BACHELOR PROJECT SCIENTIFIC COMPUTING

Numerical Integration 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 $\mathbf{r}$. Since the effective potential $V_{\text{eff}}(\mathbf{r};\rho(\mathbf{r}))$ is in general a functional of ρ, the set of PDEs in (1) needs to be solved self-consistently. Most practical implementations follow the *Linear Combination of Atomic Orbitals* approach, in which 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

$$H_{\alpha,\nu;\alpha',\nu'} = \int \varphi_{\alpha,\nu}^{(lm)}(\mathbf{r})\left[-\nabla^2 + V_{\text{eff}}(\mathbf{r};\rho(\mathbf{r}))\right]\varphi_{\alpha',\nu'}^{(l'm')}(\mathbf{r})d^3r$$

$$S_{\alpha,\nu;\alpha',\nu'} = \int \varphi_{\alpha,\nu}^{(lm)}(\mathbf{r})\varphi_{\alpha',\nu'}^{(l'm')}(\mathbf{r})d^3r$$

forming the Hamiltonian $\underline{\underline{\mathbf{H}}}$ and overlap $\underline{\underline{\mathbf{S}}}$ matrices analytically.

However, for some non-linear contributions to $V_{\text{eff}}(\mathbf{r};\rho(\mathbf{r}))$ it is necessary to perform these integrations numerically. Such numerical schemes rely on the definition of spherical integration grids around atomic centers by choices of radial (e.g., Euler-McLaurin, Gauss-Chebychev) and angular (e.g., Gauss-Legendre, Lebedev) quadratures. Additionally, partitioning and (re-)weighting schemes for appropriately superimposing these atomic grids to a single molecular quadrature rule are required.

Tasks

- Study literature (provided by the supervisor).
- Identify a suitable simple but representative test case.
- Implement several methods in Matlab or Python and apply them to a specific part of setting up $\underline{\underline{\mathbf{H}}}$.
- Analyze the convergence behavior and accuracy of the different methods.

Requirements

- Linear algebra
- Basic programming skills in Matlab or Python

Supervisor

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