Survey of Techniques in Electronic Structure Theory

Ankit Mahajan
Supervisor: Prof. Alok Shukla

Department of Physics,
IIT Bombay

B.Tech. Project, Autumn 2015

Formulating the problem

- Quantum mechanical treatment of many-body systems entails solving the Schrödinger equation for,

$$
\begin{aligned}
\boldsymbol{\mathcal{H}} = & -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + \frac{1}{4\pi\epsilon_0}\sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\
& - \frac{1}{4\pi\epsilon_0}\sum_{I,i}\frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0}\sum_{I<J}\frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \\
= & -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \boldsymbol{\mathcal{H}}_e(\mathbf{r}_i, \mathbf{R}_I)
\end{aligned}
$$

- Need for approximation: Exponential scaling of Hilbert space with size
- Born-Oppenheimer approximation: Problem reduced to finding eigenfunctions of $\boldsymbol{\mathcal{H}}_e$

- Independent electron approximation: Choosing single particle potentials

$$\mathbf{h}_i = \frac{\hbar^2}{2m_i}\nabla_i^2 + V_i$$

- Electronic band structure: Semi-empirical techniques of calculating electronic structure in solids.

- Second quantization: A convenient framework for many-body systems

- Ab initio techniques: Derived from first principles

Overview
Band structure
Second quantization
Ab initio techniques

Periodic potentials
Plane wave methods
Tight binding methods

Periodic Potentials: Bloch's Theorem

- Free electron approximation: Sommerfeld gas with plane wave wavefunctions
- Bloch's Theorem: Bloch proposed that electrons move in a static periodic potential of the lattice
- Schrödinger equation with a periodic potential can be written in the momentum space as,

$$\left(\frac{\hbar^2}{2m}(\mathbf{k} - \mathbf{K})^2 - E \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} V_{\mathbf{G}-\mathbf{K}} = 0 \qquad (1)$$

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}, \quad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}}$$

$$\psi_{\mathbf{k}n}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{R}} u_{\mathbf{k}n}(\mathbf{r}) \qquad (2)$$

Overview
Band structure
Second quantization
Ab initio techniques

Periodic potentials
Plane wave methods
Tight binding methods

Nearly free electrons

- Equation (1) can be solved directly by retaining a finite number of $\mathbf{k} - \mathbf{K}$ vectors
- Weak potential: Perturbation theory

$$E_{\mathbf{k}} = E_{\mathbf{k}}^0 + \frac{2m}{\hbar^2} \sum_{\mathbf{G} \neq 0} \frac{|V_{\mathbf{G}}|^2}{\mathbf{k}^2 - (\mathbf{k} + \mathbf{G}^2)}$$

(inside the BZ)

$$= E_{\mathbf{k}}^0 \pm \sqrt{\frac{1}{a} \left[E_{\mathbf{K}}^0 - E_{\mathbf{K}+\mathbf{G}}^0 \right]^2 + |V_{\mathbf{G}}|^2}$$
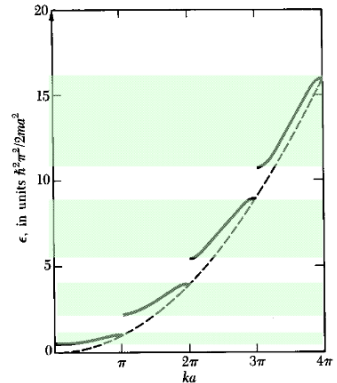
(near BZ boundary)

Figure: Dispersion relation for a weak potential (Kittel)

Overview
Band structure
Second quantization
Ab initio techniques

Periodic potentials
Plane wave methods
Tight binding methods

k.p method

- Following equation is obtained for $u_{\mathbf{k}n}(\mathbf{r})$,

$$\left[\frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar}{m}\mathbf{k}.\mathbf{p} + \frac{\hbar^2 \mathbf{k}^2}{2m}\right] u_{\mathbf{k}n}(\mathbf{r}) = E_{\mathbf{k}n} u_{\mathbf{k}n}(\mathbf{r}) \quad (3)$$

- The hamiltonian can be split as,

$$\mathcal{H}_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}), \quad \mathcal{H}_{\mathbf{k}} = \frac{\hbar}{m}\mathbf{k}.\mathbf{p} + \frac{\hbar^2 \mathbf{k}^2}{2m} \quad (4)$$

- Using perturbation theory for $\mathbf{k}$ values near $\mathbf{0}$,

$$E_n(\mathbf{k}) = E_n(\mathbf{0}) + \frac{\hbar^2 \mathbf{k}^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n \neq m} \frac{\langle u_{\mathbf{0}n}|\mathbf{k}.\mathbf{p}|u_{\mathbf{0}m}\rangle \langle u_{\mathbf{0}m}|\mathbf{k}.\mathbf{p}|u_{\mathbf{0}n}\rangle}{E_n(0) - E_m(0)}$$

$$(5)$$

Overview
Band structure
Second quantization
Ab initio techniques

Periodic potentials
Plane wave methods
Tight binding methods

Ortogonalized plane wave method

- Plane waves are not well suited to approximate the rapidly oscillating wavefunction near cores of nuclei

$$\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} + \sum_c b_c \psi_{\mathbf{k}}^c(\mathbf{r}) \qquad (6)$$

$$\langle \phi_{\mathbf{k}} | \psi_{\mathbf{k}}^c \rangle = 0$$

- OPWs mimic the behavior of electronic wavefunctions efficiently in both core and interstitial regions

