# State of the basis in electronic structure theory

### Sketching the scene beyond Gaussian-type orbitals

Michael F. Herbst

MathCCES lunch seminar

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Background | cGTO | ETOs | Grid-based | Plane waves | Addendum | A & Q
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Electronic Schrödinger operator

# Electronic structure theory

- $N_{\text{elec}}$ electrons in chemical system
- Spectrum of $\hat{\mathcal{H}}_{N_{\text{elec}}}$

$$\hat{\mathcal{H}}_{N_{\text{elec}}} \equiv \sum_{i=1}^{N_{\text{elec}}} -\frac{1}{2}\Delta_i + \sum_{i=1}^{N_{\text{elec}}} \hat{\mathcal{V}}_{\text{Nuc},i} + \sum_{i=1}^{N_{\text{elec}}} \sum_{j=i+1}^{N_{\text{elec}}} \frac{1}{r_{ij}}$$

with

$$-\frac{1}{2}\Delta_i \qquad \text{Kinetic energy of electrons}$$

$$\hat{\mathcal{V}}_{\text{Nuc},i} \qquad \text{Electron-nuclear interaction}$$

$$\frac{1}{r_{ij}} \qquad \text{Electron-electron interaction}$$

# Schrödinger operator domain

- $N_{\text{elec}}$ electrons $\Rightarrow 3N_{\text{elec}}$ coords

- Electrons are fermions:

$$D(\hat{\mathcal{H}}_{N_{\text{elec}}}) = H^2(\mathbb{R}^{3N_{\text{elec}}}, \mathbb{C}) \cap \bigwedge^{N_{\text{elec}}} L^2(\mathbb{R}^3, \mathbb{C})$$

where

$$\bigwedge^{N_{\text{elec}}} L^2(\mathbb{R}^3, \mathbb{C}) \equiv \text{span} \left\{ \psi_1 \wedge \psi_2 \wedge \cdots \wedge \psi_{N_{\text{elec}}} \right|$$
$$\left. \psi_i \in L^2(\mathbb{R}^3, \mathbb{C}) \, \forall i = 1, \ldots N_{\text{elec}} \right\}$$

- One-particle function $\psi_i$ (orbitals)

# Schrödinger operator discretisation (1)

- HVZ theorem
- Ritz-Galerkin / Courant-Fischer
- Ground state (lowest eigenvalue):

$$E_0 \leq \min_{\Phi \in \operatorname{span} \mathbb{B}_{N_{\mathrm{elec}}}} \frac{\left\langle \Phi \middle| \hat{\mathcal{H}}_{N_{\mathrm{elec}}} \Phi \right\rangle}{\langle \Phi | \Phi \rangle}$$

where

$$\mathbb{B}_{N_{\mathrm{elec}}} \subset \bigwedge^{N_{\mathrm{elec}}} H^1(\mathbb{R}^3, \mathbb{C}) \subset H^1(\mathbb{R}^{3N_{\mathrm{elec}}, \mathbb{C}})$$

is $N_{\mathrm{elec}}$-particle basis

# Schrödinger operator discretisation (2)

- Choose one-particle basis

$$\mathbb{B}_1 = \{\varphi_\nu\}_{\nu \in \mathcal{I}_{\mathrm{bas}}} \subset H^1(\mathbb{R}^3, \mathbb{C})$$

- Construct $N_{\mathrm{orb}}$ orthonormal orbitals

$$\{\psi_i\}_{i=1,\dots,N_{\mathrm{orb}}} \subset \mathrm{span}\,\mathbb{B}_1$$

- Construct Slater determinants

$$\mathbb{B}_{N_{\mathrm{elec}}} = \Big\{ \psi_{\sigma(1)} \wedge \psi_{\sigma(2)} \wedge \cdots \wedge \psi_{\sigma(N_{\mathrm{elec}})} \Big|$$

$$\sigma \text{ permutation from } \{1 \dots N_{\mathrm{elec}}\} \text{ to } \{1 \dots N_{\mathrm{orb}}\}\Big\}$$

as $N_{\mathrm{elec}}$-particle basis.

