MO-LCAO methods
(things are becoming even more complicated)

Quantum Chemistry

Lesson 10

Contents

[wiki (MO-LCAO) , wiki (AO), wiki (MO), wiki (basis sets)]

A way to solve the H-F equations

Restricted H-F method (closed electronic shells)

- even number of electrons, pairs with opposite spin projections

- one-electron wave functions (the Slater determinant of the H-F method consists of)
  - $\varphi_1(\vec{r},\xi) = \phi_1(\vec{r})\alpha(\xi),\ \varphi_2(\vec{r},\xi) = \phi_1(\vec{r})\beta(\xi)$
  - …
  - $\varphi_{n-1}(\vec{r},\xi) = \phi_{n/2}(\vec{r})\alpha(\xi),\ \varphi_n(\vec{r},\xi) = \phi_{n/2}(\vec{r})\beta(\xi)$

- Hartree-Fock equations
  - $\left\{-\frac{\hbar^2}{2m_\mathrm{e}}\Delta - \sum_{J=1}^{N}\frac{Z_J\tilde{e}^2}{\|\vec{r}-\vec{R}_J\|}\right\}\phi_k(\vec{r}) + 2\left\{\sum_{j=1,j\neq k}^{n/2}\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\phi_j^*(\vec{r}')\phi_j(\vec{r}')\,\mathrm{d}\vec{r}'\right\}\phi_k(\vec{r}) - \sum_{j=1,j\neq k}^{\frac{n}{2}}\left\{\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\phi_j^*(\vec{r}')\phi_k(\vec{r}')\,\mathrm{d}\vec{r}'\right\}\phi_j(\vec{r}) = \varepsilon_k\phi_k(\vec{r})$
  - $k = 1, \dots, n/2$

A way to solve the H-F equations

Restricted H-F method (closed electronic shells)

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molecular spin-orbital

molecular orbital (MO)

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A way to solve the H-F equations

Restricted H-F method (closed electronic shells)

$$\left\{-\frac{\hbar^2}{2m_e}\Delta - \sum_{J=1}^{N}\frac{Z_J\tilde{e}^2}{\|\vec{r}-\vec{R}_J\|}\right\}\phi_k(\vec{r}) + 2\left\{\sum_{j=1,j\neq k}^{n/2}\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\phi_j^*(\vec{r}')\phi_j(\vec{r}')\,\mathrm{d}\vec{r}'\right\}\phi_k(\vec{r}) - \sum_{j=1,j\neq k}^{n/2}\left\{\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\phi_j^*(\vec{r}')\phi_k(\vec{r}')\,\mathrm{d}\vec{r}'\right\}\phi_j(\vec{r}) = \varepsilon_k\phi_k(\vec{r})$$

Molecular orbitals (MOs) expansion

- $\phi_j(\vec{r}) = \sum_a c_{aj}\chi_a(\vec{r})$
  - $\chi_a(\vec{r})$ are given functions
  - $a = 1, \dots, +\infty \ (N < +\infty)$
  - in general, $\langle\chi_a|\chi_b\rangle \equiv S_{ab} \neq \delta_{ab}$
- H-F equations become a set of (non-differential / non-integral) equations for unknown coefficients c_{aj} (see below)
- the core of the MO-LCAO methods

A way to solve the H-F equations

Restricted H-F method (closed electronic shells)

$$\left\{-\frac{\hbar^2}{2m_e}\Delta - \sum_{J=1}^{N}\frac{Z_J\tilde{e}^2}{\|\vec{r}-\vec{R}_J\|}\right\}\phi_k(\vec{r}) + 2\left\{\sum_{j=1,j\neq k}^{n/2}\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}\,'\|}\phi_j^*(\vec{r}\,')\phi_j(\vec{r}\,')\,\mathrm{d}\vec{r}\,'\right\}\phi_k(\vec{r}) - \sum_{j=1,j\neq k}^{n/2}\left\{\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}\,'\|}\phi_j^*(\vec{r}\,')\phi_k(\vec{r}\,')\,\mathrm{d}\vec{r}\,'\right\}\phi_j(\vec{r}) = \varepsilon_k\phi_k(\vec{r})$$

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overlap integrals,
'overlaps'

- H-F equations become a set of (non-differential / non-integral) equations for unknown coefficients c_{aj} (see below)
- the core of the MO-LCAO methods

MO-LCAO methods (terminology)

MO-LCAO = **M**olecular **O**rbitals (expressed as) **L**inear **C**ombinations of **A**tomic **O**rbitals