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{K}} \phi_{\mathbf{k}+\mathbf{K}} \qquad (7)$$

Overview
Band structure
Second quantization
Ab initio techniques

Periodic potentials
Plane wave methods
Tight binding methods

Pseudopotentials: Extension of the method of OPWs

- The effect of core electrons on the valence states is expressed through an effective pseudopotential.

$$\psi_{\mathbf{k}}^{v}(\mathbf{r}) = \phi_{\mathbf{k}}^{v}(\mathbf{r}) + \sum_{c} b_c \psi_{\mathbf{k}}^{c}(\mathbf{r}) \tag{8}$$

$$\phi_{\mathbf{k}}^{v}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K}.\mathbf{r})} \tag{9}$$

- Substituting this form in the Schrödinger equation we get,

$$(\mathcal{H} + V^R)\phi_{\mathbf{k}}^{v} = E_{\mathbf{k}}^{v} \phi_{\mathbf{k}}^{v} \tag{10}$$

$$V^R \psi(\mathbf{r}) = \sum_{c} (E_{\mathbf{k}}^{v} - E_{\mathbf{k}}^{c}) \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}' \right) \psi_{\mathbf{k}}^{c}(\mathbf{r}) \tag{11}$$

- V^R is positive definite

$$V^{PS} = V + V^R \tag{12}$$

Overview
Band structure
Second quantization
Ab initio techniques

Periodic potentials
Plane wave methods
Tight binding methods

Tight binding

- In tight binding methods, a basis of localized wavefunctions is used.

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}.\mathbf{R}} a_n^{at}(\mathbf{r} - \mathbf{R})$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{n'} \mathcal{C}_{nn'} \phi_{n'k}(\mathbf{r})$$

- Substituting in the Schrödinger equation,

$$\sum_{n'} \mathcal{C}_{nn'} \mathcal{H}_{n''n'} - E_n \mathcal{S}_{n''n'} |\phi_{n'\mathbf{k}}\rangle = 0 \qquad (13)$$

- Wannier functions are designed to have zero overlap between neighbors

$$w_n(\mathbf{r} - \mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}.\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) \qquad (14)$$

Overview
Band structure
Second quantization
Ab initio techniques

Periodic potentials
Plane wave methods
Tight binding methods

Wannier functions

- Tight binding hamiltonian is give by,

$$\mathcal{H}_{TB} = \sum_{\mathbf{R}\boldsymbol{\delta}} |\mathbf{R}\rangle t \langle \mathbf{R} + \boldsymbol{\delta}| + \sum_{\mathbf{R}} |\mathbf{R}\rangle U \langle \mathbf{R}| \qquad (15)$$

$$E_{\mathbf{k}} = U + t \sum_{\boldsymbol{\delta}} e^{i\mathbf{k}.\boldsymbol{\delta}} \qquad (16)$$

- The Wannier functions can be used to solve the Schrödinger equation in a slowly varying perturbing potential $\mathcal{H}_1$

$$\left(-\frac{\hbar^2}{2m^*} \nabla^2 + \mathcal{H}_1(\mathbf{R}) \right) \Phi_n(\mathbf{R}) = E_n \Phi_n(\mathbf{R}) \qquad (17)$$

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} \Phi_n(\mathbf{R}) w_n(\mathbf{r} - \mathbf{R})$$

Overview
Band structure
Second quantization
Ab initio techniques

Occupation number representation
Fock Space
Operators in second quantization
Degenerate electron gas

Occupation number representation

- Let $|\phi_r\rangle_\alpha$ be the complete orthonormal set of vectors spanning the one particle Hilbert space $\mathcal{F}_1$. The n-particle Hilbert space is the tensor product of n such single particle spaces.

- A basis set for the n-particle femionic space, denoted by $\mathcal{F}_n$, is the set of Slater determinants given by,

$$|n[n_1 n_2...]\rangle_n = \frac{1}{n!} \begin{vmatrix} |\phi_r\rangle_1 & |\phi_r\rangle_2 & \cdots & |\phi_r\rangle_n \\ |\phi_s\rangle_1 & |\phi_s\rangle_1 & \cdots & |\phi_s\rangle_1 \\ \vdots & \vdots & \ddots & \vdots \\ |\phi_t\rangle_1 & |\phi_t\rangle_2 & \cdots & |\phi_t\rangle_n \end{vmatrix} \qquad (18)$$

where, $r < s < ... < t$.

