter M. W. Gill‡

Research School of Chemistry, Australian National University, ACT 0200, Australia, and School of Chemistry, University of Nottingham, Nottingham NG7 2RD, England

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The Initial Maximum Overlap Method

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Simple Models for Difficult Electronic Excitations

Giuseppe M. J. Barca, Andrew T. B. Gilbert, and Peter M. W. Gill*

Research School of Chemistry, Australian National University, Acton ACT 2601, Australia

Orbital overlap matrix

The orbital overlap matrix

$$\boldsymbol{O} = (\boldsymbol{C}_{\text{old}})^{\dagger} \boldsymbol{S} \boldsymbol{C}_{\text{new}} \tag{10}$$

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Projection on the old occupied space

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We select the N largest overlap!

Prevent the variational collapse for double excitations

The orbital overlap matrix

$$\boldsymbol{O} = (\boldsymbol{C}_{\text{initial}})^{\dagger} \boldsymbol{S} \boldsymbol{C}_{\text{new}} \tag{12}$$

Projection on the old occupied space

$$p_i = (\sum_i (O_{ij})^2)^{1/2} \tag{13}$$