A new 3D grid method for accurate electronic structure calculation of polyatomic molecules: The Voronoi-cell finite difference method

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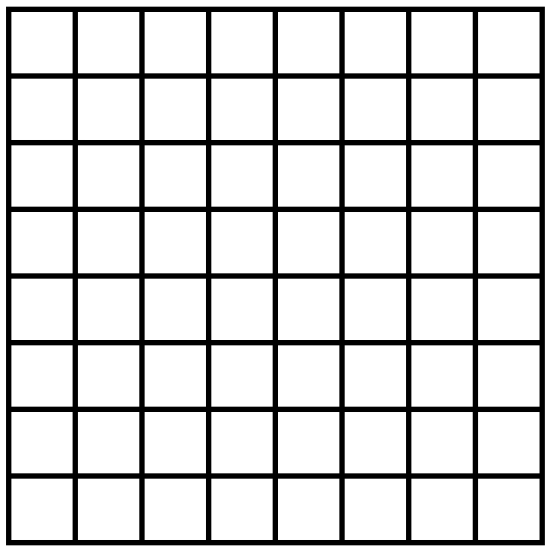
Abstract

We introduce a new computational method on *unstructured* grids in the three-dimensional (3D) spaces to investigate the electronic structure of polyatomic molecules. The Voronoi-cell finite difference (VFD) method realizes a simple discrete Laplacian operator on *unstructured* grids based on Voronoi cells and their natural neighbors. The feature of *unstructured* grids enables us to choose intuitive pictures for an optimal molecular grid system. The new VFD method achieves highly adaptability by the Voronoi-cell diagram and yet simplicity by the finite difference scheme. It has no limitation in local refinement of grids in the vicinity of nuclear positions and provides an explicit expression at each grid without any integration. This method augmented by *unstructured* molecular grids is suitable for solving the Schrödinger equation with the realistic 3D Coulomb potentials regardless of symmetry of molecules. For numerical examples, we test accuracies for electronic structures of one-electron polyatomic systems: linear H_2^+ and triangular H_3^{++}. We also extend VFD to the density functional theory (DFT) for many-electron polyatomic molecules.

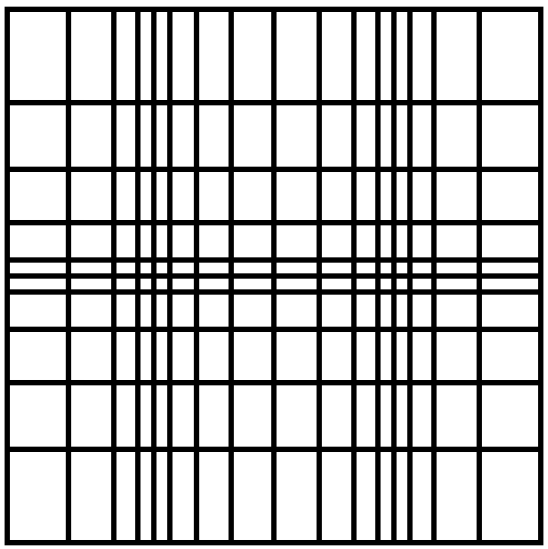
Introduction

- Voronoi-cell FD (VFD): based on Voronoi diagram and its natural neighbors
- *Unstructured* grids: optimal molecular grids
- High adaptability like FE: no limitation on local grid refinement
- Simplicity like FD: a simple and explicit matrix form of the discrete Laplacian operator
- Direct solutions of the Schrödinger / Poisson equations on *unstructured* grids
- No integration for constructing the Hamiltonian matrix
- 3D realistic Coulomb potential

