

Numerical Methods

Lecture 3

Spatial Fourier Methods

Stephen Fahy

s.fahy@ucc.ie

Ref: Chapter 12 of Numerical Recipes

Outline

- Spatial Fourier Integrals and Series
- Quantum Mechanics:
Coordinate and Momentum Representations
- Solution of Poisson Equation
- Schrodinger Equation in Periodic Systems
- “Supercell” Methods

Spatial Fourier Transforms

Forward:

$h(\mathbf{r})$ is a function of *position*,

$$H(\vec{k}) = \int_{-\infty}^{+\infty} h(\vec{r}) \exp[-i\vec{k} \cdot \vec{r}] d^3\vec{r}$$

time \rightarrow position
frequency \rightarrow wave vector

$$2\pi f = \omega \rightarrow -k$$

H is the spatial Fourier Transform of h

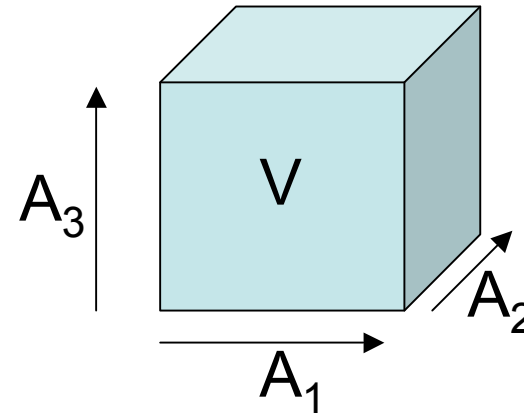
Backward:

$$h(\vec{r}) = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} H(\vec{k}) \exp[i\vec{k} \cdot \vec{r}] d^3\vec{k}$$

$h(\mathbf{r})$ is a superposition of waves of wave vector \mathbf{k}
and amplitude (including phase) $H(\mathbf{k})$

Fourier Series - 3-D Periodic Functions

$h(\mathbf{r})$ is a periodic function on the parallelepiped defined by vectors $\{\mathbf{A}_1 \mathbf{A}_2 \mathbf{A}_3\}$



forward: $H(\vec{k}) = \int_V h(\vec{r}) \exp[-i\vec{k} \cdot \vec{r}] d^3\vec{r}$

$$\vec{k} = k_1 \vec{g}^1 + k_2 \vec{g}^2 + k_3 \vec{g}^3$$

k_i are integers

where

$$\vec{A}_i \cdot \vec{g}^j = 2\pi \delta_i^j$$

reciprocal vectors, g^j

backward: $h(\vec{r}) = \frac{1}{V} \sum_{k_1, k_2, k_3} H(\vec{k}) \exp[i\vec{k} \cdot \vec{r}]$

Quantum Mechanics: Wave vectors and Momentum

De Broglie: momentum $\vec{p} = \hbar \vec{k}$

$$|p\rangle = \int_V |r\rangle \langle r|p\rangle d^3r \quad \text{Momentum eigenstate}$$

$$\text{where } \langle r|p\rangle = \frac{1}{\sqrt{V}} \exp[i(k/\hbar) \cdot r]$$

States are normalized in a volume V

$h(\mathbf{r})$ is the coordinate representation of a state h
 $H(\mathbf{k})/\sqrt{V}$ is its momentum representation

The Laplacian

coordinate representation $\vec{\nabla} = i\vec{k}$ momentum representation

$\nabla^2 = -k^2$

Translationally symmetric operators are ordinary numbers in the momentum representation
 \Rightarrow Computationally *very* sparse!

Kinetic Energy: $\frac{p^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 = \frac{(\hbar k)^2}{2m}$

Coordinate representation Momentum representation

The Laplacian in action!

Heat (Diffusion)
Equation:

$$\frac{\partial n}{\partial t} = D \nabla^2 n$$

Coordinate-time
representation

$$-i\omega N = -Dk^2 N$$

Momentum-frequency
representation

Poisson Equation:

$$\nabla^2 \Phi = -4\pi\rho$$

Φ = electrical potential
 ρ = charge density

Schrodinger Equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \varphi_i + V(\vec{r})\varphi_i = E_i \varphi_i$$

Coupled Schrodinger-Poisson:
(Hartree Eqns.)

e = charge on particle

$$\rho(\vec{r}) = e \sum_{i, E_i < E_F} |\varphi_i(\vec{r})|^2$$
$$V(\vec{r}) = V_0(\vec{r}) + e\Phi(\vec{r})$$

