Basics of periodic systems calculations
(Electronic structure theory for materials)

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Extended (periodic) systems

There are \(10^{20}\) electrons per \(1\ \text{mm}^3\) 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 form 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 \( U(r + R) = U(r) \)  
(translational symmetry)  
\[
R = n_1a_1 + n_2a_2 + n_3a_3
\]

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

\[
\psi(r + R) = \exp(ikR)\psi(r)
\]

Index \( k \) is a vector in *reciprocal space*

\[
k = x_1g_1 + x_2g_2 + x_3g_3 \quad \text{and} \quad g_i \cdot a_j = 2\pi\delta_{ij}
\]

\[
g_l = 2\pi \frac{a_m \times a_n}{\Omega} \quad \text{– reciprocal lattice vectors}
\]

Consequently:

\[
\psi(r) = \exp(ikr)u(r), \quad u(r + R) = u(r)
\]
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:

$k = 0$:

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

$k = \frac{\pi}{a}$:

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

$k$ 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 \( \mathbf{k} \):

\[
\hat{H} \psi_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}
\]

\( \psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}), \quad u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \)

For any reciprocal lattice vector

\[ \mathbf{G} = n_1 \mathbf{g}_1 + n_2 \mathbf{g}_2 + n_3 \mathbf{g}_3 \]

\[
\psi_{n\mathbf{k}+\mathbf{G}} = \exp(i\mathbf{k}\mathbf{r})[u_{\mathbf{k}+\mathbf{G}} \exp(i\mathbf{G}\mathbf{r})] = \exp(i\mathbf{k}\mathbf{r})\tilde{u} = \psi_{n'\mathbf{k}}
\]

A Bloch state at \( \mathbf{k} + \mathbf{G} \) with index \( n \)

A lattice-periodic function \( \tilde{u} \)

A Bloch state at \( \mathbf{k} \) with a different index \( n' \)

Can choose to consider only \( \mathbf{k} \) within single primitive unit cell in reciprocal space
Brillouin zones

A conventional choice for the reciprocal lattice unit cell

For a square lattice

Wigner-Seitz cell

For a hexagonal lattice

Wigner-Seitz cell

In three dimensions:

Face-centered cubic (fcc) lattice

Body-centered cubic (bcc) lattice
**Time-reversal symmetry**

For Hermitian $\hat{h}$, $\varepsilon_{n\mathbf{k}}$ can be chosen to be real

$$\hat{h} \psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}) \Rightarrow \hat{h} \psi_{n\mathbf{k}}^\ast(\mathbf{r}) = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}^\ast(\mathbf{r})$$

From Bloch’s theorem:

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(ik\mathbf{R})\psi_{n\mathbf{k}}(\mathbf{r}) \Rightarrow \psi_{n\mathbf{k}}^\ast(\mathbf{r} + \mathbf{R}) = \exp(-ik\mathbf{R})\psi_{n\mathbf{k}}^\ast(\mathbf{r})$$

$$\psi_{n\mathbf{k}}^\ast = \psi_n(-\mathbf{k}) \quad \varepsilon_n(-\mathbf{k}) = \varepsilon_{n\mathbf{k}}$$

Electronic states at $\mathbf{k}$ and $-\mathbf{k}$ are at least doubly degenerate

(in the absence of magnetic field)
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
Electronic band structure in three dimensions

Brillouin zone of the fcc lattice

Al band structure (DFT-PBE)

By convention, $\varepsilon_{nk}$ are measured (angular-resolved photoemission spectroscopy, ARPES) and calculated along lines in k-space connecting points of high symmetry.
Finite k-point mesh

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

\[ n(r) = \sum_j^{\text{occ}} \int_{\Omega_{BZ}} \left| \psi_{jk}(r) \right|^2 \frac{d^3k}{\Omega_{BZ}} \]

\[ \psi_{nk}, \varepsilon_{nk} \] – smooth functions of \( k \) →

can use a finite mesh, and then
interpolate and/or use perturbation theory to calculate integrals

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

Band gap and band width (dispersion)

- hydrogen molecule chain (DFT-PBE)

Overlap between interacting orbitals determines band gap and band width
Band structure – test example

Orbital energies are smooth functions of $k$

Example: chain of Pt-L₄ complexes ($K_2[Pt(CN)_4]$)

Insulators (MgO, NaCl, ZnO,...)

Semiconductors (Si, Ge,...)

Metals (Cu, Al, Fe,...)

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

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

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,

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

$$\frac{1}{\Omega d\varepsilon} \sum_{\varepsilon}^{\varepsilon+d\varepsilon} 1$$
Atom-Projected Density Of States (APDOS)

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

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

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 $\phi_i$. 