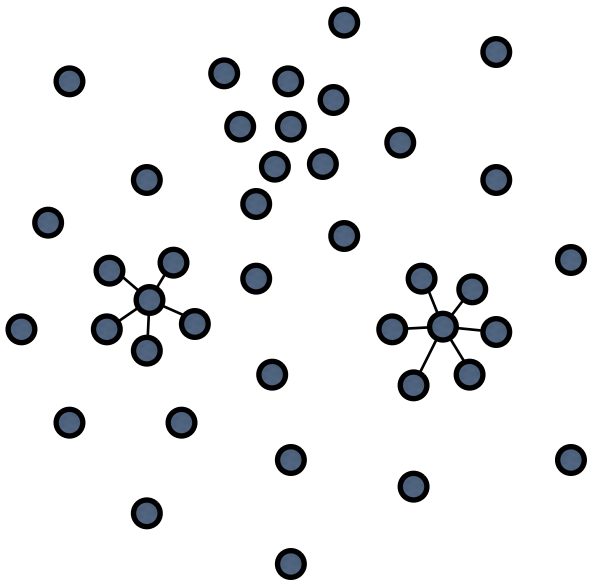
Unstructured grids



uniformly
structured

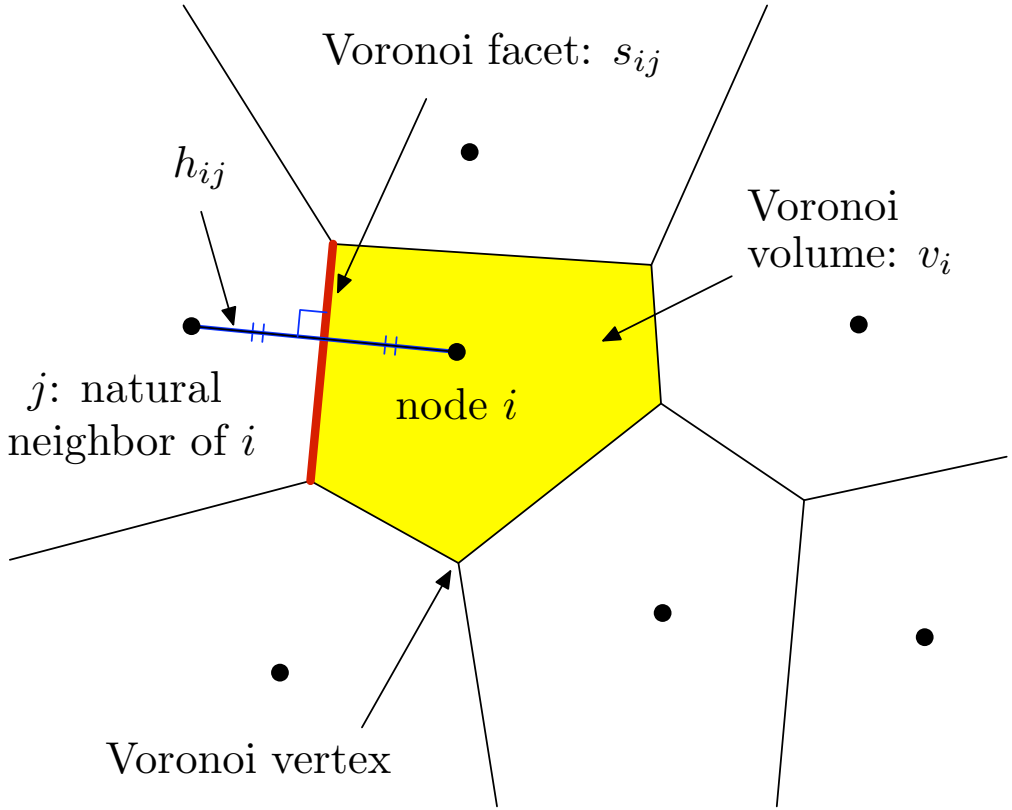


non-uniformly
structured



randomly
unstructured

Voronoi diagram



Voronoi cell: uniquely defined on *unstructured* grids in *n*-dimension

$$T_i = \{\mathbf{x} \in \mathbb{R}^n : d(\mathbf{x}, \mathbf{x}_i) \leq d(\mathbf{x}, \mathbf{x}_j) \text{ for } \forall j \neq i\}$$

Voronoi-cell FD

Differentiation

$$\nabla^2\varphi = \lim_{\int_V d\tau \to 0} \frac{\int_S \nabla\varphi \cdot \mathbf{n}\, d\sigma}{\int_V d\tau} \quad \text{(Gauss's theorem)}$$

i) volume and surface integrals are computed by Voronoi volumes and Voronoi facet areas

ii) a simple difference scheme is used for directional derivatives

Discrete Laplacian: $\left(\nabla^2\varphi\right)_i = \frac{1}{v_i} \sum_{j}^{\substack{\text{natural} \\ \text{neighbors}}} \frac{\varphi_j - \varphi_i}{h_{ij}} s_{ij}$

Integration

Simple nodal quadrature using Voronoi volumes

$$\int_V f(\mathbf{x}) d\tau \approx \sum_i f(\mathbf{x}_i) v_i$$

PDE solver by VFD

Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + U(\mathbf{x})\right)\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

$$\Rightarrow (\tilde{\mathbf{T}} + \mathbf{U})\tilde{\mathbf{C}} = \mathbf{E}\tilde{\mathbf{C}}$$

$$\tilde{T}_{ij} = \begin{cases} -\dfrac{1}{2\sqrt{v_i v_j}}\dfrac{s_{ij}}{h_{ij}} & (i \neq j), \\ \dfrac{1}{2v_i}\displaystyle\sum_{k}^{\text{neighbors}} \dfrac{s_{ik}}{h_{ik}} & (i = j) \end{cases}$$

