GRID-Based Methods for the Analysis of the Wave Function in Quantum Chemistry Accelerated by GPUs

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The electron density, $\rho(\vec{r})$, is the most important concept on the interpretation of the wave function in quantum chemistry.
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For wave-function methods or density functional theory

$$\rho(\vec{r}) = \sum_{i=1}^{\text{occ}} \omega_i \psi_i^*(\vec{r}) \psi_i(\vec{r})$$
Orbitals

For atoms, molecules or extended systems, in general, the orbitals are represented in a basis set functions

\[ \psi_i(\vec{r}) = \sum_{\mu=1}^{K} c^{(i)}_{\mu} f_{\mu}(\vec{r}) \]

- \( \{f_{\mu}\} \) : basis set functions.
- \( \{c_{\mu}\} \) : coefficients obtained from a quantum chemistry method.
- \( K \) : number of the basis functions.
Gaussian functions

\[ f_{\mu}(\vec{r}) = (x - X)^{m_{\mu}} (y - Y)^{l_{\mu}} (z - Z)^{n_{\mu}} e^{-\zeta r^2} \]

with

\[ r^2 = (x - X)^2 + (y - Y)^2 + (z - Z)^2 \]

\((X, Y, Z)\): coordinates of a center (nucleus). Codes where gaussian functions are used to describe orbitals or electron density for atoms, molecules or solids:

- CRYSTAL (www.crystal.unito.it)
- GAMMMESS-UK (www.cfs.dl.ac.uk)
- GAMESS US (www.msg.ameslab.gov)
- Gaussian Inc. (www.gaussian.com)
- NWChem (www.nwchem-sw.org)
Summary to obtain the electron density

1. Basis set \( \{ f_\mu \} \)
2. \( \{ c_\mu \} \) from a quantum chemistry code.
3. 

\[
\rho(\vec{r}) = \sum_{i=1}^{occ} \sum_{\mu=1}^{K} \sum_{\nu=1}^{K} \omega_i c^i_\mu^* c^i_\nu f^*_\mu(\vec{r}) f_\nu(\vec{r})
\]
Visualization of orbitals and electron density

In quantum chemistry, orbitals or electron density are evaluated typically on a mesh to be displayed on a screen by using the marching cubes algorithm.
New code to analyze scalar and vector fields in quantum chemistry

Evaluation of scalar and vector fields on GPUs

Rendering by using GPUs

Code based on CUDA

Coefficients from NWChem or G09 in WFX format
The evaluation of $\rho$ is considered as a reduction problem.

- One thread is associated to each point on the mesh.

Mesh for the electron density

Mesh on the GPU
The evaluation of $\rho$ is considered as a reduction problem

- 64 threads are associated to each point on the mesh.
The evaluation of $\rho$ is viewed as a reduction problem:

- One thread is associated to each point on the mesh.
- 64 threads are associated to each point on the mesh.

720 basis set functions
932800 points in the mesh
1 thread per node in the mesh: 73 s.
The evaluation of $\rho$ is viewed as a reduction problem:

- One thread is associated to each point on the mesh.
- 64 threads are associated to each point on the mesh.

720 basis set functions
932800 points in the mesh
1 thread per node in the mesh : 73 s.
64 threads per node in the mesh : 25 s.
Our code is designed to evaluate electron density and others scalar or vector fields on GPUs. Additionally, the isosurfaces are rendering by the marching cubes algorithm also on GPUs.
Grid-based methods

Additionally to the visual part related with the electron density, there are tools to understand the chemical bond concept. The Atoms in Molecules (AIM) analysis predicts a chemical bond in a molecule if the condition

$$\nabla \rho(\vec{r}) = 0$$

is satisfied. All points that satisfy this condition are known as critical points.
Grid-based methods

Example of critical points indicated by small spheres
Grid-based methods

For the AIM analysis the critical points searching is an important challenge, in particular when the size of the system and the number of basis functions are large!
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- Graeme Henkelman, Andri Arnaldsson and Hannes Jónsson.  
  A fast and robust algorithm for Bader decomposition of charge.  

- Juan I. Rodríguez.  
  An efficient method for computing the QTAIM topology of a scalar field: The electron density case.  
  Journal of Computational Chemistry 34, 681 (2013)
Rodríguez algorithm:

- Molecule immersed in a Grid
- Newton-Raphson method on each point of the grid
  \( \rho(\vec{r}) \) and \( \nabla \rho(\vec{r}) \)
  are evaluated for each iteration.
- Stop if \( \rho < \epsilon \) or if a critical point is found
- Unique critical points
- Characterization of critical points
Our algorithm

- Same than Rodríguez but..
Our algorithm

- Same than Rodríguez but...
- Newton-Raphson just within one cube.
- Each thread of the GPU applied the Newton-Raphson method.
AIM on GPUs

20 bond critical points
6 ring critical points
1 cage critical point

B3LYP/6-311++G(2d,p)
408 Gaussian functions

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<th>CPU</th>
<th>Time (s)</th>
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AIM on GPUs

20 bond critical points
6 ring critical points
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CPU : AMD Opteron 6282 SE, 2.60GHz. GPU : Tesla M2090.

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<td>2 GPUs</td>
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Grid-based methods

12 H$_2$O + 1 CH$_4$

720 gaussian functions
58 bond critical points
18 Ring critical points

- 1 GPU : 456 s.
- 2 GPUs : 263 s.
- 4 GPUs : 188 s.
- 32 CPUs :
Grid-based methods

12 \( \text{H}_2\text{O} \) + 1 \( \text{CH}_4 \)

720 gaussian functions
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- 1 GPU: 456 s.
- 2 GPUs: 263 s.
- 4 GPUs: 188 s.
- 32 CPUs: 7688 s.

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AIM on GPUs

Jorge Garza (UAMI)

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Conclusions

- One code accelerated by GPUs gives scalar and vector fields in short times.
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- One code accelerated by GPUs gives scalar and vector fields in short times.
- The marching cubes algorithm on GPUs allows a visualization in real time.
- The critical points search on grid-based methods is implemented in a transparent way on GPUs.
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www.fqt.izt.uam.mx