# Questions

- $\mathbb{B}_{N_{\text{elec}}}$ grows as $O(N_{\text{bas}}^{N_{\text{elec}}})$
  - $\Rightarrow$ Use $\{\psi_i\}_i$ to construct subset

- How to construct $\psi_i$?
  - Yield best single determinant
  - $\Rightarrow$ Hartree-Fock (HF) or density-functional theory (DFT)

- Construction of subset of $\mathbb{B}_{N_{\text{elec}}}$?
  - e.g. Post-HF

- Which functions to choose in $\mathbb{B}_1$?

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# Self-consistent field methods (HF and DFT)

- Single determinant minimiser to trial energy functional

- Euler-Lagrange equations:

$$\underbrace{\left(-\frac{1}{2}\Delta + \hat{\mathcal{V}}_{\mathrm{Nuc}} + \hat{\mathcal{V}}_{2\mathrm{e}}\left[\,\{\psi_i\}_{i\in I}\,\right]\right)}_{=\hat{\mathcal{F}}}\psi_i = \varepsilon_i\psi_i$$

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}$$

with

$-\dfrac{1}{2}\Delta$        Kinetic energy of electrons

$\hat{\mathcal{V}}_{\mathrm{Nuc}}$        Electron-nuclear interaction

$\hat{\mathcal{V}}_{2\mathrm{e}}\left[\,\{\psi_i\}_{i\in I}\,\right]$        Electron-electron interaction

- Non-linear system of partial differential equations

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Seeking a basis

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Seeking a basis

# An ideal basis

- Represents physics well
- Results reliable
  - Error margin known
  - Systematic improvement possible
- Prior knowledge
  - Little required
  - If available: Can be incorporated
- Integrals and eigenproblem are feasible
- ⇒ In reality need a good compromise

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# An ideal basis

- E.g. hydrogen atom ground state

$$\Psi_{1s}(r, \theta, \phi) = \sqrt{\frac{Z^3}{\pi}} \exp(-Zr)$$

- Kato's electron-nuclear cusp condition[1]:

$$\frac{\partial \langle \Psi(\underline{\boldsymbol{x}}) \rangle}{\partial r_i} \bigg|_{\underline{\boldsymbol{r}}_i = \underline{\boldsymbol{R}}_A} = -Z_A \langle \Psi(\underline{\boldsymbol{x}}) \rangle |_{\underline{\boldsymbol{r}}_i = \underline{\boldsymbol{R}}_A}$$

where $\langle \Psi(\underline{\boldsymbol{x}}) \rangle |_{\underline{\boldsymbol{r}}_i = \underline{\boldsymbol{R}}_A}$ is the average value if $\underline{\boldsymbol{r}}_i = \underline{\boldsymbol{R}}_A$ fixed.

- electron-electron cusp[1] as $r_{ij} \to 0$

- Energy-dependent exponential decay[1]

[1]Kato 1957

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# An ideal basis

Matrix representation of $\hat{\mathcal{H}}_{N_{\text{elec}}}$ involves integrals

$$(\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\varphi_\mu^*(\underline{r}_1)\varphi_\nu(\underline{r}_1)\,\varphi_\kappa^*(\underline{r}_2)\varphi_\lambda(\underline{r}_2)}{\|\underline{r}_1 - \underline{r}_2\|_2}\,\mathrm{d}\underline{r}_1\,\mathrm{d}\underline{r}_2.$$

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contracted Gaussian-type orbitals

# Atom-centred basis functions

- Molecular density to good approximation sum of atomic densities

- Typical ansatz

$$\varphi(\underline{r}_\mu) = R(r_\mu) Y_l^m(\theta_\mu, \phi_\mu)$$

where

$$(r_\mu, \theta_\mu, \phi_\mu) \equiv \underline{r}_\mu = \underline{r} - \underline{R}_\mu$$

- $\underline{R}_\mu$ is the centre, i.e. atom position
- $\Rightarrow$ Intrinsic assumption: Electrons close to atoms

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contracted Gaussian-type orbitals

# Gaussian-type orbitals

- Use Gaussian radial part

$$R_\mu^{\mathrm{GTO}}(r) = N_\mu r^{l_\mu} \exp(-\alpha_\mu r^2)$$

- Dense in $H^1$, but slow convergence
- Not physical
- Very feasible integrals $(\mu\nu|\kappa\lambda)$
- Not used in practice