After symmetrization

$$U_{ij} = \delta_{ij} U(\mathbf{x}_i)$$

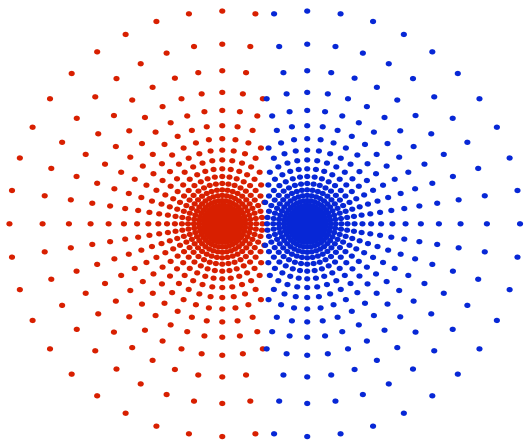
Potential is given by a diagonal matrix without any integration

Poisson equation

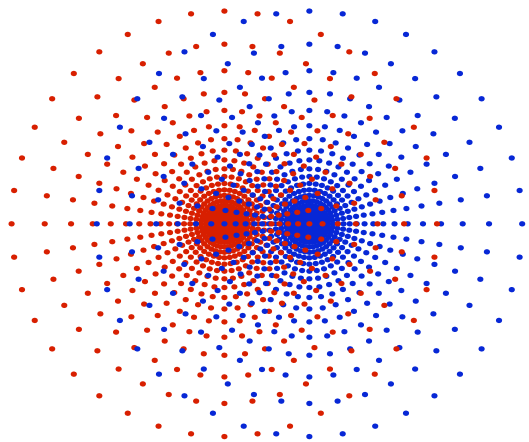
$$\nabla^2 v_{\mathrm{h}}(\mathbf{x}) = -4\pi\rho(\mathbf{x}) \Rightarrow \mathbf{v}_{\mathrm{h}} = -4\pi\mathbf{L}^{-1}\boldsymbol{\rho}$$

Easy to incorporate the boundary condition within **L**

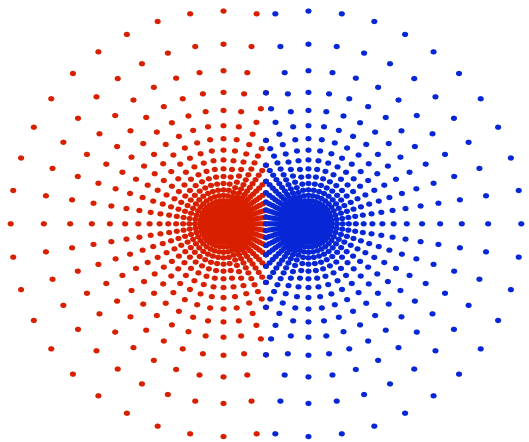
Molecular grids



non-overlap



overlap



squeezed

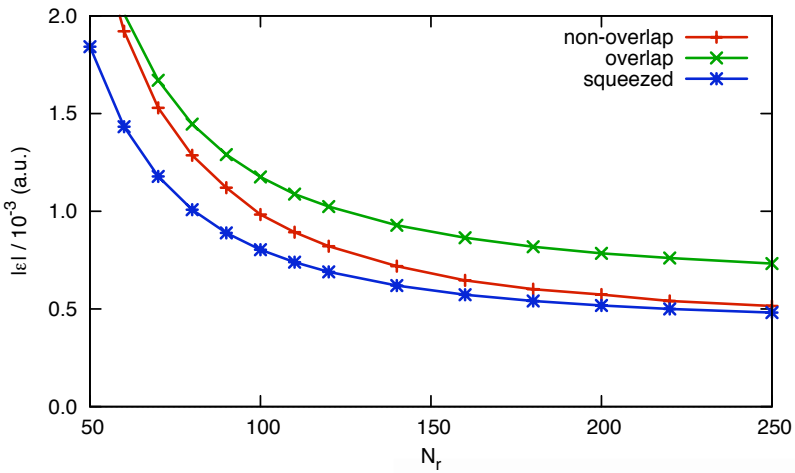
Molecular grids are intuitively constructed by combination of spherical atomic grids in 3D