Diagram showing band structures and orbital contributions.
Potential of an array of point charges

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

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

\[ V(r) = \sum_{R} \sum_{i=1}^{N} \frac{q_i}{|r - r_i - R|} + \sum_{i,G \neq 0} q_i \frac{4\pi}{G^2 \Omega} \exp \left( -\frac{\eta^2 G^2}{4} + iG \cdot (r - r_i) \right) \]

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

Decays fast with \(|R|\)

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 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)
Shockley surface states

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

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

Experimental results from angular-resolved photo-emission spectroscopy

Electron-repulsion integrals in periodic systems
**Standard DFT and the self-interaction error**

\[
E_{\text{tot}} = T[n] - \sum_{l=1}^{M} Z_l \int \frac{n(r)}{|r - R_l|} d^3r + \frac{1}{2} \sum_{l=1}^{M} \sum_{j=1}^{M} \frac{Z_l Z_j}{|R_l - R_j|} + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} d^3r d^3r' + E_{\text{XC}}[n]
\]

\( n(r) \) -- electron density

\( E_{\text{XC}}[n] \) -- exchange-correlation (XC) energy

\( (\text{includes self-interaction}) \)

**LDA, GGA, meta-GGA:**

\[
E_{\text{XC}}[n] = E_{X}^{\text{loc}}[n] + E_{C}^{\text{loc}}[n]
\]

**Standard DFT:** (Semi)local XC operator \( \rightarrow \) low computational cost

Removing self-interaction + preserving fundamental properties (e.g., invariance with respect to subspace rotations) is non-trivial \( \rightarrow \) residual self-interaction (error) in standard DFT

**Consequences of self-interaction** (no cancellation of errors):
localization/delocalization errors, incorrect level alignment (charge transfer, reactivity, etc.)
Hybrid DFT

\[ E_{XC}[\{\psi\}] = \alpha E_{X}^{HF}[\{\psi\}] + (1 - \alpha) E_{X}^{loc}[n] + E_{C}^{loc}[n] \]

-- easy in Kohn-Sham formalism ( \( n = \sum_{n} f_{n} |\psi_{n}|^{2} \) )

Perdew, Ernzerhof, Burke (J. Chem. Phys. 105, 9982 (1996)): \( \alpha = 1/N \)

MP4 \( \Rightarrow \) \( N = 4 \), but “An ideal hybrid would be sophisticated enough to optimize \( N \) for each system and property.”

\[ E_{XC}^{PBE0} = \alpha E_{X}^{HF} + (1 - \alpha) E_{X}^{PBE} + E_{C}^{PBE} \]
Hartree-Fock exchange – the problem

\[ E_{X}^{\text{HF}} = -\frac{1}{2} \sum_{i,j,k,l} D_{il} D_{jk} \int \frac{\phi_i(\mathbf{r})\phi_k(\mathbf{r})\phi_j(\mathbf{r'})\phi_l(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d^3rd^3r' \]

electron repulsion integrals

Lots of integrals, naïve implementation \( \rightarrow N^4 \) scaling (storage impractical for \( N > 500 \) basis functions)

- need fast evaluation
- need efficient use of sparsity (screening)
"Resolution of identity" (RI) (density fitting)

\[(ij \mid kl) = \int \frac{\varphi_i(r)\varphi_j(r)\varphi_k(r')\varphi_l(r')}{|r - r'|} d^3r d^3r'\]

\[\varphi_i(r)\varphi_j(r) = \sum_{\mu} C_{ij}^{\mu} P_{\mu}(r)\]

\[\varphi_k(r)\varphi_l(r) = \sum_{\mu} C_{kl}^{\mu} P_{\mu}(r)\]

independent auxiliary basis

Basis-pair space is overcomplete, since \(\{\varphi_i(r)\}\) approaches completeness \(\rightarrow\) size of \(\{P_{\mu}(r)\}\) \(\sim 4-5\) times size of \(\{\varphi_i(r)\}\)
“Resolution of identity” (RI) (density fitting)

\[(ij \mid kl) = \int \frac{\varphi_i(r)\varphi_j(r)\varphi_k(r')\varphi_l(r')}{|r-r'|} d^3r d^3r' \]

\[\varphi_i(r)\varphi_j(r) = \sum_{\mu} C_{ij}^{\mu} P_{\mu}(r) \]
\[\varphi_k(r)\varphi_l(r) = \sum_{\mu} C_{kl}^{\mu} P_{\mu}(r) \]

independent auxiliary basis

Finding the RI coefficients: RI-SVS

$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \approx \sum_{\mu} C_{ij}^\mu P_\mu(\mathbf{r}) \Rightarrow (ij \mid kl) \approx I_{ij,kl} = \sum_{\mu,\nu} C_{ij}^\mu V_{\mu\nu} C_{kl}^\nu$$

