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

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

where \(\psi_i(r)\) is a single-electron wave function, and \(\epsilon_i\) its energy. With \(N\) electrons in the system, \(\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2\) is the probability density to find an electron at point \(r\). Since the effective potential \(V_{\text{eff}}(r; \rho(r))\) is in general a functional of \(\rho\), 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 \(\psi_i(r)\) are expanded in terms of atom-centered Gaussian-type functions

\[
\varphi_{\alpha,\nu}^{(lm)}(r) = N^{(lm)}_\alpha Y^{lm}_{\lambda \mu}(\theta, \phi) e^{-a(r-a\nu)^2}
\]

with \(a\nu\) the position of atom \(\nu\) and \(Y^{lm}_{\lambda \mu}(\theta, \phi)\) spherical harmonics. With \(\psi_i(r) = \sum_{\alpha,\nu} c_{\alpha,\nu} \varphi_{\alpha,\nu}^{(lm)}(r)\), Eq. (1) turns into a generalized eigenvalue problem in matrix form \(H c_i = \epsilon_i S c_i\), which can be solved with Linear Algebra techniques. The particular choice of functions in (2) allows to calculate most of the real-space integrals

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

forming the Hamiltonian \(H\) and overlap \(S\) matrices analytically.

However, for some non-linear contributions to \(V_{\text{eff}}(r; \rho(r))\) 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 \(H\).
- 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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