Quantum Mechanics Methods

Energy model

Energy $E(R_i)$

Hierarchy of energy models

Accuracy

- Quantum mechanical methods
- Semi-empirical models
- Empirical models

Energies, Relaxations, Transition states, Molecular dynamics, Speed
Short Review of Quantum Mechanics

Why do we need quantum mechanics?
• Bonding and structure
• Electronic, magnetic and optical properties of materials
• Chemistry and reactions

Standard model of matter
• Matter consists of atoms
• Atoms consist of
  ‣ Massive, point-like nuclei (protons + neutrons)
  ‣ That are surrounded by tightly bound core electrons
  ‣ And held together in molecules, liquid and solids by the bonds formed by valence electrons
Short Review of Quantum Mechanics

Wave-particle duality
• Planck’s uncertainty relationship
  \[ \lambda \cdot p = \hbar \]

Schrödinger equation
• Time dependent
  \[ -\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r, t) \Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t} \]
1) List as many mathematical characteristics of the Schrödinger equation as you can think of.
   - Think: Quadratic?, Homogeneous? etc.

\[-\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r, t) \Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t}\]
2) Solve the Schrödinger equation by separation of variables

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r, t) \Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t}
\]

\[
\Psi(r, t) = \varphi(r) \cdot f(t)
\]
Solutions of the Schrödinger Equation (1)

Free particle

- \( V(\mathbf{r}) = 0 \)  \( \Rightarrow \)  Solutions are plane waves

\[
\Psi_k(\mathbf{r}, t) = \exp(i \mathbf{k} \cdot \mathbf{r} - \omega t)
\]

\[
E_k = \frac{\hbar^2 k^2}{2m} = \omega \hbar
\]

Harmonic oscillator

\[
V(x) = \frac{1}{2} k x^2
\]

\[
\varphi_n(x) = c_n \cdot \exp\left(-\frac{m\omega^2 x^2}{2\hbar}\right) \cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right)
\]

\[
E_n = \left(n + \frac{1}{2}\right) \hbar \omega
\]
Solutions of the Schrödinger Equation (2)

Infinite square well

- Plane waves that vanish at the boundary

\[ V(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{otherwise} \end{cases} \]

\[ \varphi_n(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{\pi n x}{a} \right) \]

\[ E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \]
Solutions of the Schrödinger Equation (3)

Metal surface

- Potential step $\Rightarrow$ Plane wave inside metal, exponential decay outside
Solutions for the Coulomb Potential

Spherical Symmetry

\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]
\[ = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \]

Separation of variables

\[ \Psi_{nlm}(\mathbf{r}) = R_{nl}(r) \cdot Y_{lm}(\theta, \varphi) \]

Equation for radial wave functions

\[
\left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} + V(r) \right] R_{nl}(r) = E R_{nl}(r)
\]
The Periodic System of Elements

http://www.orbitals.com/orb/orbtable.htm
Matrix Formulation

Expand wave function in set of $n$ orthogonal functions

$$|\psi\rangle = \sum_{n=1}^{k} c_n |\varphi_n\rangle$$

Plugging this solution into the Schrödinger equation yields and multiplying with function $\varphi_m$ yields

$$\langle \varphi_m | H | \psi \rangle = E \langle \varphi_m | \psi \rangle$$

$$\sum_{n=1}^{k} c_n \langle \varphi_m | H | \varphi_n \rangle = E c_m$$

$$\sum_{n=1}^{k} H_{mn} c_n = E c_m$$

$$\begin{pmatrix}
H_{11} & \cdots & H_{1k} \\
\vdots & \ddots & \vdots \\
H_{k1} & \cdots & H_{kk}
\end{pmatrix} \begin{pmatrix}
c_1 \\
\vdots \\
c_k
\end{pmatrix} = E \begin{pmatrix}
c_1 \\
\vdots \\
c_k
\end{pmatrix}$$
Variational Principle

\[
E[\Phi] = \frac{\langle \Phi | \mathcal{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0
\]

\[
E[\Phi] = E_0 \iff \text{If } \Phi \text{ is the groundstate}
\]