– radial part:

$$r(x) = L\frac{1+x}{1-x} \quad (-1 < x < 1)$$

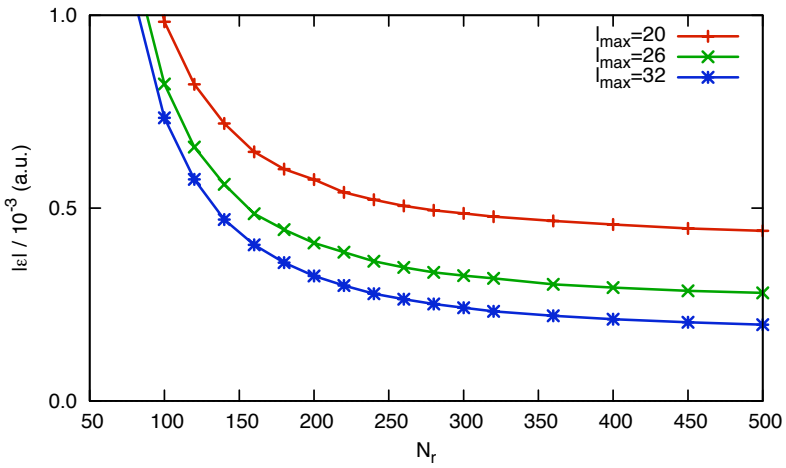
– angular part: Lebedev grids

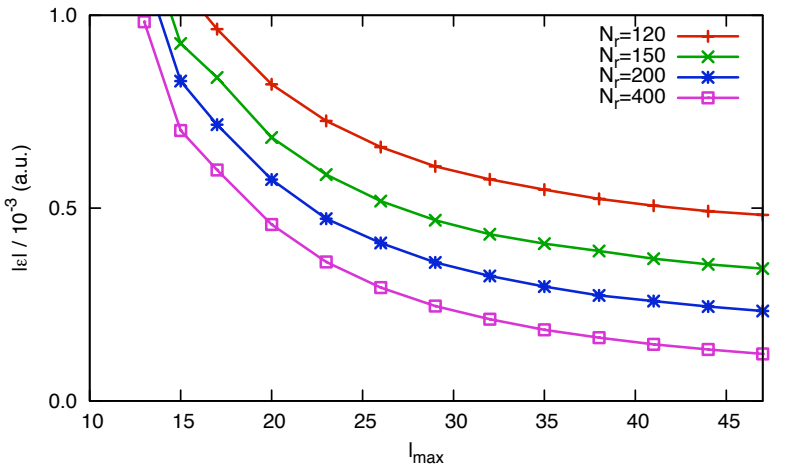
Comparison of different types



Accuracy assessment

Errors of H_2^+ ground energies by varying N_r and l_{max}





Errors of H_2^+ bound energies

Symmetry	Exact	LCAO–GTO		VFD	
		ε(a.u.)	$\lvert\varepsilon\rvert$(%)	ε(a.u.)	$\lvert\varepsilon\rvert$(%)
$1\sigma_g$	−1.102 634 21	1.41×10^{-6}	0.000	-1.22×10^{-4}	0.011
$1\sigma_u$	−0.667 534 39	1.69×10^{-6}	0.000	-1.55×10^{-4}	0.023
$1\pi_u$ (2)	−0.428 771 82	1.09×10^{-4}	0.026	-7.92×10^{-5}	0.018
$2\sigma_g$	−0.360 864 88	5.29×10^{-5}	0.015	-6.65×10^{-5}	0.018
$2\sigma_u$	−0.255 413 17	2.49×10^{-4}	0.097	-7.14×10^{-5}	0.028
$3\sigma_g$	−0.235 777 63	3.46×10^{-3}	1.468	-1.20×10^{-4}	0.051
$1\pi_g$ (2)	−0.226 699 63	4.23×10^{-3}	1.867	-1.81×10^{-4}	0.080

Basis set: aug-cc-pV6Z / Grid parameters: N_r=400, L=1, l_{max}=47 / H_2^+: R=2.0 a.u.