- MO (molecular orbitals): $\varphi_1(\vec{r},\xi) = \boldsymbol{\phi_1(\vec{r})}\alpha(\xi),\ \varphi_2(\vec{r},\xi) = \boldsymbol{\phi_1(\vec{r})}\beta(\xi), \ldots$
- LC (linear combinations): $\phi_j(\vec{r}) = \sum_a c_{aj}\chi_a(\vec{r})$
- AO (atomic orbitals): $\chi_a(\vec{r}) = \chi_{Kb_K}(\vec{r} - \vec{r}_K)$ (functions 'centered' at particular atoms, K)

Basis sets of AOs

Basis sets (in quantum chemistry)

- $\phi_j(\vec{r}) = \sum_a c_{aj}\chi_a(\vec{r})$
  - $a = 1, \dots, N < +\infty$: not necessarily a complete set on the one-electron state space (a Schauder basis set)
  - in general, non-orthogonal: $\langle \chi_a | \chi_b \rangle \equiv S_{ab} \neq \delta_{ab}$; often, however, normalized: $S_{aa} = 1$
  - chosen so that the one-electron state space is 'sufficiently accurately' represented
  - infinitely many possibilities, many proposals found in the literature

Hydrogen-like AOs

- AOs of a hydrogen-like ion
  - $\chi_{a=\{K;n,l,m\}}(r,\theta,\phi) = R_{nl}(r_{\cancel{K}})Y_{lm}(\theta_{\cancel{K}},\phi_{\cancel{K}}) \sim L^{2l+1}_{n-l-1}\left(\frac{2Zr}{na_0}\right) e^{-\frac{Zr}{na_0}} P_l^m(\cos\theta)e^{im\phi} = L^{2l+1}_{n-l-1}(2\zeta\tilde{r})e^{-\zeta\tilde{r}} P_l^m(\cos\theta)e^{im\phi}$

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$\zeta = Z/n$
$\tilde{r} = r/a_0$

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Hydrogen-like AOs

Why?
'real-valued' Hamiltonian → real-valued wave functions

$$\dots R_{nl}(r_{\cancel{K}})Y_{lm}(\theta_{\cancel{K}}, \phi_{\cancel{K}}) \sim L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right) e^{-\frac{Zr}{na_0}} P_l^m(\cos\theta)e^{im\phi} = L_{n-l-1}^{2l+1}(2\zeta\tilde{r})e^{-\zeta\tilde{r}} P_l^m(\cos\theta)e^{im\phi}$$

- real-valued hydrogen-like AOs
  - $\chi_{a=\{K;n,l,m\}}(r,\theta,\phi) \sim L_{n-l-1}^{2l+1}(2\zeta\tilde{r})e^{-\zeta\tilde{r}} P_l^m(\cos\theta)\cos(m\phi)$ for $m \neq 0$ $(m > 0)$
  - $\chi_{a=\{K;n,l,m\}}(r,\theta,\phi) \sim L_{n-l-1}^{2l+1}(2\zeta\tilde{r})e^{-\zeta\tilde{r}} P_l^m(\cos\theta)\sin(m\phi)$
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Basis sets of AOs

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Hydrogen-like AOs

- AOs of a hydrogen-like ion
  - $\chi_{a=\{K;n,l,m\}}(r,\theta,\phi) = R_{nl}(r_K)Y_{lm}(\theta_K, \ldots$ $\ldots e^{im\phi} = L_{n-l-1}^{2l+1}(2\zeta\tilde{r})e^{-\zeta\tilde{r}}\,P_l^m(\cos\theta)e^{im\phi}$

$$Y_{lm}^{(\mathrm{re})}(\theta,\phi) \sim \begin{cases} P_l^m(\cos\theta)\cos(m\phi) \\ P_l^m(\cos\theta) \\ P_l^m(\cos\theta)\sin(m\phi) \end{cases}$$

- real-valued hydrogen-like AOs
  - $\chi_{a=\{K;n,l,m\}}(r,\theta,\phi) \sim L_{n-l-1}^{2l+1}(2\zeta\tilde{r})e^{-\zeta\tilde{r}}\,P_l^m(\cos\theta)\cos(m\phi)$ for $m \neq 0$ $(m > 0)$
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Basis sets of AOs

Slater AOs

- $\chi_{a=\{K;n,l,m\}}(r,\theta,\phi) \sim \tilde{r}^{n-1} e^{-\zeta\tilde{r}} Y_{lm}^{(\mathrm{re})}(\theta,\phi)$

Gaussian AOs

- $\chi_{a=\{K;n,l,m\}}(r,\theta,\phi) \sim \tilde{r}^{n-1} e^{-\zeta\tilde{r}^2} Y_{lm}^{(\mathrm{re})}(\theta,\phi)$
  - pros (analytically integrable) *vs.* contras (not fully correct behavior at $\tilde{r} \to 0$ and for $\tilde{r} \to +\infty$)
  - contracted Gaussian AOs (Slater-like AOs expressed as optimized linear combinations of Gaussian ones)