Example: The hydrogen atom

\[
\Psi_\alpha = c \cdot \exp(-\alpha r)
\]

\[
E[\Phi_\alpha] = \frac{\langle \Phi_\alpha | \mathcal{H} | \Phi_\alpha \rangle}{\langle \Phi_\alpha | \Phi_\alpha \rangle}
\]
The Hydrogen Atom

Ansatz:
\[ \Psi_\alpha = c \cdot \exp(-\alpha r) \]

\[ E[\Phi_\alpha] = \frac{\langle \Phi_\alpha | \mathcal{H} | \Phi_\alpha \rangle}{\langle \Phi_\alpha | \Phi_\alpha \rangle} \]

Calculate:
\[ \langle \Phi_\alpha | \Phi_\alpha \rangle \quad \langle \Phi_\alpha | - \frac{1}{2} \nabla^2 | \Phi_\alpha \rangle \quad \langle \Phi_\alpha | - \frac{1}{r} | \Phi_\alpha \rangle \]

Use:
\[ \langle \ldots | \ldots \rangle = \int_0^\infty 4\pi r^2 \ldots d^3r \quad \int_0^\infty r^n \exp(-ar) = \frac{n!}{a^{n+1}} \]

\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]
\[ = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \]
The Hydrogen Atom

Result:

\[ \langle \Phi_\alpha | \Phi_\alpha \rangle = \pi \frac{c^2}{\alpha^3}, \quad \langle \Phi_\alpha | -\frac{1}{2} \nabla^2 | \Phi_\alpha \rangle = \pi \frac{c^2}{2\alpha}, \quad \langle \Phi_\alpha | -\frac{1}{r} | \Phi_\alpha \rangle = \pi \frac{c^2}{\alpha^2} \]

Write out the energy as a function of \( \alpha \) and minimize with respect to \( \alpha \):

\[
E(\alpha) = \frac{\pi \frac{c^2}{2\alpha} - \pi \frac{c^2}{\alpha^2}}{\pi \frac{c^2}{\alpha^3}} = \frac{1}{2} \alpha^2 - \alpha
\]

\[
\frac{d}{d\alpha} E(\alpha) = \alpha - 1 = 0
\]
## Atomic Units

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Name</th>
<th>Symbol</th>
<th>SI value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>Hartree energy</td>
<td>Ha</td>
<td>$4.359,744,17(75)\times10^{-18}$ J</td>
</tr>
<tr>
<td>Length</td>
<td>Bohr radius</td>
<td>$a_0$</td>
<td>$5.291,772,108(18)\times10^{-11}$ m</td>
</tr>
<tr>
<td>Mass</td>
<td>Electron rest mass</td>
<td>$m_e$</td>
<td>$9.109,3826(16)\times10^{-31}$ kg</td>
</tr>
<tr>
<td>Electric charge</td>
<td>Elementary charge</td>
<td>$e$</td>
<td>$1.602,176,53(14)\times10^{-19}$ C</td>
</tr>
<tr>
<td>Electrostatic force</td>
<td>Coulombs constant</td>
<td>$1/4\pi\varepsilon_0$</td>
<td>$8.9875516\times10^9$ C$^{-2}$Nm$^2$</td>
</tr>
</tbody>
</table>
The Many-Electron Problem

\[ \left[ -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Z}{r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{|r_i - r_j|} \right] \psi(r_1, \ldots, r_n) = E \psi(r_1, \ldots, r_n) \]

Example: Fe atom

- Fe has 26 electrons ⇒ wave function has 3×26 = 78 variables
- Store wave function on a grid
- Use a coarse grid of only 10 points along each direction
- To store wave function would require storage of \(10^{78}\) numbers
- Single precision 1 number = 4 Bytes

- Compare that to all the data stored worldwide 1 zettabyte = \(10^{21}\) Bytes
The Hartree Method

