Periodic systems: Concepts

Sergey V. Levchenko

FHI Theory department
Reminder: electronic-structure problem

\[ \hat{h} \psi_i = \epsilon_i \psi_i \]

\[ \hat{h} = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' + \hat{V}_{\text{XC}} \]

\( \psi_i \) - unknown functions (one-electron wave functions)

\[ \psi_i(\mathbf{r}) = \sum_p C_{ip} \phi_p(\mathbf{r}) \] - basis set expansion

\( \phi_p(\mathbf{r}) \) - known functions (basis functions)

Generalized eigenvalue problem:

\[ \sum_q \langle \phi_p | \hat{h}[\mathbf{C}] | \phi_q \rangle C_{iq} = \epsilon_i \sum_q \langle \phi_p | \phi_q \rangle C_{iq} \]
Extended (periodic) systems

There are $10^{20}$ electrons per 1 mm$^3$ of bulk Cu

Position of every atom in the crystal (Bravais lattice):

$$\mathbf{r}(n_1, n_2, n_3) = \mathbf{r}(0,0,0) + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

lattice vector: $$\mathbf{R}(n_1, n_2, n_3) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

$$n_1, n_2, n_3 = 0, \pm 1, \pm 2, \ldots$$
Example: two-dimensional Bravais lattice

The shape of the primitive unit cell is not unique
From molecules to solids

Electronic bands as limit of bonding and anti-bonding combinations of atomic orbitals:

Bloch’s theorem

Periodic potential \( U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \) (translational symmetry)

\[
\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3
\]

In an infinite periodic solid, the solutions of the one-particle Schrödinger equations must behave like

\[
\psi(\mathbf{r} + \mathbf{R}) = \exp(ik\mathbf{R})\psi(\mathbf{r})
\]

Index \( \mathbf{k} \) is a vector in reciprocal space

\[
\mathbf{k} = x_1 \mathbf{g}_1 + x_2 \mathbf{g}_2 + x_3 \mathbf{g}_3 \quad \mathbf{g}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}
\]

\[
\mathbf{g}_l = 2\pi \frac{\mathbf{a}_m \times \mathbf{a}_n}{\Omega} \quad \text{– reciprocal lattice vectors}
\]

Consequently:

\[
\psi(\mathbf{r}) = \exp(ik\mathbf{r})u(\mathbf{r}), \quad u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r})
\]
The meaning of $k$

$\psi_k = \sum_j \exp(ikx_j) \chi_{1s}(j \cdot a)$

$k$ shows the phase with which the orbitals are combined:

$k = 0$: $\psi_0 = \sum_j \exp(0) \chi_{1s}(j \cdot a) = \chi_{1s}(a) + \chi_{1s}(2a) + K$

$k = \frac{\pi}{a}$: $\psi_0 = \sum_j \exp(i\pi \cdot j) \chi_{1s}(j \cdot a) = -\chi_{1s}(a) + \chi_{1s}(2a) - \chi_{1s}(3a) + K$

$k$ is a symmetry label and a node counter, and also represents electron momentum

Bloch’s theorem: consequences

In a periodic system, the solutions of the Schrödinger equations are characterized by an integer number $n$ (called band index) and a vector $k$:

$$\hat{h}\psi_{nk} = \varepsilon_{nk}\psi_{nk}$$

$$\psi_{nk}(r) = \exp(ikr)u_{nk}(r), \quad u_{nk}(r + R) = u_{nk}(r)$$

For any reciprocal lattice vector

$$G = n_1g_1 + n_2g_2 + n_3g_3$$

$$\psi_{nk+G} = \exp(ikr)[u_{k+G}\exp(iGr)] = \exp(ikr)\tilde{u} = \psi_{n'k}$$

a Bloch state at $k+G$ with index $n$

a lattice-periodic function $\tilde{u}$

a Bloch state at $k$ with a different index $n'$

Can choose to consider only $k$ within single primitive unit cell in reciprocal space
Brillouin zones

A conventional choice for the reciprocal lattice unit cell

For a square lattice

For a hexagonal lattice

In three dimensions:

- Face-centered cubic (fcc) lattice
- Body-centered cubic (bcc) lattice
Time-reversal symmetry

For Hermitian \( \hat{h} \), \( \varepsilon_{n,k} \) can be chosen to be \textit{real}

\[
\hat{h} \psi_{n,k}(\mathbf{r}) = \varepsilon_{n,k} \psi_{n,k}(\mathbf{r}) \implies \hat{h} \psi_{n,k}^*(\mathbf{r}) = \varepsilon_{n,k} \psi_{n,k}^*(\mathbf{r})
\]

From Bloch’s theorem:

\[
\psi_{n,k}(\mathbf{r} + \mathbf{R}) = \exp(ik\mathbf{R})\psi_{n,k}(\mathbf{r}) \implies \psi_{n,k}^*(\mathbf{r} + \mathbf{R}) = \exp(-ik\mathbf{R})\psi_{n,k}^*(\mathbf{r})
\]

\[
\psi_{n,k}^* = \psi_{n,-k} \quad \varepsilon_{n,-k} = \varepsilon_{n,k}
\]

