BACHELOR/MASTER PROJECT SCIENTIFIC COMPUTING

Resolution of Identity: Optimization of auxiliary basis sets in Molecular Quantum Chemistry

Problem Description

Quantum Chemistry is a branch of chemistry whose primary focus is the application of quantum mechanics in physical models of chemical systems. One of the most popular techniques is *Density Functional Theory*. The behavior of electrons is described by solving Schrödinger-type equations of the form

$$\hat{H}\psi_i(\mathbf{r}) = \left[-\nabla^2 + V_{\text{eff}}(\mathbf{r};\rho(\mathbf{r}))\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{1}$$

where $\psi_i(\mathbf{r})$ is a single-electron wave function, and ϵ_i its energy. With N electrons in the system, $\rho(\mathbf{r}) = \sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2$ is the probability density to find an electron at point $\mathbf{r}$. In most practical implementations the $\psi_i(\mathbf{r})$ are expanded in terms of atom-centered Gaussian-type functions

$$\varphi_{\alpha,\nu}^{(lm)}(\mathbf{r}) = N_\alpha^{(lm)} r^l Y_{lm}(\theta,\phi) e^{-\alpha(\mathbf{r}-\mathbf{a}_\nu)^2} \tag{2}$$

with $\mathbf{a}_\nu$ the position of atom ν and $Y_{lm}(\theta,\phi)$ spherical harmonics. With $\psi_i(\mathbf{r}) = \sum_{\alpha,\nu} c_{\alpha,\nu}^i \varphi_{\alpha,\nu}^{(lm)}(\mathbf{r})$, Eq. (1) turns into a generalized eigenvalue problem in matrix form $\underline{\underline{\mathbf{H}}}\mathbf{c}^i = \epsilon_i \underline{\underline{\mathbf{S}}}\mathbf{c}^i$, which can be solved with Linear Algebra techniques. The particular choice of functions in (2) allows to calculate most of the real-space integrals forming the Hamiltonian $\underline{\underline{\mathbf{H}}}$ and overlap $\underline{\underline{\mathbf{S}}}$ matrices analytically. For the contribution of Coulomb interaction to the Hamiltonian this includes four-center integrals

$$V_{ijkl} = \iint \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}')\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'$$

which are computationally demanding. One can ease this by using *auxiliary* basis functions $\chi(\mathbf{r})$ of the same type as Eq. (2) to, e.g., approximate

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} \approx \sum_{\beta\beta'} \chi_\beta(\mathbf{r}) \left\langle \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right\rangle_{\beta\beta'} \chi_{\beta'}(\mathbf{r}')$$

so that

$$V_{ijkl} \approx \sum_{\beta\beta'} \left\langle \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right\rangle_{\beta\beta'} \int \varphi_i(\mathbf{r})\chi_\beta(\mathbf{r})\varphi_l(\mathbf{r}) d^3r \int \varphi_j(\mathbf{r}')\chi_{\beta'}(\mathbf{r}')\varphi_k(\mathbf{r}') d^3r'.$$

Tasks

- Study literature (provided by the supervisor).
- Identify and/or develop optimization techniques to determine an optimal auxiliary basis.
- Implement automatic optimization methods in Matlab or Python and apply them to a specific test case.
- Analyze the convergence behavior and accuracy of the different approaches.

Requirements

- Linear algebra
- Basic programming skills in Matlab or Python

Supervisor

Björn Baumeier—MF 7.142—040-2472205—b.baumeier@tue.nl