**Independent electron method**

- Assume that electrons move independently of each other
- Each electron moves in an effective potential that consists of
  - Attraction of nuclei
  - Average repulsive interaction of other electrons
- Many-body wave function as product of single-particle orbitals

\[ \psi(r_1, r_2, \ldots, r_n) = \varphi_1(r_1) \varphi_2(r_2) \ldots \varphi_n(r_n) \]
The Hartree Method

\[
\begin{align*}
-\frac{1}{2} \nabla_i^2 + \sum_{I} V(R_I - r_i) + \sum_{j \neq i} \int |\varphi_j(r_j)|^2 \frac{1}{|r_i - r_j|} d^3 r_j
\end{align*}
\]

Hartree potential

\[
\varphi_i(r_i) = \epsilon \varphi_i(r_i)
\]

Douglas Rayner Hartree and Porter Meccano differential analyzer built in 1934 at a cost of £20. It achieved an accuracy of about 2%.
Illustration of Electron Correlations

Uncorrelated
Cars are smeared out

Correlated
Cars avoid each other

Uncorrelated
Electrons described by their independent density, electrons can get arbitrary close

Correlated
Electrons avoid each other due to the Coulomb interaction between them

http://www.flickr.com/photos/88943727@N00/101166668/
The Hartree-Fock Method

What is missing in the Hartree approximation

• Wave function is not **antisymmetric**
• Does not include electron **correlation**

Antisymmetry for Fermions

• Exchanging two identical (indistinguishable) fermions changes the sign of the wave function

\[
\psi(r_1, r_2, \ldots, r_j, \ldots, r_k, \ldots, r_n) = -\psi(r_1, r_2, \ldots, r_k, \ldots, r_j, \ldots, r_n)
\]

Pauli Exclusion Principle

• Two electrons cannot be in the same quantum state
• Consequence of the antisymmetry
Slater Determinants

Slater determinant

- Antisymmetric product of single particle orbitals

\[ \psi(r_1, r_2, \ldots, r_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(r_1) & \varphi_2(r_1) & \cdots & \varphi_n(r_1) \\ \varphi_1(r_2) & \varphi_2(r_2) & \cdots & \varphi_n(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(r_n) & \varphi_2(r_n) & \cdots & \varphi_n(r_n) \end{vmatrix} \]

- Swapping rows in a determinant changes the sign
The Hartree-Fock Method

Hartree-Fock equation for orbitals $\varphi_\lambda$

- Use of variational principle leads to set of equations for $\varphi_\lambda$

$$
\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(R_I - r_i) \right] \varphi_\lambda(r_i) + \\
\sum_\mu \left[ \int \varphi_\mu^*(r_j) \frac{1}{|r_i - r_j|} \varphi_\mu(r_j) d^3r_j \right] \varphi_\lambda(r_i) - \\
\sum_\mu \left[ \int \varphi_\mu^*(r_j) \frac{1}{|r_i - r_j|} \varphi_\lambda(r_j) d^3r_j \right] \varphi_\mu(r_i) = \epsilon \varphi_\lambda(r_i)
$$
The Exchange Term

\[ \sum_{\mu} \left[ \int \frac{\varphi^*_\mu(r_j)}{|r_i - r_j|} \varphi_\lambda(r_j) \, d^3r_j \right] \varphi_\mu(r_i) \]

- Describes effect of exchange of electrons
- \textit{Cannot} be written in the form

\[ V^x_\lambda(r_i) \varphi_\lambda(r_i) \]

- Instead it is of the form

\[ \int V^x_\lambda(r_i, r_j) \varphi_\lambda(r_j) \, d^3r_j \]

- This is called a \textit{non-local potential}
Successes and Limitations of Hartree-Fock

Successes

• Good for atomic properties
• Self-interaction free
• Good starting point for correlated-electron methods

Limitations

• Schrödinger equation: $H \Psi = E \Psi \Rightarrow E_{\text{exact}}$
• Hartree-Fock equations: $F \phi_i = \varepsilon_i \phi_i \Rightarrow E_{\text{HF}}$
• Any effect beyond HF is called correlation $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$
• Size of correlation energy
  Example: N$_2$ molecule: $E_{\text{corr}} = 14.9$ eV $\leq 1\%$ of $E_{\text{exact}}$
• However: binding energy N$_2 \rightarrow$ N + N is
  $D_e(\text{Hartree-Fock}) = 5.1$ eV, $D_e(\text{exp}) = 9.9$ eV