Overview
Band structure
Second quantization
Ab initio techniques

Occupation number representation
Fock Space
Operators in second quantization
Degenerate electron gas

Fock Space

- The Fock space is defined as,

$$\mathcal{F} = \mathcal{F}_0 \bigoplus \mathcal{F}_1 \bigoplus ... \bigoplus \mathcal{F}_n \bigoplus ...$$

  A basis can be defined on $\mathcal{F}$ as follows,

$$|n[n_1 n_2...]\rangle = (0, 0, ..., |n[n_1 n_2...]\rangle_n, ...)$$

- Creation and annihilation operators

$$F_r^\dagger = \sum_{nn_1 n_2...}^{f} (-1)^{m_r}(1-n_r)|n+1[n_1 n_2...n_r+1...]\rangle\langle n[n_1 n_2...n_r...]|$$

$$F_r = \sum_{nn_1 n_2...}^{f} (-1)^{m_r} n_r |n[n_1 n_2...n_r-1...]\rangle\langle n+1[n_1 n_2...n_r...]|$$

Overview
Band structure
Second quantization
Ab initio techniques

Occupation number representation
Fock Space
Operators in second quantization
Degenerate electron gas

Operators in second quantization

$$F_r^\dagger |n\, [n_1 n_2 ... 0...]\rangle = (-1)^{m_r} |n+1\, [n_1 n_2 ... 1...]\rangle$$
$$F_r |n+1\, [n_1 n_2 ... 1...]\rangle = (-1)^{m_r} |n\, [n_1 n_2 ... 0...]\rangle$$
$$\{F_r^\dagger, F_s^\dagger\} = \{F_r, F_s\} = 0, \quad \{F_r, F_s^\dagger\} = \delta_{rs} \qquad (19)$$

- One particle operators can be written as,

$$A = \sum_{r,s} \langle \phi_r | A | \phi_s \rangle F_r^\dagger F_s \qquad (20)$$

- Two particle operators can be written as,

$$A = \sum_{r,s,t,u} \langle \phi_r \phi_s | A | \phi_u \phi_t \rangle F_r^\dagger F_s^\dagger F_t F_u \qquad (21)$$

Overview
Band structure
Second quantization
Ab initio techniques

Occupation number representation
Fock Space
Operators in second quantization
Degenerate electron gas

Degenerate electron gas

- Consider the system of interacting electrons placed in a uniformly distributed positive background

$$\mathcal{H} = T + V^{el-b} + V^{el} + V^b$$

$$= \sum_{\mathbf{k}\sigma} \frac{\hbar^2 \mathbf{k}^2}{2m} F_{\mathbf{k},\sigma}^\dagger F_{\mathbf{k},\sigma} + \frac{e^2}{2V} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\neq 0 \sigma_1 \sigma_2} \frac{4\pi}{\mathbf{q}^2} F_{\mathbf{k}-\mathbf{q},\sigma_1}^\dagger F_{\mathbf{k}'+\mathbf{q}\sigma_2}^\dagger F_{\mathbf{k}',\sigma_2} F_{\mathbf{k},\sigma_1}$$

- The interaction potential can be treated as a perturbation in the high density limit

$$\frac{E}{N} \approx \frac{e^2}{2a_0} \left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right]$$

Overview
Band structure
Second quantization
Ab initio techniques

Hartree-Fock theory
Configuration interaction

Hartree-Fock theory

Hamiltonian in $\mathcal{F}$ can be written as,

$$\boldsymbol{\mathcal{H}} = \sum_r E_r F_r^\dagger F_r + \frac{1}{2} \sum_{r,s,t,u} \langle \phi_r \phi_s | V | \phi_u \phi_t \rangle F_r^\dagger F_s^\dagger F_t F_u - \sum_{r,s} \langle \phi_r | \mathcal{V} | \phi_s \rangle F_r^\dagger F_s$$

$$[T(\xi_\alpha) + U(\xi_\alpha) + \mathcal{V}(\xi_\alpha)] \, |\phi_r\rangle = E_r |\phi_r\rangle$$

$$\boldsymbol{\mathcal{H}}_0 = \sum_\alpha [T(\xi_\alpha) + U(\xi_\alpha) + \mathcal{V}(\xi_\alpha)]$$

The choice of $\mathcal{V}$ that gives the best approximation is given by the Hartree-Fock potential,

$$\langle \phi_r | \mathcal{V}_{HF} | \phi_s \rangle = \sum_t \langle \phi_r \phi_t | V | \phi_s \phi_t \rangle - \langle \phi_r \phi_t | V | \phi_t \phi_s \rangle \qquad (22)$$

Overview
Band structure
Second quantization
Ab initio techniques

Hartree-Fock theory
Configuration interaction

Configuration interaction

- The basic idea behind CI is to use the linear combination of multiple Slater determinants as a solution ansatz

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{ar} c_a^t |\Psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + ... \quad (23)$$

$$E_{corr} = \sum_{a<b,r<s} c_{ab}^{rs} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle$$

- Doubly excited CI:

$$|\Phi_{DCI}\rangle = |\Phi_0\rangle + \sum_{c<d,t<u} c_{cd}^{tu} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle$$

$$\begin{bmatrix} 0 & B^{\dagger} \\ B & D \end{bmatrix} \begin{bmatrix} 1 \\ c \end{bmatrix} = E_{corr} \begin{bmatrix} 1 \\ c \end{bmatrix}$$