Minimize the error norm: $$\min_C \int \left( \sum_{\mu} C_{ij}^\mu P_\mu(\mathbf{r}) - \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \right)^2 d^3r$$

$$I_{ij,kl} = \sum_{\nu} O_{ij}^\nu S_{\nu\sigma}^{-1} V_{\sigma\sigma'} S_{\sigma'\mu}^{-1} O_{kl}^\mu, \quad O_{ij}^\nu = \int \varphi_i(\mathbf{r})\varphi_j(\mathbf{r})P_\nu(\mathbf{r})d^3r$$

![Graph showing the error in total energy (meV) with respect to the number of molecules in the S22 set.](image)
Finding better RI coefficients

\[ \rho_{ij}(\mathbf{r}) = \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}), \quad (ij | kl) = \int \frac{\rho_{ij}(\mathbf{r})\rho_{kl}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r \]

Let us calculate the error in \((ij | ij)\) – the largest integrals:

\[ \delta(ij | ij) = 2\int \frac{\delta\rho_{ij}(\mathbf{r}) \left( \sum_v C_{ij}^v P_v(\mathbf{r}') \right)}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + \Delta(\delta\rho_{ij}^2) \]

first-order correction does not vanish in RI-SVS!

Is it possible to do better without increasing the size of the auxiliary basis?
Finding better RI coefficients: RI-V

Set the first-order correction to zero, minimize second-order:

\[ \Delta(\delta \rho_{ij}^2) \rightarrow \min \implies \Delta(\delta \rho_{ij}) \rightarrow 0 \]

\[
I_{ij,kl} = \sum_v Q_{ij}^v V^{-1}_{v\mu} Q_{kl}^{\mu}, \quad Q_{ij}^v = \int \frac{\varphi_i(r)\varphi_j(r)P_v(r')}{|r-r'|} d^3rd^3r'
\]
Finding better RI coefficients: RI-V

\[ O_{ij}^\nu = \int \varphi_i(r) \varphi_j(r) P_v(r) d^3r \]

\[ Q_{ij}^\nu = \int \frac{\varphi_i(r) \varphi_j(r) P_v(r')}{|r - r'|} d^3rd^3r' \]

Distant aux. functions contribute to the integrals \( \rightarrow \) a lot of memory and operations \( \rightarrow \) scaling \( N^3 \)
Localized RI-V (RI-LVL, Jürgen Wieferink)

\[ \varphi_i(r)\varphi_j(r) \approx \sum_{\mu} C_{ij}^\mu P_\mu(r), \quad \mu \in \text{atom}(i) \text{ or atom}(j) \]

\[ \Delta(\delta\rho_{ij}^2) \to \min \quad \Rightarrow \quad \Delta(\delta\rho_{ij}) \to 0 \]

\[ I_{ij,kl} = \sum_{\sigma\sigma'} \left( \sum_{\nu} Q_{ij}^\nu L_{\nu\sigma} \right) V_{\sigma\sigma'} \left( \sum_{\mu} L_{\sigma'\mu} Q_{kl}^\mu \right), \quad L_{\nu\sigma} = (V^{-1})_{\nu\sigma} \]
Hartree-Fock exchange in extended systems

\[ E_X^\text{HF} = -\frac{1}{2} \sum_{m,n} \int \psi_{mk}^*(r, \sigma) \psi_{nk'}(r, \sigma) \psi_{nk'}^*(r', \sigma') \psi_{mk}(r', \sigma') \frac{d^3rd^3r'd\sigma d\sigma'}{|r-r'|} \]

\[ \psi_{mk}(r, \sigma) = s(\sigma) \sum_{i,R} c_{mi}^{k\sigma} \varphi_i(r-R) e^{ikR} \]

\[ E_X^\text{HF} = -\frac{1}{2} \sum_{i,j,k,l} D_{il}(R+R'') D_{jk}(R'-R) \times \]

\[ \times \int \frac{\varphi_i(r) \varphi_k(r-R') \varphi_j(r'-R) \varphi_l(r'-R-R'')}{|r-r'|} d^3rd^3r' \]
Electron repulsion integrals in periodic systems

RI-V is impractical for extended systems

$$\varphi_j(r - R)$$

$$\varphi_i(r)$$

$$P_\mu(r - Q)$$

$$C_{\mu \nu}^{\mu \nu} \equiv 0$$

RI-LVL: Sparse, easier to calculate, linear scaling is possible!

$$I_{ijR',kR/R+R''} = \sum_{\mu Q'} \sum_{\nu Q''} C_{i,jR'}^{\mu Q'} V_{\mu \nu (R+Q''-Q')} C_{k,lR''}^{\nu Q''}$$
Hybrid functionals -- scaling with system size

Zincblende GaAs

Periodic GaAs, HSE06 hybrid functional

Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler,
Hybrid functionals -- CPU scaling

Periodic GaAs, HSE06 hybrid functional

Zincblende GaAs

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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 Noble 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
From molecules to solids

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

Shockley surface states

For nearly-free electrons:

\[ \varepsilon(k_{\perp}) \]

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

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