Thus, there are large contribution from the correlation energy to relative energies, i.e. chemical reaction energies.
Beyond Hartree-Fock

Hartree Fock configuration
• HF Slater determinant is built from lowest energy 1-e orbitals
  \[ \Psi_{\text{HF}}^0 = | \varphi_1 \varphi_2 \cdots \varphi_K | \]
• Slater determinant is also called a configuration since it refers to certain filled orbitals

Configuration interaction method
• Add additional configurations to the wave functions that mix in “excited” states
• Excite electron from orbital \(i\) to orbital \(K+1\)
  \[ \Psi_{\text{HF}}^1 = | \varphi_1 \varphi_2 \cdots \varphi_{K+1} \cdots \varphi_K | \]
  \[ \Psi_{\text{CI}} = c_0 \Psi_0 + c_1 \Psi_1 + c_2 \Psi_2 + \ldots \]
Thomas-Fermi Approach

Motivation

\[ \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \quad \text{Function of } 3N \text{ variables} \]

\[ \rho(\mathbf{r}) \quad \text{Function of } 3 \text{ variables} \]

Electron density

Position

Locally homogeneous electron gas
Density Functional Theory

- Theory for the ground state energy of a system as a function of the electron density instead of the wave function
- Walter Kohn received the Nobel prize in 1998 for his development of density functional theory

**Motivation**

\[ \Psi(r_1, r_2, \ldots, r_n) \quad \text{Function of } 3N \text{ variables} \]

\[ \rho(r) \quad \text{Function of } 3 \text{ variables} \]
The Hohenberg-Kohn Theorems

- The external potential and the number of electrons define the problem
- Schrödinger’s equation in principle uniquely determines the wave functions
- All system properties follow from the wave functions

\[ \Rightarrow \quad \text{Hence the energy and everything else} \]
\[ \text{is a functional of } V_{\text{ext}} \text{ and } N_{\text{el}} \]

\[
\begin{array}{ccc}
V_{\text{ext}}(\mathbf{r}) & \iff & \rho_0(\mathbf{r}) \\
\text{Schrödinger equation} & \downarrow & \uparrow \\
\Psi_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) & \Rightarrow & \Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \\
\text{Integration of } |\Psi_0|^2 \text{ over } & N-1 \text{ electron coordinates} \\
\end{array}
\]
The Universal Functional

• Since the ground state density determines all properties, the ground state energy and its components are a functional of the density

\[ E_{\text{tot}}^0 = E_{\text{kin}}[\rho^0] + V_{\text{ext}}[\rho^0] + V_{\text{el-el}}[\rho^0] \]

• \( V_{\text{ext}} \) is known

\[ V_{\text{ext}}[\rho^0] = \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d^3r \]

• For the kinetic energy and the e-e interaction

\[ F[\rho^0] = E_{\text{kin}}[\rho^0] + V_{\text{el-el}}[\rho^0] \]

• Form of this functional is the same for any molecule or solid

⇒ Universal functional \( F[\rho] \)

Functional form unknown
2nd Hohenberg-Kohn Theorem

- The groundstate energy can be obtained variationally.
- The density that minimizes the total energy is the exact groundstate density.

\[ E[\rho(r)] = F[\rho(r)] + \int V_{\text{ext}}(r)\rho(r) d^3r \geq E_0 \]
The Kohn-Sham Equations

Mapping to a non-interacting system

\[ \rho(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2 \]

• Why? The kinetic energy of the non-interacting system is well defined.

\[ T_S[\rho(r)] = -\frac{1}{2} \sum_{i=1}^{N} \int \varphi_i^*(r) \nabla^2 \varphi_i(r) \]

• Universal functional now takes the form

\[ F[\rho(r)] = T_S[\rho(r)] + E_H[\rho(r)] + E_{xc}[\rho(r)] \]