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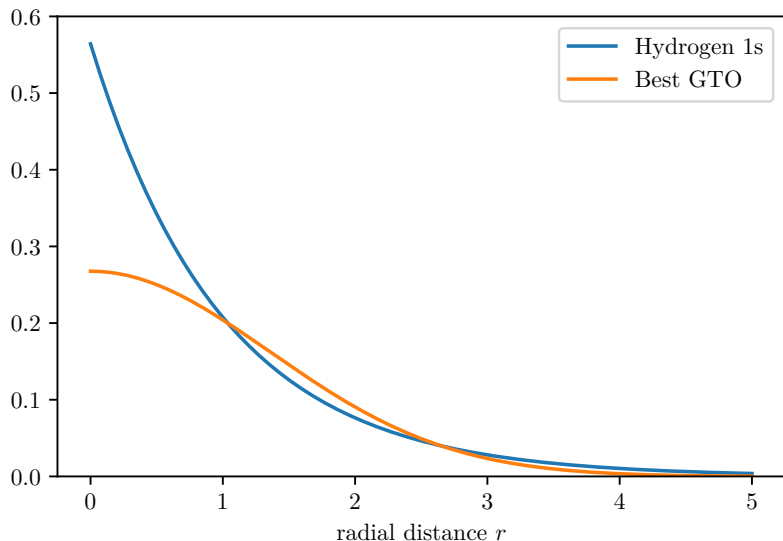- Very feasible integrals $(\mu\nu|\kappa\lambda)$
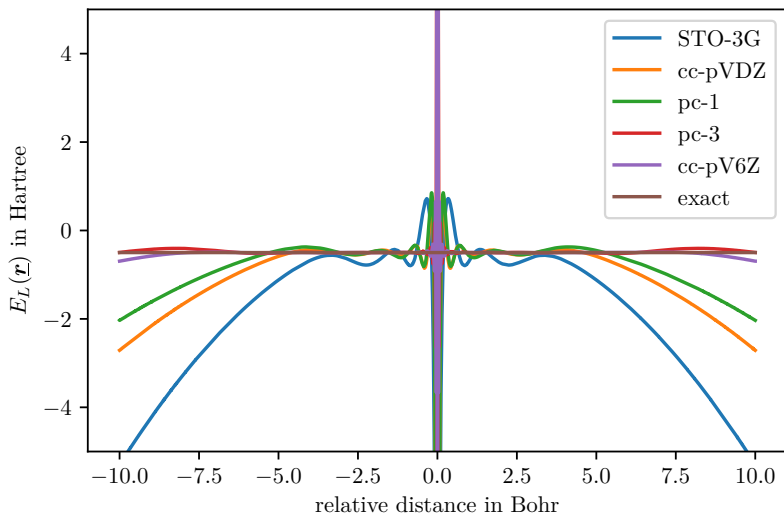- Not used in practice

# Gaussian-type orbitals

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contracted Gaussian-type orbitals

# contracted Gaussian-type orbitals

- *Fixed* linear combination of primitive Gaussians

$$R_\mu^{\mathrm{cGTO}}(r) = r^{l_\mu} \sum_i^{N_{\mathrm{contr}}} c_{\mu,i} \exp(-\alpha_{\mu,i} r^2)$$

- Integrals still feasible
- Fitted to
    - exponential shape
    - achieve best energies
    - achieve best properties
$\Rightarrow$ Effectively split parameter space

# Discretising hydrogen

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contracted Gaussian-type orbitals

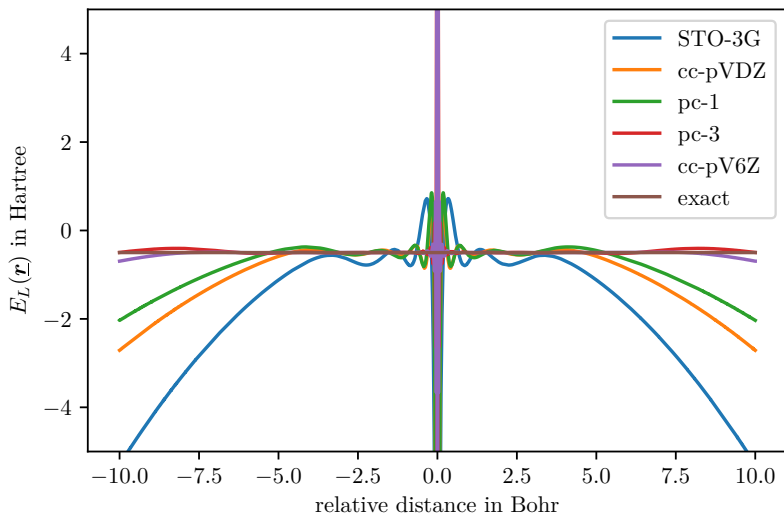# Discretising hydrogen

Local energy

$$E_L(\underline{r}) = \frac{\left(\hat{\mathcal{H}}_{N_{\mathrm{elec}}}\Phi\right)(\underline{r})}{\Phi(\underline{r})}$$

