Solid State Theory: Band Structure Methods

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Wed., 12:00-13:30

HS P3 (PH02112)

http://itp.tugraz.at/LV/boeri/ELE/
- **DFT1+2**: Hohenberg-Kohn Theorem and Kohn and Sham equations.
- **DFT3+4**: Solving K-S in practice; basis functions, augmented methods and psp theory.
- **DFT5**: Practical problems in DFT (k space integration, convergence etc)
- **P1**: EOS and band structure of silicon.
- **ADV1+2**: Linear Response theory (mostly for phonons).
- **P2**: Phonons of silicon
- **ADV3**: Wannier Functions and TB approximation.
- **P3**: Wannier Functions and BOM for silicon.
Important Dates (exercises):

13/5 (Tuesday, next week): 14-15:30 (Electronic structure, \textit{pw.x})
23/5 (Friday): 14-> 17 (Phonons, \textit{ph.x})
30/5 (Friday): 14-> 17 (Wannier Functions, \textit{wannier90.x}).

We will employ quantum espresso: http://www.quantum-espresso.org/
Before the break:

- Density Functional Theory: Hohenberg and Kohn Theorem, Kohn-Sham equations (Density is the basic variable).
- Density Functional Theory: practical problems (convergence, basis functions).
- Pseudopotential Theory.

“A primer in Density Functional Theory” (Springer), chapter 1 and 6.

- Pseudopotential Theory.

_Pseudopotential Method, G.B. Bachelet and A. Filippetti (notes)._
Solids: Quantum Mechanical Problem

\[ \hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 + \sum_i \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \]

- **Density functional theory:**

  - “Smart” method to approximate the electron-electron interaction: the interacting many-body wavefunction for electrons is replaced by the electron density (function of one variable).

- **Pseudopotential Method:**

  - Approximate the electron-nuclei term: DFT equations in plane waves can be practically implemented.
Main Concepts of Density Functional Theory:

The quantum-mechanical many-electron problem can be greatly simplified if we are only interested in its ground-state properties.

\[
\Psi_0(r_1\sigma_1, \ldots, r_N\sigma_N) \rightarrow n_0^\sigma(r) = \sum_{\sigma_2 \ldots \sigma_N} \int d^3r_2 \ldots d^3r_N |\Psi_0(r_\sigma, \ldots, r_N\sigma_N)|^2
\]

- **Hohenberg-Kohn Theorem:** The ground-state energy of a system of interacting electrons is a function of its ground-state density only. The complications induced by the electron-electron interaction are "dumped" into an effective exchange and correlation energy, whose exact form is unknown (but good approximation exists).

- **Kohn-Sham Equations:** It is possible to find the ground-state density of the interacting system solving self-consistently a system of single-particle equations for the **auxiliary (effective) Kohn-Sham quasi-particles**.
Kohn-Sham Equations:

The Schrödinger's equation for the Kohn-Sham quasi-particles depends on the ground-state density; on the other hand, the ground-state density is obtained summing over the occupied K-S orbitals.

\[
\left( -\frac{1}{2} \nabla^2 + v(\mathbf{r}) + u([n]; \mathbf{r}) + u_{xc}(n_\uparrow, n_\downarrow; \mathbf{r}) \right) \psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma} \psi_{\alpha\sigma}(\mathbf{r})
\]

\[
n_{\sigma}(\mathbf{r}) = \sum_{\alpha} \theta(\mu - \epsilon_{\alpha\sigma}) |\psi_{\alpha\sigma}(\mathbf{r})|^2
\]

1. Start from a set of “guess functions”.
2. Calculate the corresponding charge density.
3. Compute the Hartree and xc potentials
4. Insert into the Schrödinger equations.

Iterate until the charge densities at step \(t\) and \((t+1)\) differ by less than a given threshold
Kohn-Sham Equations (plane waves):

The most convenient way to solve K-S equations is to expand the K-S Bloch orbitals on given basis functions. **Plane waves** are a very common choice:

\[
\psi_{nk}(\mathbf{r}) = \sum_{\mathbf{G}} c_{nk}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}
\]

\[
\sum_{\mathbf{G}'} \left[ \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + \tilde{\nu}(|\mathbf{G} - \mathbf{G}'|) \right] c_{nk}(\mathbf{G}') = \varepsilon_{nk} c_{nk}(\mathbf{G})
\]

The computational time scales exponentially with the number of plane-waves. The length-scale (number of G components) of the scf potential is given by the external (lattice potential).

\[
t_{\text{comp}} \propto \left( N_{pw} \right)^3
\]

\[
|\mathbf{k} + \mathbf{G}|^2 < E_{\text{cut}} \quad \lambda_{\text{min}} = \frac{2\pi}{G_{\text{cut}}}
\]

In order to reduce the number of plane waves, we have to “cut out” the core electrons, which have small-scale oscillations (pseudopotential).
Model Pseudopotentials:

The solid can be approximated as isolated (rigid) pseudo-atoms + valence electrons which re-arrange self-consistently due to different environment (chemical bonds). The tail of the potential of the pseudo-atoms must behave as $-Z_v/r$.