• Electron-electron interaction is separated into two terms, the Hartree term and the unknown exchange-correlation energy term

\[ E_H = \frac{1}{2} \int \int \frac{\rho(r) \rho(r')}{|r - r'|} d^3r \, d^3r' \]
Euler-Lagrange Equations

Minimize energy with respect to variations of the density

$$\frac{\delta}{\delta \rho} \left\{ F[\rho(r)] + \int V_{\text{ext}}(r)\rho(r) d^3r - \mu \left( \int \rho(r) d^3r - N \right) \right\} = 0$$

$$\frac{\delta F[\rho(r)]}{\delta \rho(r)} + V_{\text{ext}} = \mu$$

• Resulting equations have a similar form as the Schrödinger equation and are known as the Kohn-Sham equations

$$\left[ -\frac{1}{2} \nabla^2 + V_H(r) + V_{xc}(r) + V_{\text{ext}}(r) \right] \varphi_i(r) = \epsilon_i \varphi_i(r)$$

$$\mathcal{H}_{\text{KS}}$$
Summary

Hohenberg-Kohn theorem

\( V_{\text{ext}}(\mathbf{r}) \leftrightarrow \varrho_0(\mathbf{r}) \)

\[ \downarrow \]

Kohn-Sham

\[ \uparrow \]

\( \Psi_i(\mathbf{r}_1, \ldots \mathbf{r}_N) \Rightarrow \Psi_0(\mathbf{r}_1, \ldots \mathbf{r}_N) \)

Hohenberg-Kohn theorem applied to non-interacting electrons

\( \varrho_0(\mathbf{r}) \Rightarrow V_{\text{ext}}(\mathbf{r}) \)

\[ \uparrow \]

\[ \downarrow \]

\( \varphi_{i=1,N}(\mathbf{r}) \leftrightarrow \varphi_i(\mathbf{r}) \)

\[ E[\{\varphi_i(\mathbf{r})\}] = \sum_{i=1}^{N} \left( \frac{1}{2} \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) d^3r + E_{\text{H}}[\rho(\mathbf{r})] + E_{\text{xc}}[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d^3r \right) \]

\[ = \sum_{i=1}^{N} \epsilon_i - V_{\text{H}}[\rho(\mathbf{r})] + E_{\text{xc}}[\rho(\mathbf{r})] - \int \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) d^3r \]
The Local Density Approximation

The Phases of Silicon

Under pressure Si displays 11 crystal phases

• LDA correctly predicts the energetic order of all these phases

Compression

Si(I) diamond 11 GPa  
Z=4

Si(II) β–tin 13 GPa  
Z=6

Si(XI) Imma 16 GPa  
Z=6

Si(V) hexagonal 36 GPa  
Z=8

Si(VI) orthorhombic 42 GPa  
Z=10

Si(VII) hcp 79 GPa  
Z=12

Si(X) fcc
Z=12

Decompression

Slow pressure release

Si(II) β–tin 9 GPa  
Z=6

Si(XII) R8 2 GPa  
Z=4

Si(III) BC~8 >480 K  
Z=4

Si(IV) hex. diamond

Fast pressure release

→ Si(VIII) and Si(IX) tetragonal

Exchange-Correlation Functionals

Local density approximation (LDA)
• Based on Ceperley & Alder’s calculations for the uniform electron gas by quantum Monte Carlo (a stochastic method for quantum particles)

Generalized gradient approximations (GGA: PW91, PBE)
• Gradients of the density are introduced
• Preserve analytic scaling features of the unknown exact functional

Meta-GGA (TPSS)
• Include information about curvature of the density

Hybrid density functionals (B3LYP, HSE)
• Based on GGA or meta-GGA approximations
• Add some non-local Hartree-Fock exchange to the functional
Density Functional Theory in Practice

1. Remove tightly bound core electrons: the pseudopotential approach

2. Represent orbitals with a basis (plane waves or Gaussians)

3. Calculate total energy for trial orbitals
   - Kinetic and hartree energy in reciprocal space
   - Exchange-correlation energy and external potential in real space
   - Method can take advantage of Fast Fourier Transformations
   - Sum over all states: BZ integrations