Convolutions - Solution of Poisson Equation

Convolution of ρ and *Coulomb interaction* $V_{e-e}(r-r')$

$$\Phi(\vec{r}) = \rho * V_{e-e}(\vec{r}) = \int V_{e-e}(|\vec{r} - \vec{r}'|) \rho(\vec{r}') d^3\vec{r}'$$

$$\boxed{V_{e-e}(\vec{r} - \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|^2}} \quad \Rightarrow \quad V(k) = \frac{4\pi}{k^2} \quad \leftarrow \boxed{\text{Exercise: prove this!}}$$

Convolution theorem:

Fourier transform of $g*h = G(f)H(f)$

$$\boxed{\Phi(\vec{k}) = \frac{4\pi\rho(\vec{k})}{k^2}}$$

$$\begin{aligned} \nabla^2\Phi &= -4\pi\rho \\ -k^2\Phi(\vec{k}) &= -4\pi\rho(\vec{k}) \end{aligned}$$

Hartree Potential

$$\rho(\vec{r}) = e \sum_{i, E_i < E_F} |\varphi_i(\vec{r})|^2$$

Calculate in coord rep. and
FT to wave vector rep.

$$\Phi(\vec{k}) = \frac{4\pi\rho(\vec{k})}{k^2}$$

Calculate in wave vector rep.
and FT to coord rep. $\Phi(\mathbf{r})$

Note: $\Phi(k=0)$ must = 0,
i.e. system is charge neutral -
Add compensating +ve background

$$V(\vec{k}) = V_0(\vec{k}) + e \Phi(\vec{k})$$

Schrodinger Eqn. - Momentum Rep.

$$-\frac{\hbar^2}{2m}\nabla^2\varphi_i + V(\vec{r})\varphi_i = E_i\varphi_i$$

Transform to Fourier (momentum) representation:

$$\frac{(\hbar k)^2}{2m}\varphi_i(\vec{k}) + \sum_{k'} V(\vec{k} - \vec{k}')\varphi_i(\vec{k}') = E_i\varphi_i(\vec{k})$$

$$\sum_{k'} H_{kk'}\varphi_i(\vec{k}') = E_i\varphi_i(\vec{k}) \quad \text{Diagonalize } H_{kk'}$$

$$H_{kk'} = \frac{(\hbar k)^2}{2m}\delta_{kk'} + V(k - k') \quad \boxed{\text{Matrix representation of } H}$$

Schrodinger Eqn. - Periodic Potential V

$$V(\vec{k} - \vec{k}') = V(\vec{G}) \quad \text{for } \vec{k} - \vec{k}' = \vec{G} = m_1 \vec{g}^1 + m_2 \vec{g}^2 + m_3 \vec{g}^3 \\ = 0 \quad \text{otherwise}$$

$$\vec{A}_i \cdot \vec{g}^j = 2\pi \delta_i^j$$

Transform to Fourier (momentum) representation:

$$\frac{(\hbar k)^2}{2m} \varphi_i(\vec{k}) + \sum_{\vec{G}} V(\vec{G}) \varphi_i(\vec{k} - \vec{G}) = E_i \varphi_i(\vec{k})$$

$$\sum_{\vec{G}} H_{k k-G} \varphi_i(\vec{k} - \vec{G}) = E_i \varphi_i(\vec{k})$$

$$H_{k k-G} = \frac{(\hbar k)^2}{2m} \delta_{k k'} + V(\vec{G})$$

Matrix representation of H

Periodic Potential V - Bloch's Theorem

Eigenstates of Hamiltonian:

$$\varphi_{nk} = \exp[ik \cdot r] u_{nk}(r) = \exp[ik \cdot r] \sum_G c_{nG} e^{iG \cdot r}$$

Function with period of lattice

Eigenvector of matrix $H_{k, k+G}$

$$\rho(\vec{r}) = e \sum_{nk, E_{nk} < E_F} |u_{nk}(\vec{r})|^2$$

Sample Algorithm

- *FT c_{nG} to get $u_n(r)$
- *find $e|u_n(r)|^2$
- *Sum to get $\rho(r)$
- *FT to get $\rho(G)$
- *Find $V(G)$ from Poisson Eq.

Assignment

Hartree (Schrodinger-Poisson) Eqn.

Write complete pseudo-code to solve the Hartree Eqns. for a 1-D lattice with potential $V(x)$, given on a uniform grid, with m electrons per unit cell

“Supercell” Method:

make system period (even if it is not physically periodic). This allows us to make use of Bloch’s Theorem and Fourier Transforms.

e.g a single defect becomes an array of defects

Summary

- Spatial Fourier Integrals and Series
- Quantum Mechanics:
Coordinate and Momentum Representations
- Solution of Poisson Equation
- Schrodinger Equation in Periodic Systems
- “Supercell” Method - solve 1-D lattice

Next Class

- * Matrix Diagonalization
- * Dynamical Matrices