Background | cGTO | ETOs | Grid-based | Plane waves | Addendum | A & Q
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contracted Gaussian-type orbitals

# Discretising hydrogen

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contracted Gaussian-type orbitals

# Notes and observations

- Pragmatic compromise:
  - Not physical
  - Chemistry is about energy differences
  - Mostly work by error compensation
- Special basis sets for special use cases:
  - correlation-consistent construction
  - Core polarisation
  - Augmentation
- Over-complete:
  - Numerical issues

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Explicitly correlated methods

# Explicitly correlated methods

- Fundamental problem of one-electron basis functions:
  - electron-electron cusp *not* taken into account
- ⇒ Slow convergence of Post-HF methods
- ⇒ Include dependency $r_{ij}$ in basis

- Boys, Singer: Exponentially correlated Gaussians (ECG):

$$\Phi_k(\underline{x}) = \exp\left(-\sum_{i=1}^{N_{\text{elec}}} \alpha_{k,i} \left\|\underline{r}_i - \underline{R}_{k,i}\right\|^2 - \sum_{i<j} \gamma_{k,ij} r_{ij}^2\right)$$

where $\underline{R}_{k,i}$ are Gaussian centres

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Explicitly correlated methods

# Properties of ECGs

- Analytically evaluatable many-electron integrals
- Dense $N_{\text{elec}}$-electron basis
- Cusp condition not perfect
- Many non-linear parameters $\gamma_{k,ij}$

$\Rightarrow$ Only keep one $\gamma_{k,ij}$ per $k$.

$\Rightarrow$ Gaussian-type geminals:

$$g_k(\underline{r}_1, \underline{r}_2) = \exp\left(-\alpha_{k,1}\left\|\underline{r}_1 - \underline{R}_{k,1}\right\| - \alpha_{k,2}\left\|\underline{r}_2 - \underline{R}_{k,2}\right\| - \gamma_k r_{12}^2\right)$$

- Maximal 4-electron integrals

# Geminal methods

$$g_k(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2) = f(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2) \exp\left(-\alpha_{k,1} \left\| \underline{\boldsymbol{r}}_1 - \underline{\boldsymbol{A}}_k \right\|\right) \exp\left(-\alpha_{k,2} \left\| \underline{\boldsymbol{r}}_2 - \underline{\boldsymbol{B}}_k \right\|\right)$$

- Generalised geminal:
  - linear $f(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2) = r_{12}$
  - Slater-type $f(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2) = \exp(-\gamma_k r_{12})$

- Introduced in context of *pair theories*
  - Post-HF methods: MP2, CCD, CCSD(T)
  - R12 or F12 methods

- Lead to additional terms and geminal parameters
- Optimised alongside vs. predetermined

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Explicitly correlated methods

# Notes and observations

- Leads to challenging equations
- 4-electron integrals are very expensive
  - ⇒ Aproximations allow factorisation into one- and two-electron integrals

- Effect diminishes for:
  - large Gaussian basis sets
  - higher-order Post-HF methods
- Minor effect on fundamental cGTO issues

# Contents

## Exponential-type orbitals (ETO)

- Hydrogen-atom radial part

$$R_{nl}(r) = N_{nl} \left( \frac{2Zr}{n} \right)^l \exp\left( -\frac{Zr}{n} \right) \ {}_1F_1\left( l+1-n \middle| 2l+2 \middle| \frac{2Zr}{n} \right)$$

- Not used as basis:
  - Classical turning point: $O(n^2)$
  - Too fast expansion
  - Not complete

- Template for exponential-type orbitals

# Slater-type orbitals

- Functional form:

$$R_\mu(r) = N_\mu r^{n_\mu - 1} \exp(-\zeta_\mu r)$$

- $\zeta_\mu$: Fitted / predetermined atomic exponents

- Physical shape

- BUT: Integrals difficult

- Not complete

- Fast convergence of e.g. NMR properties[1]