4. Minimize energy and iterate charge density to self-consistency
Pseudopotentials

Electrons in the inner shells do not contribute to bonding

- Core electrons are effectively frozen
- Replace Coulomb potential between electrons and nuclei with effective potential, the pseudopotential

\[
\begin{align*}
\text{Valence states} & : \quad \begin{array}{c}
3p \quad \begin{array}{c}
\uparrow \\
-2.7 \text{ eV}
\end{array} \\
3s \quad \begin{array}{c}
\downarrow \downarrow \\
-7.8 \text{ eV}
\end{array}
\end{array} \\
\text{Core states} & : \quad \begin{array}{c}
2p \quad \begin{array}{c}
\uparrow \uparrow \uparrow \uparrow \\
-69.8 \text{ eV}
\end{array} \\
2s \quad \begin{array}{c}
\uparrow \\
-108 \text{ eV}
\end{array} \\
1s \quad \begin{array}{c}
\downarrow \\
-1512 \text{ eV}
\end{array}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{Al} & \quad Z = 13 \\
\text{Pseudo Al} & \quad Z = 3
\end{align*}
\]
Pseudopotentials

The pseudopotential and the wave function

- Real potential and wave function are shown in blue
- Pseudopotential and pseudo wave function in red
- Outside the cutoff region (vertical black line) the two are identical
Non-Local Pseudopotentials

- Electron states with different angular momenta scatter differently from the core.
- States that have shell below them with same angular momentum feel stronger repulsion due to orthogonality constraint.
Basis Set Choices and Convergence

Basis set choices

• Real potential and wave function are shown in blue
• For molecules: often atomic orbitals, or localized functions like Gaussians
• For solids, periodic functions such as sines and cosines (plane waves)
• Use of Bloch theorem for periodic solids

\[ [\mathcal{H}, \mathcal{T}_R] = 0 \implies \varphi(r) = u_{nk}(r) \exp(i\mathbf{k} \cdot \mathbf{r}) \]

⇒ Remember the importance of \( k \)-point sampling

Convergence

• Increase size of basis set to approach completeness
Plane Wave Basis Set

- Superposition of plane waves to represent orbitals

\[ u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}| \leq \mathbf{G}_{\text{max}}} c_{nk}(\mathbf{G}) \exp(i \mathbf{G} \cdot \mathbf{r}) \]
Band structure of crystals (1)

Bloch states and Brillouin zones

- Crystal structures defined by Bravais lattice \( \{a_i\} \) and basis
- Periodic density \( \Rightarrow \text{Bloch theorem} \)  
  \[ \psi(r + R) = \psi(r) \cdot \exp(ik \cdot r) \]
- Fourier transformation  
  \[ n(r) = \sum_G n_G \cdot \exp(iG \cdot r) \]
- Reciprocal lattice  
  \[ b_k = 2\pi \cdot \frac{a_l \times a_m}{a_k \cdot (a_l \times a_m)} \]
- Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice
Band structure of crystals (2)

**Diffraction picture for origin of the energy gap**

- Start with a 1D crystal and consider diffraction of electron wave
  
  \[
  n\lambda = 2d \cdot \sin \theta \quad \text{with} \quad d = a \quad \text{and} \quad \sin \theta = 1
  \]
  
  \[
  n\lambda = 2a
  \]
  
  \[
  k = \frac{2\pi}{\lambda}
  \]
  
  \[
  k = \frac{n\pi}{a}
  \]

- Take lowest order \((n = 1)\) and consider incident and reflected electron wave
  
  \[
  \psi_i = e^{ikx} = e^{i \frac{\pi}{a} \cdot x} \quad \text{and} \quad \psi_r = e^{-i \frac{\pi}{a} \cdot x}
  \]

- Total wave function for electrons with diffracted wave length
  
  \[
  \psi = \psi_i \pm \psi_r \quad \Rightarrow \quad \psi_+ = \psi_i + \psi_r = 2\cos \frac{\pi x}{a} \quad \text{and} \quad \psi_- = \psi_i - \psi_r = 2\sin \frac{\pi x}{a}
  \]