A model pseudopotential has two important physical parameters:

- $Z_v$: Valence charge
- $r_c$: Core radius

Good agreement for charge density distributions (defects, impurities), bad results for total energy.

Figure 3: Model bare pseudopotentials. Lower panel: two-parameter pseudopotential. Upper and middle panels: one-parameter pseudopotentials, where the only parameter is the core radius $r_c$, roughly corresponding to the spatial extent of the outermost core orbitals, or to the outermost radial node of the true valence orbitals (see Figure 2 and text).
Ab-initio Pseudopotentials:

Hamann-Schlueuter-Chiang (1979): A fully ab-initio pseudopotential can be constructed, requiring that the solution of the radial Schroedinger equation for the full and the pseudo atoms are the same, above a cut-off radius $r_c$:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + v_{\text{screen}}(r)\right] \chi_{nl} = \varepsilon_{nl} \chi_{nl}$$

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_{l,\text{screened}}(r)\right] \chi_{l}^{ps} = \varepsilon_{l} \chi_{l}^{ps}$$

The pseudo wave function is a smooth function without nodes. Norm conservation ensures optimal transferability.

$$\int_{0}^{r_c} |\chi_{l}^{ps}(r)|^2 dr = \int_{0}^{r_c} |\chi_{nl}(r)|^2 dr$$
Second Part (Advanced Topics)

PHONONS AND DENSITY FUNCTIONAL PERTURBATION THEORY
Outline:

- Phonons: Physical Properties, experiments and theory (history).
- Phonon Eigenvectors and Supercells.
- Limitations of the supercell method (Kohn Anomalies in metals).

Phonons:

Physical Properties:

- Specific heat, lattice expansion, heat conduction, melting.
- Electron-Phonon interaction (metals): transport (resistivity), superconductivity, optical spectra.

Experimental Methods:

- $\Gamma$ point (Raman/IR spectroscopy)
- Inelastic scattering (full dispersion): neutrons, X-ray, Helium.
Phonons:

**Theory (early approaches):**

- Quantum theory of lattice vibrations (*Born et al, 30’s*): dynamical properties, relation to crystal symmetries
- Shell Model: semi-empirical model to account for the effect of electrons on lattice properties.

**Modern Approaches (*Ab-initio*):**

- Based on the total energy of the quantum-mechanical problem of the crystal (electrons+ions): include self-consistently the effect of electrons on phonon properties. (*De Cicco et al, Pick et al; with DFT: Cohen et al,... + many others*).
Lattice Dynamics from electronic-structure Theory:

The Schroedinger equation for the nuclei reads:

$$ \left[ -\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial R_I^2} + E(R) \right] \Phi(R) = \varepsilon \Phi(R) $$

$E(R)$ is the Born-Oppenheimer energy surface (solution of the electronic Schroedinger’s equation for *clamped ions*).

$$ H_{BO}(R) = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial r_i^2} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + E_N(R) $$

$$ E_N(R) = \frac{e^2}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|} $$
The equilibrium geometry is given by the condition that the forces on individual nuclei vanish:

\[ F_I = - \frac{\partial E(R)}{\partial R_I} = 0 \]

While Phonon Frequencies can be calculated from the determinant of the Hessian matrix:

\[
\det \left| \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(R)}{\partial R_I \partial R_J} - \omega^2 \right| = 0
\]
**Ab-initio Lattice Dynamics:**

To calculate the *phonon* frequencies of a given system we have to compute the *second-order* variations of the energy. There are two methods for this:

1) **Frozen-phonon:** Direct method (brute-force). Calculate the total energy for (small) finite displacements using *supercells*.

2) **Linear Response:** “Elegant” Method: perturbations are “monochromatic”, all q points can be calculated with the same computational effort.
Lattice dynamics (linear chain)

\[
\omega(k) = \sqrt{\frac{2k(1 - \cos(ka))}{M}} = 2\sqrt{\frac{k}{M}} \left| \sin \frac{ka}{2} \right|
\]

\[u(na) = e^{i(ka - \omega t)}\]

Linear chain with 2 force constants:

\[
\omega^2(k) = \frac{K + G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos(ka)}
\]

+ = optical
- = acoustical

Eigenvector:

\[
\frac{\varepsilon_2}{\varepsilon_1} = \frac{K + Ge^{ika}}{K + Ge^{ika}}
\]

\[u_i(na) = \varepsilon_i e^{i(ka - \omega t)}\]
How to construct supercells?
Metals have many small-scale structures due to electron-phonon coupling (Kohn anomalies).
Energy Gaps and Kohn Anomalies in Elemental Superconductors

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Fig. 4. (A) Linewidths of transverse acoustic phonons along $q = (\xi, 0, 0)$ in Nb at two different temperatures. The gray symbols are the results of lattice-dynamical calculations, as described in the text. (B) Blowup of the low-$q$ segment of (A). The corresponding $E$ is provided by the scale at the top. The lines are guides to the eye. Error bars indicate the statistical errors.