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[1]Hoggan 2009

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Sturmian-type orbitals

# Coulomb-Sturmians

- Iso-energetic solutions $\varphi_{nlm}$ to hydrogen-like equation[1]

$$\left(-\frac{1}{2}\Delta - \beta_n \frac{Z}{r}\right)\varphi_{nlm}(\underline{r}) = E\varphi_{nlm}(\underline{r})$$

- Scaling factor $\beta_n$ chosen to uniform energy:

$$\beta_n = \frac{kn}{Z} \quad \Rightarrow \quad E = -\frac{k^2}{2}$$

- $\varphi_{nlm}$ look like hydrogenic orbitals with $\frac{Z}{n}$ replaced by $k$
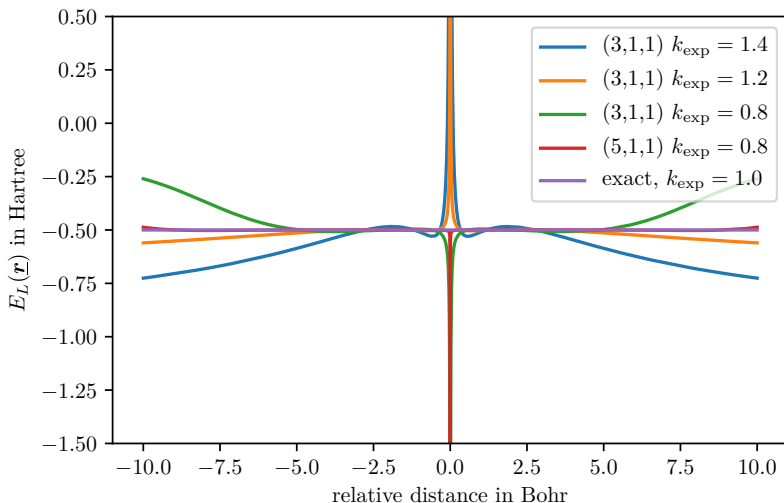
- Radial part $R_{nl}$ satisfies

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l(l+1)}{2r^2} - \frac{nk_{\exp}}{r} - E\right)R_{nl}(r) = 0.$$

$\Rightarrow$ Sturm-Liouville equation[2]

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[1]Shull and Löwdin 1959
[2]Rotenberg 1962, Rotenberg 1970

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Sturmian-type orbitals

# Discretising hydrogen

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Sturmian-type orbitals

# Coulomb-Sturmians properties

- Only atoms: Different Sturmians for molecules required

- Complete (Schauder) basis for $H^1(\mathbb{R}^3)$[1]

- Correctly represent nuclear cusp

- Proper exponential decay for large $r$

- All functions have the same $k_{exp}$

- One-electron integrals sparse and analytic

- Two-electron integrals sparse tensor contraction

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[1]Klahn and Bingel 1977

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Sturmian-type orbitals

# Other Sturmian-type orbitals

- Molecular Sturmians
  - One-to-one onto hyperspherical harmonics[1]

- Generalised Sturmians[2]
  - Geometry built into basis ($N_{\text{elec}}$-particle basis)

- $d$-dimensional hyperspherical harmonic basis sets[3]
  - Strongly interacting few-body systems

- Ionising Sturmians[4]

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[1]Aquilanti 1992, Aquilanti 2003, Coletti 2013, Calderini 2012
[2]Avery 2012
[3]Avery 2018
[4]Mitnik 2011, Randazzo 2015, Granados 2016

## Contents

# Grid-based approaches

- Fully numerical vs. radial only

- Challenges:
  - Discontinuity at nuclei
  - Non-locality of $\hat{\mathcal{H}}_{N_{\mathrm{elec}}}$
  - Basis size

- Perspectives:
  - Error control
  - No implicit bias

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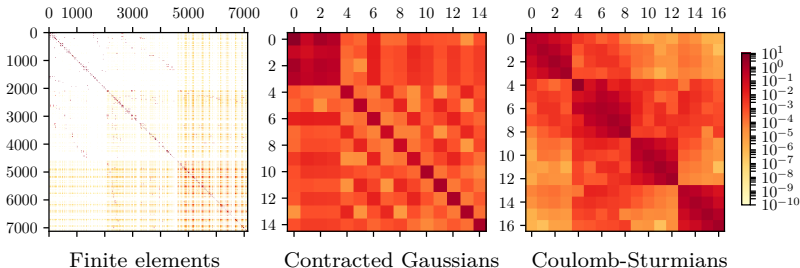  - No implicit bias