- Only two solutions for \(k = \pi/a\): Electron density on atoms or between

- No traveling wave solution
Band structure of crystals (3)

Diffraction picture for origin of the energy gap

- If ion potential is a weak perturbation $U$, the electrons near diffraction condition have two possible solutions
  - Electron density between ions: $E = E_{\text{free}} - U$
  - Electron density on ions: $E = E_{\text{free}} + U$
- Near diffraction condition energy is parabolic in $k$, $E \propto k^2$
- Electron near diffraction conditions are not free
- Their properties can still be described as “free” with an effective mass $m^*$
Band Structure: Free Electron Gas and Si

Free electron gas

$$E = \frac{\hbar^2 k^2}{2m} \text{ and } \varphi(r) = \exp(ik \cdot r)$$

Silicon
Example of metallic band structure: Cu

- Copper: Band structure calculated with Wien2k
- Nearly free electron $s$-band dominates at low and high energies
- Electron near diffraction conditions have different effective mass
- Hybridization between nearly-free $s$ and atomic-like $d$ orbitals at intermediate energies
- Necking of Fermi surface in [111] directions ⇒ Hume-Rothery stabilization
Successes and Failures of DFT

Structural and elastic properties
- Lattice parameters are typically within a few percent of experimental values and often accurate to better than 1%
- The bulk modulus and other elastic constants are usually within 10%

Vibrational Properties
- Forces = 1\textsuperscript{st} derivative of energy with respect to atomic displacement
- Forces are accurate to better than 10% (similar to elastic constants)
- Vibrational frequencies are the 2\textsuperscript{nd} derivatives
- Their accuracy is about 1/2 the accuracy of the forces or about 5%
Successes and Failures of DFT

Defect energies
• In many cases such as for metals, vacancy and interstitial energies are highly accurate (within 0.1 eV)
• In some cases such as interstitial defects in silicon, DFT is too low by about 1 eV predicting a 3–3.5 eV formation energy instead of the 4.5 eV of experiments and QMC [Phys. Rev. B 74, 121102(R) (2006)]

Excited states and gaps
• Local density approximation fails for excited states
• Bandgaps in LDA and GGA are usually underestimated by 20–50%
• In some cases such as Ge, LDA predicts a metallic instead of semiconducting state
• Hybrid functionals (e.g. B3LYP and HSE) improve the accuracy to about 10%
The bandgap problem of DFT

Example: Bandstructure of InAs

- LDA, no gap: -0.42 eV
- PBE, no gap: -0.13 eV
- B3LYP 20%, gap: 0.54 eV

- Experimental bandgap: 0.41 eV

**Band gap problem:** LDA and GGA yield a metallic ground state!

- Practical solution: **Hybrid functionals** B3LYP & HSE (0.39 eV)
- Better solution: **GW approximation or QMC methods**
Beyond DFT – The GW approximation

Energy gap (eV)

-2  0  2  4  6  8  10

Si
Ge
diamond
3C SiC
LiCl
β-C3N4
BN
BP
BAs
AlN
AlP
AlAs
AlSb
GaN
GaP
GaAs
GaSb
InP
InAs
InSb
Al0.5Ga0.5As
GaAs0.47N0.53
GaAs0.75N0.25
ZnO
ZnS
ZnSe
ZnTe
CdS
CdSe
CdTe
MgO
MnO
NiO
CaCu2O6
Li2O
ZrO2
SnO2

LDA
GWA
Expt., indirect gap
Expt., direct gap
Summary of Density Functional Theory

**LDA**
- Lattice constants: 1-3% too small
- Cohesive Energies: 5-20% too strongly bound
- Bulk Modulus: 5-20% (largest errors for late TM)
- Bandgaps: too small

**GGA**
- Improves cohesive energies
- Often but not always better for lattice parameters
- Important for magnetic systems

**Hybrid functionals**
- Improved band gaps, often very accurate

Always check the accuracy of the computational method by benchmarking against experimental data or more accurate theory.