Electronic states at \( k \) and \( -k \) are at least doubly degenerate 
(in the absence of magnetic field)
**Basis sets**

\[ \psi_i(r) = \sum_p C_{ip} \varphi_p(r) \]

Commonly used basis sets:

- **plane waves** \( \exp(ik \cdot r) \) (delocalized, analytic integrals)
- **gaussians** \( x^i y^j z^k \exp(-\alpha r^2) \) (localized, analytic integrals)
- **Slater-type** \( x^i y^j z^k \exp(-\alpha r) \) (localized, nuclear cusp)
- **Numeric atomic orbitals** \( \frac{u(r)}{r} Y_{lm}(\theta, \phi) \) (localized, flexible)
- **grid-based** \( \delta(r - r_i) \) (localized)

Core electrons are often treated separately (pseudopotentials, plane-wave + localized basis)
Localized basis sets and periodic systems

\[
\chi_{pk}(r) = \sum_R e^{-ikR} \phi_p(r + R)
\]

New basis functions satisfying Bloch’s theorem:

\[
\chi_{pk}(r + R) = e^{ikR} \chi_{pk}(r)
\]

\[
\psi_{ik}(r) = \sum_p C_{ik,p} \chi_{pk}(r) \quad \psi_{ik}(r + R) = e^{ikR} \psi_{ik}(r)
\]
Localized basis sets and periodic systems

\[
\hat{h} \left[ \sum_p \sum_R C_{ik}^p e^{-ikR} \phi_p(r + R) \right] = \varepsilon_{ik} \left[ \sum_p \sum_R e^{-ikR} \phi_p(r + R) \right]
\]

Multiply by \(\phi_q\) and integrate over all space:

\[
\sum_p \sum_R C_{ik}^p e^{-ikR} \langle \phi_q | \hat{h} | \phi_p (r + R) \rangle = \varepsilon_{ik} \sum_p \sum_R e^{-ikR} \langle \phi_q | \phi_p (r + R) \rangle
\]

In practice, all integration points and pieces of \(\phi_p\) are mapped back to the original unit cell:
For a periodic (infinite) crystal, there is an infinite number of states for each band index $n$, differing by the value of $k$. Band structure represents dependence of $\varepsilon_{nk}$ on $k$. Electronic band structure
By convention, $\varepsilon_{n\mathbf{k}}$ are measured (angular-resolved photoemission spectroscopy, ARPES) and calculated along lines in $\mathbf{k}$-space connecting points of high symmetry.
Finite k-point mesh

Charge densities and other quantities are represented by Brillouin zone integrals:

\[ n(r) = \sum_{j} \sum_{\Omega_{BZ}} \left| \psi_{jk}(r) \right|^2 \frac{d^3k}{\Omega_{BZ}} \]

\[ \psi_{nk}, \varepsilon_{nk} \text{ – smooth functions of } k \rightarrow \text{ can use a finite mesh, and then } \text{interpolate and/or use perturbation theory to calculate integrals} \]

\[ n(r) \approx \sum_{j} \sum_{m=1}^{N_{kpt}} w_m \left| \psi_{jk_m}(r) \right|^2 \]

Band gap and band width (dispersion)

\[ \varepsilon(k) \]

- Hydrogen molecule chain (DFT-PBE)

Overlap between interacting orbitals determines band gap and band width
Orbital energies are smooth functions of $k$

Example: chain of Pt-L$_4$ complexes ($K_2[Pt(CN)_4]$)

$$k = 0 \quad k = \pi/a$$

$$\varepsilon(k)$$

Insulators, semiconductors, and metals

- Insulators (MgO, NaCl, ZnO, …)
  \[ E_g \gg k_B T \]

- Semiconductors (Si, Ge, …)
  \[ E_g \sim k_B T \]

- Metals (Cu, Al, Fe, …)
  \[ E_g = 0 \]

In a metal, some (at least one) energy bands are only partially occupied.

The Fermi energy \( \varepsilon_F \) separates the highest occupied states from lowest unoccupied.
Fermi surface

Plotting the relation

$$\varepsilon_n(k) = \varepsilon_F$$

in reciprocal space for different $n$ yields different parts of the Fermi surface.

For free electrons, Fermi surface is a sphere

$$\frac{\eta^2 k^2}{2m_e} = \varepsilon_F$$

Periodic table of Fermi surfaces: http://www.phys.ufl.edu/fermisurface/

The grid used in $k$-space must be sufficiently fine to accurately sample the Fermi surface.
Density Of States (DOS)

Number of states in energy interval \( d\varepsilon \) per unit volume,

\[
g(\varepsilon) = \sum_n \int_{\Omega_{\text{BZ}}} \delta(\varepsilon - \varepsilon_n(k))d^3k \approx \sum_n \sum_{j=1}^{N_{\text{kpt}}} w_j \delta(\varepsilon - \varepsilon_n(k_j))
\]

\[
\frac{1}{\Omega d\varepsilon} \sum_{\varepsilon} 1
\]
Atom-Projected Density Of States (APDOS)