Terminology (classification of basis sets of AOs)

- *minimal BS*: only AOs which are occupied in the particular atom are included
- *extended BS*: additional AOs are included (additional AOs for 'occupied' values of l, higher values of l), double-zeta, triple-zeta, etc.
- *valence BS*: only valence shell electrons are considered explicitly, inner-shell electrons are approximated by a pseudopotential
- *polarization functions* (AOs): $l \geq 1$
- *diffusion functions* (AOs): small-values ζ (highly delocalized functions)

Roothaan equations (closed-shell variant)

Ingredients

- Hartree-Fock equations

$$\left\{-\frac{\hbar^2}{2m_\mathrm{e}}\Delta-\sum_{J=1}^{N}\frac{Z_J\tilde{e}^2}{\|\vec{r}-\vec{R}_J\|}\right\}\phi_k(\vec{r})+2\left\{\sum_{j=1,j\neq k}^{n/2}\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\phi_j^*(\vec{r}')\phi_j(\vec{r}')\,\mathrm{d}\vec{r}'\right\}\phi_k(\vec{r})-$$

$$-\sum_{j=1,j\neq k}^{n/2}\left\{\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\phi_j^*(\vec{r}')\phi_k(\vec{r}')\,\mathrm{d}\vec{r}'\right\}\phi_j(\vec{r})=\varepsilon_k\phi_k(\vec{r})$$

- the MO-LCAO expansion of MOs

$$\phi_j(\vec{r})=\sum_a c_{aj}\chi_a(\vec{r})$$

- with generally non-orthonormal AOs

$$\langle\chi_a|\chi_b\rangle\equiv S_{ab}$$

- orthonormal MOs

$$\langle\phi_j|\phi_k\rangle\equiv\delta_{jk}\rightarrow\sum_{a,b}c_{ai}^*c_{bj}S_{ab}=\delta_{ij}$$

Roothaan equations (closed-shell variant)

Ingredients

- Hartree-Fock equations

$$\ldots \phi_j^*(\vec{r}')\phi_j(\vec{r}')\,\mathrm{d}\vec{r}'\Big\}\phi_k(\vec{r}) - \ldots$$

> - new unknowns which represent the solution of the H-F equations we are looking for
> - in general, $c_{aj} \in \mathbb{C}$, but usually real-valued $c_{aj} \in \mathbb{R}$ are used

- the MO-LCAO expa... of MOs

$$\phi_j(\vec{r}) = \sum_a c_{aj}\chi_a(\vec{r})$$

- with generally non-orthonormal AOs

$$\langle\chi_a|\chi_b\rangle \equiv S_{ab}$$

- orthonormal MOs

$$\langle\phi_j|\phi_k\rangle \equiv \delta_{jk} \rightarrow \sum_{a,b} c_{ai}^* c_{bj} S_{ab} = \delta_{ij}$$

Roothaan equations (closed-shell variant)

Insertion of the MO-LCAO expansion into the H-F equations ...

$$\left\{-\frac{\hbar^2}{2m_\mathrm{e}}\Delta - \sum_{J=1}^{N}\frac{Z_J\tilde{e}^2}{\|\vec{r}-\vec{R}_J\|}\right\}\overbrace{\phi_k(\vec{r})}^{\sum_a c_{ak}\chi_a(\vec{r})} + 2\left\{\sum_{j=1,j\neq k}^{n/2}\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\overbrace{\phi_j^*(\vec{r}')}^{\sum_b c_{bj}^*\chi_b^*(\vec{r})}\overbrace{\phi_j\;(\vec{r}')}^{\sum_g c_{gj}\chi_g\,(\vec{r})}\,\mathrm{d}\vec{r}'\right\}\overbrace{\phi_k(\vec{r})}^{\sum_a c_{ak}\chi_a(\vec{r})} -$$

$$-\sum_{j=1,j\neq k}^{\frac{n}{2}}\left\{\int_{\mathbb{R}^3}\frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|}\underbrace{\phi_j^*(\vec{r}')}_{\dots}\underbrace{\phi_k(\vec{r}')}_{\dots}\mathrm{d}\vec{r}'\right\}\underbrace{\phi_j(\vec{r})}_{\dots} = \varepsilon_k\underbrace{\phi_k(\vec{r})}_{\dots}$$

$$\langle\chi_s| \rightarrow \equiv \int_{\mathbb{R}^3}\mathrm{d}\vec{r}\;\underbrace{\chi_s(\vec{r})}_{\text{real valued functions}}$$

