Lecture 21: Finite Basis Sets

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Chem 150/250 Fall 2023

12/06/2023

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Choosing a Spin Basis

- Generalized Hartree-Fock (GHF) method: Each spin orbital is two-component "spinor",

$$\phi_p(\mathbf{r}, \sigma) = \phi_{p\alpha}(\mathbf{r})\delta_{\sigma\alpha} + \phi_{p\beta}(\mathbf{r})\delta_{\sigma\beta}.$$

  GHF determinant need not be $\hat{S}_z$ or $\hat{\mathbf{S}}^2$ eigenstate. Important for spin-orbit relativistic theory, spin-frustrated systems

- Spin unrestricted Hartree-Fock (UHF) method: Each spin orbital ϕ_p is either $\sigma(p) = \alpha$ or $\sigma(p) = \beta$ spin eigenstate,

$$\phi_p(\mathbf{r}, \sigma) = \phi_{k(p)\sigma(p)}(\mathbf{r})\delta_{\sigma\sigma(p)}.$$

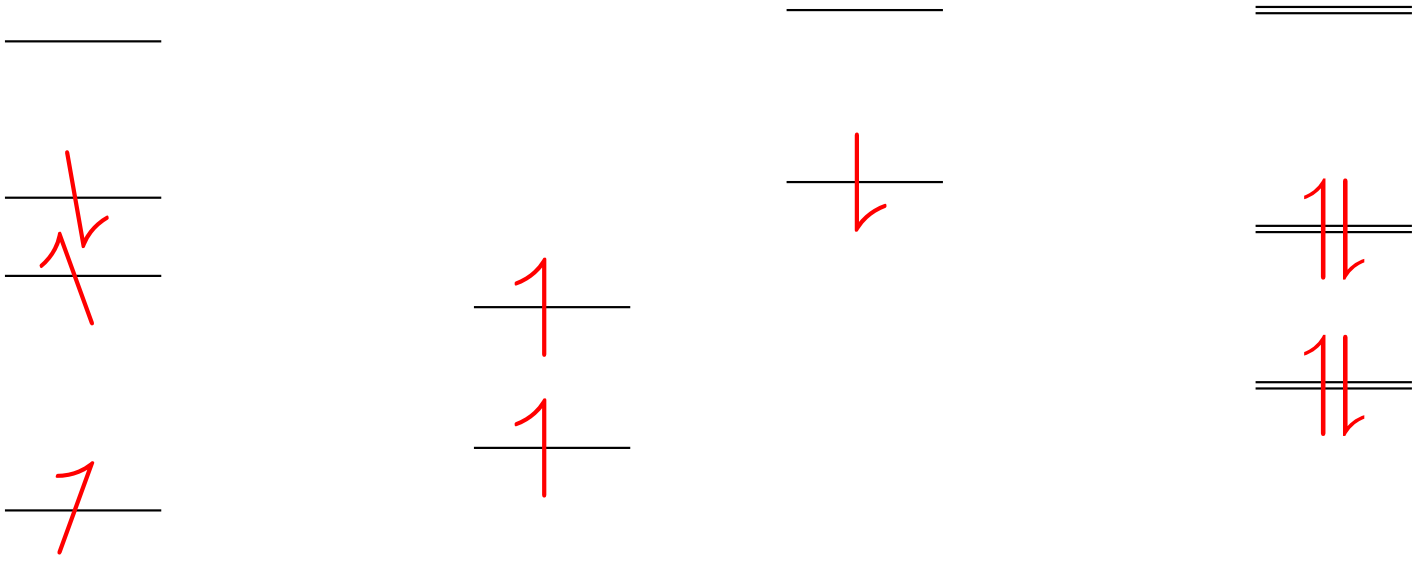
  $k(p)$ indexes each spin. UHF determinant is $\hat{S}_z$ but not necessarily $\hat{\mathbf{S}}^2$ eigenstate. Important for states with unpaired electrons, e.g. radicals, biradicals

Choosing a Spin Basis

- Spin restricted Hartree-Fock (RHF) method: UHF α and β orbitals are restricted to be identical, in pairs i.e.,

$$\phi_{k\alpha}(\mathbf{r}) = \phi_{k\beta}(\mathbf{r}).$$

  RHF determinants are $\hat{S}_z$ eigenstates and they are $\hat{\mathbf{S}}^2$ eigenstates for closed-shell and high-spin open shell states.
- $E^{\mathrm{RHF}} \geq E^{\mathrm{UHF}} \geq E^{\mathrm{GHF}}$. If "$>$", then HF solution breaks spin symmetry
- Will use UHF in the following, unless otherwise stated



Choosing a Spatial Basis

- LCAO-MO method:

$$\phi_{p\sigma}(\mathbf{r}) = \sum_{\mu} C_{\mu p\sigma} \chi_{\mu}(\mathbf{r})$$

- $\{\chi_\mu\}$: "Atomic" orbital (AO) basis functions, nonorthogonal
- For polyatomic molecules, contracted Cartesian Gaussians are most common
- $\mathbf{C}_\sigma$: σ spin MO coefficient matrix, satisfies

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1},$$

  where $\mathbf{S}$ is the overlap matrix.
- It is conventional to use indices $i, j, \ldots$ for occupied, $a, b, \ldots$ for virtual, and $p, q, \ldots$ for general MOs
- Need at least $\max(N_\alpha, N_\beta)$ basis functions ("minimal basis")

AO Density Matrix

- Inserting LCAO-MO expansion ($2\times$) yields

$$\gamma_\sigma(\mathbf{r},\mathbf{r}') = \sum_{\mu\nu} D_{\mu\nu\sigma}\chi_\mu(\mathbf{r})\chi^*_\nu(\mathbf{r}')$$

- AO density matrix

$$D_{\mu\nu\sigma} = \sum_p n_{p\sigma} C_{\mu p\sigma} C^*_{\nu p\sigma}.$$

- Mulliken electronic/net charge populations:

$$q_{I\sigma} = \sum_{\mu,\nu\in I} D_{\mu\nu\sigma} S_{\mu\nu} \tag{1}$$

- Mulliken overlap populations:

$$p_{IJ\sigma} = \sum_{\mu\in I,\nu\in J} D_{\mu\nu\sigma} S_{\mu\nu} \tag{2}$$

Roothaan-Hall Equations

$$\mathbf{F}_\sigma \mathbf{C}_\sigma = \mathbf{S}\mathbf{C}_\sigma \boldsymbol{\epsilon}_\sigma$$

- UHF Fock operator

$$F_{\mu\nu\sigma} = \frac{\partial E}{\partial D_{\mu\nu\sigma}} = h_{\mu\nu} + \sum_{\kappa\lambda\sigma'} \left[(\mu\nu|\kappa\lambda) - \delta_{\sigma\sigma'} (\mu\lambda|\kappa\nu) \right] D_{\lambda\kappa\sigma'}$$

- Generalized eigenvalue problem with operator $\mathbf{F}_\sigma$ depending nonlinearly on the occupied MO coefficients through $\mathbf{D}_\sigma$.
- Solved iteratively using damping, level shifting, DIIS extrapolation
- Integral direct SCF (Almlöf, Häser, Ahlrichs): Integrals $(\mu\nu|\kappa\lambda)$ are not stored, but computed "on the fly" in each iteration (if needed). Avoids large I/O bottleneck.