Development of a Computer Program to Solve Electronic Structure using Lagrange Basis Functions

Fadjar Fathurrahman

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Outline

- Kohn-Sham equations
- Lagrange basis functions

Total energy functional

Within LDA, Kohn-Sham energy functional can be written as:

$$E_{\mathrm{LDA}}\left[\{\psi_i(\mathbf{r})\}\right] = E_{\mathrm{kin}} + E_{\mathrm{ion}} + E_{\mathrm{Ha}} + E_{\mathrm{xc}} \tag{1}$$

with the following energy terms.
(1) kinetic energy:

$$E_{\mathrm{kin}} = -\frac{1}{2}\sum_{i_{st}} \int f_{i_{st}}\, \psi^*_{i_{st}}(\mathbf{r})\, \nabla^2\, \psi_{i_{st}}(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{2}$$

(2) ion-electron interaction energy:

$$E_{\mathrm{ion}} = \int V_{\mathrm{ion}}(\mathbf{r})\, \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{3}$$

(3) Hartree (electrostatic) energy:

$$E_{\mathrm{Ha}} = \int \frac{1}{2}\, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{4}$$

(4) Exchange-correlation energy (using LDA):

$$E_{\mathrm{xc}} = \int \epsilon_{\mathrm{xc}}\left[\rho(\mathbf{r})\right] \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{5}$$

Kohn-Sham equations

Central to the density functional theory is the so-called Kohn-Sham equation. This equation can be written as:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right]\psi_{i_{st}}(\mathbf{r}) = \epsilon_{i_{st}}\psi_{i_{st}}(\mathbf{r}) \tag{6}$$

where ϵi_{st} and $\psi_{i_{st}}(\mathbf{r})$ is known as Kohn-Sham eigenvalues and eigenvectors (orbitals). Quantity V_{KS} is called the Kohn-Sham potential, which can be written as sum of several potentials:

$$V_{\mathrm{KS}}(\mathbf{r}) = V_{\mathrm{ion}}(\mathbf{r}) + V_{\mathrm{Ha}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) \tag{7}$$

Lagrange basis functions

For a given interval $[0, L]$, with $L > 0$, the grid points x_i appropriate for periodic Lagrange function are given by:

$$x_i = \frac{L}{2}\frac{2i-1}{N} \tag{8}$$

with $i = 1, \ldots, N$. Number of points N should be an odd number.
The periodic cardinal functions $L_i^{\mathrm{per}}(x)$, defined at grid point i are given by:

$$L_i^{\mathrm{per}}(x) = \frac{1}{\sqrt{NL}} \sum_{n=1}^{N} \cos\left(\frac{\pi}{L}(2n - N - 1)(x - x_i)\right). \tag{9}$$

The expansion of periodic function in terms of Lagrange functions:

$$f(x) = \sum_{i=1}^{N} c_i L_i^{\mathrm{per}}(x) \tag{10}$$

with expansion coefficients $c_i = \sqrt{L/N} f(x_i)$. When doing variational calculation, the cofficients c_i are the variational parameters. The actual function values $f(x_i)$ at grid points x_i is obtained by $f(x_i) = \sqrt{N/L} c_i$. The prefactor is sometimes abbreviated by $h = L/N$ and is also referred to as scaling factor.

Cluster LF

For a given interval $[A, B]$, with $B > A$, the grid points x_i appropriate for cluster Lagrange function are given by:

$$x_i = A + \frac{B-A}{N+1} i$$

where $i = 1, \ldots, N$. Number of points N can be either odd or even number. The cluster Lagrange functions $L_i^{\mathrm{clu}}(x)$, defined at grid point i are given by:

$$L_i^{\mathrm{clu}}(x) = \frac{2}{\sqrt{(N+1)(B-A)}} \sum_{n=1}^{N} \sin\left(k_n(x_i - A)\right) \sin\left(k_n(x - A)\right). \tag{11}$$

where $k_n = \pi n/(B-A)$. The expansion of a function $f(x)$ in terms of cluster Lagrange functions:

$$f(x) = \sum_{i=1}^{N} c_i L_i^{\mathrm{clu}}(x) \tag{12}$$

with expansion coefficients $c_i = \sqrt{(B-A)/(N+1)} f(x_i)$. When doing variational calculation, the cofficients c_i are the variational parameters. The actual function values $f(x_i)$ at grid points x_i is obtained by $f(x_i) = \sqrt{(N+1)/(B-A)} c_i$.

Matrix elements $D_{jl}^{(2)}$ of the second derivatives for cluster Lagrange functions are

$$D_{jl}^{(2)} = \begin{cases} -\frac{1}{2}\left(\frac{\pi}{B-A}\right)^2 \frac{2(N+1)^2+1}{3} - \frac{1}{\sin^2\left[\pi j/(N+1)\right]} & j = l \\ -\frac{1}{2}\left(\frac{\pi}{B-A}\right)^2 (-1)^{j-l} \left[\frac{1}{\sin^2\left[\frac{\pi(j-l)}{2(N+1)}\right]} - \frac{1}{\sin^2\left[\frac{\pi(j+l)}{2(N+1)}\right]} \right] & j \neq l \end{cases}$$

Expansion in Lagrange basis function

in 1D Schrodinger equation blah

Solution to Kohn-Sham equations

Self-consistent field
Direct minimization

Result for Gaussian potentials

Gaussian potential

Hydrogen atom

Gaussian potential