Roothaan equations (closed-shell variant)

... and some algebra

- symbols used to simplify the resulting equations
  - $H_{ab} \equiv \left\langle \chi_a \middle| \left\{ -\frac{\hbar^2}{2m_\mathrm{e}} \Delta - \sum_{J=1}^{N} \frac{Z_J \tilde{e}^2}{\|\vec{r}-\vec{R}_J\|} \right\} \middle| \chi_b \right\rangle \equiv \int_{\mathbb{R}^3} \chi_a(\vec{r}) \left\{ -\frac{\hbar^2}{2m_\mathrm{e}} \Delta - \sum_{J=1}^{N} \frac{Z_J \tilde{e}^2}{\|\vec{r}-\vec{R}_J\|} \right\} \chi_b(\vec{r})$
  - $P_{ab}(\mathbf{c}) \equiv 2 \sum_k c_{ak}^* c_{bk}$
  - $I_{ab,pq} \equiv \left\langle \chi_a \chi_b \middle| \frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|} \middle| \chi_p \chi_q \right\rangle \equiv \int_{\mathbb{R}^3 \times \mathbb{R}^3} \chi_a(\vec{r}) \chi_b(\vec{r}) \frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|} \chi_p(\vec{r}') \chi_q(\vec{r}') \mathrm{d}\vec{r} \mathrm{d}\vec{r}'$
  - $F_{ab}(\mathbf{c}) = H_{ab} + \sum_{p,q} P_{pq}(\mathbf{c}) \left(I_{ab,pq} - \frac{1}{2} I_{aq,pb} \right)$

- Roothaan equations

$$\sum_b [F_{ab}(\mathbf{c}) - \varepsilon_k S_{ab}] c_{bk} = 0$$

Roothaan equations (closed-shell variant)

… and some algebra

- symbols used to simplify the resulting equations
  - $H_{ab} \equiv \left\langle \chi_a \middle| \left\{ -\frac{\hbar^2}{2m_\mathrm{e}}\Delta - \sum_{J=1}^{N} \frac{Z_J \tilde{e}^2}{\|\vec{r}-\vec{R}_J\|} \right\} \middle| \chi_b \right\rangle \equiv \int_{\mathbb{R}^3} \chi_a(\vec{r}) \left\{ -\frac{\hbar^2}{2m_\mathrm{e}}\Delta - \sum_{J=1}^{N} \frac{Z_J \tilde{e}^2}{\|\vec{r}-\vec{R}_J\|} \right\} \chi_b(\vec{r})$
  - $P_{ab}(\mathbf{c}) = 2\sum_k c_{ak}^* c_{bk}$
  - $\ldots \|\vec{r}-\vec{r}'\| \, \middle| \chi_p \chi_q \right\rangle \equiv \int_{\mathbb{R}^3\times\mathbb{R}^3} \chi_a(\vec{r})\chi_b(\vec{r}) \frac{\tilde{e}^2}{\|\vec{r}-\vec{r}'\|} \chi_p(\vec{r}')\chi_q(\vec{r}') \mathrm{d}\vec{r}\mathrm{d}\vec{r}'$
  - $F_{ab}(\mathbf{c}) = H_{ab} + \sum_{p,q} P_{pq}(\mathbf{c}) \left(I_{ab,pq} - \frac{1}{2} I_{aq,pb} \right)$

Fock matrix

- Roothaan equations

$$\sum_b [F_{ab}(\mathbf{c}) - \varepsilon_k S_{ab}] c_{bk} = 0$$

Roothaan equations (closed-shell variant)

Remarks

- non-linear algebraic (i.e., neither differential nor integral) equations
- if F_{ab} did not depend on $\mathbf{c}$, we would get a generalized eigenvalue/eigenvector problem:
  - $\sum_b [F_{ab} - \varepsilon_k S_{ab}] c_{bk} = 0 \rightarrow \mathbf{Fc} = \varepsilon\mathbf{Sc}$
- a simple iterative solution is possible for F_{ab} depending on $\mathbf{c}$
  - $\mathbf{c}_0$
  - $\mathbf{F}(\mathbf{c}_0)\mathbf{c}_1 = \varepsilon_1 \mathbf{S}\mathbf{c}_1$
  - …
  - $\mathbf{F}(\mathbf{c}_{i-1})\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_i$
- or more sophisticated modifications, e.g. the *Direct Inversion in Iterative Subspace* (DIIS) method [see here]
- # solutions = # AOs, usually much more than we actually need to construct the H-F Slater determinant → post H-F methods

The end of lesson 10.