Errors of triangular H_3^{++} bound energies

Symmetry	FE	LCAO–GTO	VFD	Difference
$1a_1'$	−1.909 570 99	−1.909 569	−1.909 787	-2.18×10^{-4}
$1e'$(2)		−1.138 578	−1.138 979	-4.02×10^{-4}
$1a_2''$		−0.869 699	−0.870 008	-3.10×10^{-4}
$2a_1'$		−0.704 969	−0.705 131	-1.62×10^{-4}
$2e'$(2)		−0.534 978	−0.535 372	-3.93×10^{-4}
$3e'$(2)		−0.484 387	−0.485 081	-6.94×10^{-4}

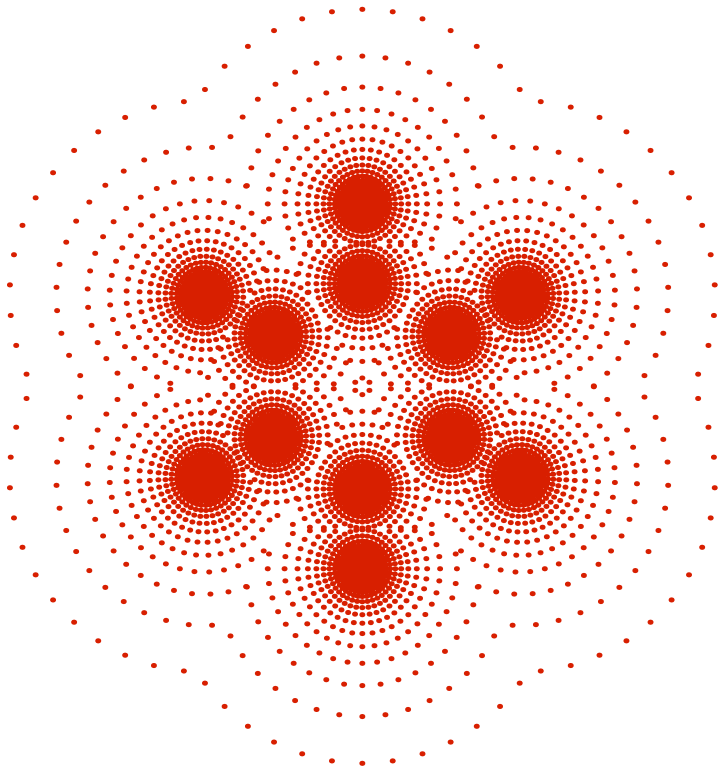
Basis set: aug-cc-pV6Z / Grid parameters: N_r=400, L=1, l_{max}=41 / H_3^{++}: R=1.68 a.u.

DFT results

LDA energies (in a.u.) of benzene

Symmetry	LCAO–GTO	VFD	Difference
$1a_{1g}$	−9.791	−9.797	−0.006
$1e_{1u}(2)$	−9.791	−9.797	−0.006
$1e_{2g}(2)$	−9.790	−9.797	−0.007
$1b_{2u}$	−9.790	−9.796	−0.006
$2a_{1g}$	−0.778	−0.775	0.003
$2e_{1u}(2)$	−0.676	−0.673	0.003
$2e_{2g}(2)$	−0.545	−0.543	0.002
$3a_{1g}$	−0.478	−0.477	0.001
$2b_{2u}$	−0.411	−0.410	0.001
$1b_{1u}$	−0.407	−0.404	0.003
$3e_{1u}(2)$	−0.379	−0.377	0.002
$1a_{2u}$	−0.341	−0.340	0.001
$3e_{2g}(2)$	−0.305	−0.303	0.002
$1e_{1g}(2)$	−0.240	−0.240	0.000
E_{total}	−230.177	−230.211	−0.034

Basis set: 6-311++G(3df,3pd) / Grid parameters: N_r=200, L=0.5, $l_{\max}$=26



2D sketch of *unstructured* molecular grids for benzene

Conclusion

- VFD is a new numerical grid method based on Voronoi diagram and applied for electronic structure calculations of polyatomic molecules.
- VFD allows us to employ intuitive pictures for *unstructured* molecular grids.
- With realistic Coulomb potential, eigenvalues of 1-e systems are solved within ~10^{-4} a.u. accuracy. DFT calculations show ~0.01% total energy difference from large-basis-set LCAO results.
- VFD is extensible to time-dependent problems due to ease of the potential matrix and applicable to problems demanding highly adaptive refinement.

References

- Voronoi diagram
  - G. Voronoï, *J. Reine Angew. Math.* **133**, 97 (1907); **134**, 198 (1908); **136**, 67 (1909)
  - F. Aurenhammer, *ACM Comput. Surv.* **23**, 345 (1991)
  - A. Okabe, B. Boots, K. Sugihara, S. N. Chiu, *Spatial Tessellations: Concepts and Applications of Voronoi Diagrams* (2000)
- Discrete Laplacian operator
  - N. Sukumar and J. E. Bolander, *CMES* **4**, 691 (2003)
  - N. Sukumar, *Int. J. Numer. Meth. Engng* **57**, 1 (2003)