Decomposition of DOS into contributions from different atomic functions $\varphi_i$:

$$g_i(\varepsilon) = \sum_n \int_{\Omega_{\text{BZ}}} \left| \int \varphi_i(\mathbf{r}) \psi_{nk}(\mathbf{r}) d^3r \right|^2 \delta(\varepsilon - \varepsilon_n(\mathbf{k})) d^3k$$

Recovery of the chemical interpretation in terms of orbitals

Qualitative analysis tool; ambiguities must be resolved by truncating the $r$-integral or by Löwdin orthogonalization of $\varphi_i$
Potential of an array of point charges

\[ V(r) = \sum_{i=1}^{N} \sum_{R} \frac{q_i}{|r - r_i - R|}, \quad \sum_{i=1}^{N} q_i = 0 \]

Convergence of the potential with number of charges is extremely slow.
Ewald summation

\[ V(r) = \sum_{\mathbf{R}} \sum_{i=1}^{N} \frac{q_i}{|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|} - \frac{1}{\eta \sqrt{\pi}} \exp\left(-\frac{(|\mathbf{r} - \mathbf{r}_i|)^2}{\eta^2}\right) \]

screening gaussian charge distribution

\[ \nabla^2 V(r) = -4\pi \rho(r) \] (Poisson's equation)

\[ V_1(r) = \sum_{i, \mathbf{R}} q_i \left( \text{erfc}\left(\frac{|\mathbf{r} - \mathbf{r}_i - \mathbf{R}|}{\eta}\right) \right) \]

Decays fast with $|\mathbf{R}|$

\[ V_2(r) = \sum_{i, G \neq 0} q_i \frac{4\pi}{G^2 \Omega} \exp\left(-\frac{\eta^2 G^2}{4} + iG \cdot (\mathbf{r} - \mathbf{r}_i)\right) \]

Decays fast with $|G|$

Diverges at $G = 0$, but divergence is cancelled for $\sum_i q_i = 0$

There is no universal potential energy reference (like vacuum level) for 3D periodic systems – important when comparing different systems.
Modeling surfaces, interfaces, and point defects – the supercell approach
The supercell approach

Can we benefit from periodic modeling of non-periodic systems?
Yes, for interfaces (surfaces) and wires (also with adsorbates), and defects (especially for concentration or coverage dependences)

Supercell approach to surfaces (slab model)

- Approach accounts for the lateral periodicity
- Sufficiently broad vacuum region to decouple the slabs
- Sufficient slab thickness to mimic semi-infinite crystal
- Semiconductors: saturate dangling bonds on the back surface
- Non-equivalent surfaces: use dipole correction
- Alternative: cluster models (for defects and adsorbates)
Surface band structure

Example: fcc crystal, (111) surface

surface Brillouin zone
Surface band structure of Cu(111)

Energy, eV

Shockley surface state

Tamm surface state

Cu(111)
Shockley surface states

For near-free electrons: \( \psi_k(r) \sim \exp(ik \cdot r) \)

Matching condition

Decaying states can be treated as Bloch states with complex \( k \) (W. Kohn, Phys. Rev., 115, 809 (1959))

Complex band structures can give useful information about conductance through interfaces and molecular junctions
Tamm surface states

In the tight-binding (localized orbital) picture, surface states may appear due to ‘dangling orbitals’ split off from the band edge.
Surface reconstruction and band structure

Dimerization at (001)-surface of group IV-elements

bulk-terminated atomic structure
Surface reconstruction and band structure

Buckling of dimers at Si (100) surface

π-bond

re-hybridization and charge transfer (from down to up)

Surface reconstruction and band structure

- Symmetric dimer model (SDM)
- Asymmetric dimer model (ADM)
- Experimental results from angular-resolved photo-emission spectroscopy

Contour plot of electron density difference with respect to free Si atoms (dashed = decrease)

Total density contour plot

Concluding remarks

1) Periodic models can be efficiently used to study concentration/coverage dependence, including infinitely dilute limit (low-dimensional systems, defects, etc.)

2) A lot of useful and experimentally testable information on material’s properties can be obtained from the analysis of its electronic structure (band structure, DOS, APDOS, etc.)

3) A lot of development (in both computational methods and code efficiency) is still necessary to go beyond standard DFT for periodic systems, and to approach accuracy that can be achieved nowadays for molecules.
Recommended literature


Axel Groß, “Theoretical surface science: A microscopic perspective”

Roald Hoffmann (1981 Nobel Prize in Chemistry (shared with Kenichi Fukui)):


2) “A chemical and theoretical way to look at bonding on surfaces”, Reviews of modern physics, 60, 601-628 (1988)
Surface modeling: important issues

1) Finite slab thickness (surface-surface interaction)

2) Finite vacuum layer thickness (image-image interactions)

3) Long-range interactions (charge, dipole moment)

4) Surface polarity

\[ \Delta \varphi \]
From molecules to solids

Electronic bands as limit of bonding and anti-bonding combinations of atomic orbitals:

bands

band gap

Shockley surface states

For nearly-free electrons:

\[ \varepsilon(k_\perp) \]

\[ \sim \exp[\kappa z] \]

\[ \sim \exp[i(k_\perp + i\kappa)z] \]