# Finite elements

- Affine, conformal mesh, continuous FEs

- Example: Hartree-Fock problem

- After discretisation:

$$\mathbf{F}[\mathbf{C}]\,\mathbf{C} = \operatorname{diag}(\varepsilon_1, \ldots, \varepsilon_n)\,\mathbf{S}\,\mathbf{C}$$

# Finite elements

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Finite elements       Contracted Gaussians       Coulomb-Sturmians

# Example: Evaluating the Coulomb integral

$$J_{jk} = \int_\Omega \varphi_j(\underline{r}) \, \hat{\mathcal{V}}_H(\underline{r}) \, \varphi_k(\underline{r}) \, \mathrm{d}\underline{r}$$

$$\hat{\mathcal{V}}_H(\underline{r}_1) = \sum_{i \in \mathrm{occ}} \int_\Omega \frac{|\psi_i(\underline{r}_2)|^2}{r_{12}} \, \mathrm{d}\underline{r}_2$$

- $\hat{\mathcal{V}}_H(\underline{r})$ is a local potential
- Obtained by solving Poisson eq$^n$:

$$-\Delta \hat{\mathcal{V}}_H(\underline{r}) = 4\pi\rho(\underline{r}) \qquad\qquad \underline{r} \in \Omega$$

- Need higher polynomial degree for Poisson problem
- Which boundary conditions?
- Hartree-Fock exchange non-local $\Rightarrow$ More challenging

Background | cGTO | ETOs | **Grid-based** | Plane waves | Addendum | A & Q
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Finite elements

## Notes and observations

- Non-locality of HF exchange:
  - Contraction-based ansatz
  - Focus on density-functional theory

- No general rigorous error estimates (yet):
  - Use simple heuristics
  - ⇒ Adaptive refinement
  - Error controlable

- Discontinuity at nuclei
  - Employ effective core potentials
  - But: No longer fully black box

| Background | cGTO | ETOs | **Grid-based** | Plane waves | Addendum | A & Q |
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Multiwavelets

# Multi-resolution analysis (MRA)

- Sequence of subspaces

$$0 \subset V_0 \subset V_1 \subset \cdots \subset V_n \subset L^2([0,1])$$

- Necessary to form MRA:
  - For all $m \in \mathbb{Z}$: $f \in V_i \Rightarrow f(x - m2^{-i})$ in $V_i$
  - $j > i \Rightarrow \forall f \in V_i \ \exists g \in V_j : \ \forall x \in \mathbb{R} \ g(x) = f(2^{j-i}x)$
  - $j > i \Rightarrow V_i \subset V_j$
  - $\bigcup_{i=0}^{n} V_i \subset L^2([0,1])$ dense

- Telescoping series:

$$V_n = V_0 \oplus \underbrace{(V_1 \ominus V_0)}_{=W_1} \oplus \underbrace{(V_2 \ominus V_1)}_{=W_2} \oplus \cdots \oplus \underbrace{(V_n \ominus V_{n-1})}_{=W_n}$$

where $\oplus$ is direct sum, $\ominus$ is orthogonal complement

| Background | cGTO | ETOs | **Grid-based** | Plane waves | Addendum | A & Q |
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Multiwavelets

## Multiwavelets

- MRA for solving PDEs[1]

$$V_0^k \subset V_1^k \subset \cdots \subset V_n^k \subset L^2([0,1])$$

where

$$V_n^k = \left\{ f \,\middle|\, \forall l = 0, \ldots 2^{n-1} : \text{Restriction of } f \text{ to } \left(2^{-n}l, 2^{-n}(l+1)\right) \right.$$
$$\left. \text{is polynomial with degree less than } k \right\}$$

- Computational domain mapped to $[0, 1]$

- Tensor-product generalisation

- Systematic construction for $V_n^k$ and $W_n^k$

- Discontinuous polynomials on grid: In $V_0^k$: Roughly DG FE

[1]Alpert 2002

| Background | cGTO | ETOs | **Grid-based** | Plane waves | Addendum | A & Q |
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Multiwavelets

# Multiwavelets: Systematic construction

- Basis for $V_0^k$: $\{\phi_j\}_j$ where

$$\phi_j = \sqrt{2i+1}P_i(2x+1)$$

  scaled Legendre polynomials

- Mother scaling functions
  - $\{\phi_{jl}^n\}_{jl}$ basis for $V_n^k$ with $j = 0, \ldots, k-1$, $l = 0, \ldots, 2^n - 1$,

$$\phi_{jl}^n = 2^{n/2}\phi_j(2^n x - l)$$

- Mother wavelets: Basis to $W_1^k$
  - First $k$ moments are zero
  - Bases for $W_n^k$ analogous to $V_n^k$
- $V_n^k$ and $W_n^k$ of dimension $2nk$

Background | cGTO | ETOs | **Grid-based** | Plane waves | Addendum | A & Q
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Multiwavelets

# Multiwavelets: Properties

- Function has two discrete representations:
  - On finest $V_n^k$
  - On $V_0^k$ plus corrections via $W_1^k, \ldots, W_n^k$
- Multiwavelets: Basis organised in groups of functions

- Error estimate:
  - Based on moments of interpolated
  - Can always increase $n$
  - Local refinement and coarsening
  - $\Rightarrow$ Adaptive refinement strategy
- $\Rightarrow$ Adaptive, sparse, hierarchical decomposition

# Notes and observations

- Fully hidden numerics[1]
⇒ Simple error control and no bias
- Massively parallel

- Regularisation of nuclear cusp[2]
  - Related to explicitly correlated methods
⇒ Multiple electronic structure theory methods with guaranteed accuracy

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[1]Harrison 2016
[2]Bischoff 2014

# Contents

## Plane waves

- Modelling solid-state / condensed matter physics

- Periodic boundary conditions

- Plane-wave expansion

$$\psi_i(\underline{\boldsymbol{x}}) = \frac{1}{\sqrt{\Omega}} \sum_{\underline{\boldsymbol{G}}} c_{\underline{\boldsymbol{G}}} e^{\imath \underline{\boldsymbol{G}} \cdot \underline{\boldsymbol{x}}}$$

where

- Unit cell volume $\Omega$

- Reciprocal lattice vectors $\underline{\boldsymbol{G}}$

- Range of $\mathbf{G}$ limited by kinetic energy cutoff

$$\frac{G^2}{2} < E_{\text{cut}}$$

## Pseudopotentials (Problem)

- Core orbitals:
    - Localised in atomic sphere
    - Largely unaffected by chemistry

- Valence orbitals:
    - Interstitial region: Rather regular
    - Atomic sphere: Oscillations
    - Small energy gaps (e.g. metals)
    - Pauli exclusion / orthogonality

$\Rightarrow$ Need larger energy cutoff

# Pseudopotentials (Idea)[1]

- Remove core orbitals by projection
- Use repulsive potential term $\hat{\mathcal{V}}_{\mathrm{PP}}$
  - Model Pauli exclusion
  - Smoother valence orbitals
  - Lower energy cutoff
- Pseudopotentials generated from atomic calculations
- Valence orbital energies should stay unchanged

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[1]Hamann 1979, Bachelet 1982, Vanderbilt 1990, Kresse 1999

## Pseudopotentials (Mechanism)

- Original SCF problem $\hat{\mathcal{F}}\psi_i = \varepsilon_i \psi_i$

- Introduce pseudo wavefunction (and orbitals)

$$\psi_i = \tilde{\psi}_i - \sum_{c \in \text{core}} \psi_c \left\langle \psi_c | \psi_i \right\rangle$$

where $\psi_c$ Atomic core orbital inside cutoff

- Construct

$$\hat{\mathcal{V}}_{\text{PP}} \tilde{\psi}_i = \sum_c \left( \varepsilon_i - \varepsilon_c \right) \psi_c \left\langle \psi_c \middle| \tilde{\psi}_i \right\rangle$$

- Solve

$$\left( \hat{\mathcal{F}} + \hat{\mathcal{V}}_{\text{PP}} \right) \tilde{\psi}_i = \varepsilon_i \tilde{\psi}_i$$

- Outside cutoff radius: All-electron and pseudo wavefunction identical

## Projector-augmented wave method

- Generalisation of pseudopotentials[1]

- Smoothening is linear transformation

$$\psi = \hat{\mathcal{T}}\tilde{\psi}$$

  transforms pseudo orbital to all-electron orbital

- Augmentation region $\Omega_M$ around nuclei

- Obtain

$$\hat{\mathcal{T}} = 1 + \sum_{\nu} \left( \phi_\nu - \tilde{\phi}_\nu \right) p_\nu$$

  - $\phi_\nu$: Set of all-electron partial waves

  - $\tilde{\phi}_\nu$: Set of pseudo partial waves

  - $p_\nu$: Set of projector functions

[1]Kresse 1999

# PAW parameters[1]

- $\phi_\nu$ determined by atomic DFT

- Inside $\Omega_M$: $\tilde{\phi}_\nu$ chosen smooth (Polynomial or Bessel)
- Outside $\Omega_M$: $\tilde{\phi}_\nu = \phi_\nu$

- $\left\langle p_\nu \middle| \tilde{\phi}_\mu \right\rangle = \delta_{\mu\nu}$
- $p_\nu$ determined by solving correction equation in $\Omega_M$

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[1]Enkovaara 2010

# Notes and observations

- Pseudopotentials:
  - Not all-electron: Core and virtuals altered
  - State-of-the-art

- Projector-augmented wave:
  - Usually combined with frozen core
  - Fully grid based implementations[1]
  - Resemblance with regularisation of electron-nuclear cusp in MRA

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[1]Enkovaara 2010

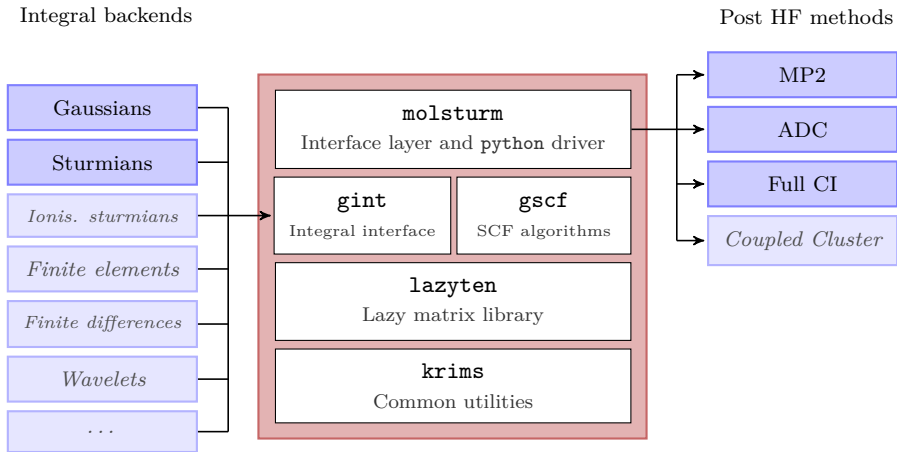# Contents

## Other approaches worth mentioning

- Grid-based fast multipole method[1]

- Finite-differences[2]

- Dual grids and mixed bases[3]

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[1]Toivanen 2015
[2]Soler 2002
[3]Yamakawa 2005, Kurashige 2007, Watson 2008

| Background | cGTO | ETOs | Grid-based | Plane waves | **Addendum** | A & Q |
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molsturm

# molsturm structure



Integral backends

Post HF methods

Background | cGTO | ETOs | Grid-based | Plane waves | **Addendum** | A & Q
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Conclusions

# Conclusions

- Contracted Gaussian-type orbitals
  - well-established

- Exponential-type orbitals
  - physical for bound systems

- Grid-based approaches
  - Error control and no bias
  - Locality built into basis

- Plane wave basis
  - Physical for extended systems

# Outlook

- Massively parallel architectures:
  - Grid-based approaches
  - Contraction-based methods
- Highly accurate calculations:
  - Grid-based approaches challenging beyond single determinant
- Probing nucleus-electron interaction:
  - Exponential-type orbitals
- Exploring further basis functions
  - Molecular Sturmians
  - Mixed basis sets

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**HGS MathComp**

# Questions?

- michael.herbst@iwr.uni-heidelberg.de
- https://michael-herbst.com

- Download PhD thesis:

        https://michael-herbst.com/phd-thesis.html