Fundamentals: the quantum-mechanical many-electron problem and the Density Functional Theory approach

\[ \hat{H}\psi = E\psi \]

Javier Junquera
Most important reference followed in the tutorial:

The SIESTA method for *ab initio* order-\(N\) materials simulation

José M Soler\(^1\), Emilio Artacho\(^2\), Julian D Gale\(^3\), Alberto García\(^4\), Javier Junquera\(^1,5\), Pablo Ordejón\(^6\) and Daniel Sánchez-Portal\(^7\)
Most important reference followed in the tutorial:

- Richard M. Martin
  - Electronic Structure
    - Basic Theory and Practical Methods

Comprehensive review of DFT, including most relevant references and exercises.
Rigorous and unified account of the *fundamental principles* of DFT
More intended for researchers and advanced students
Iterative minimization techniques for *ab initio* total-energy calculations: molecular dynamics and conjugate gradients

M. C. Payne

*Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom*

M. P. Teter and D. C. Allan

*Applied Process Research, Corning Incorporated, Corning, New York 14831*

T. A. Arias and J. D. Joannopoulos

*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
Other interesting references:
Nobel lectures by W. Kohn and J. A. Pople

Nobel prize in Chemistry 1998

Walter Kohn

ELECTRONIC STRUCTURE OF MATTER – WAVE FUNCTIONS AND DENSITY FUNCTIONALS

Nobel Lecture, January 28, 1999
by
WALTER KOHN

Department of Physics, University of California, Santa Barbara, CA 93106-9530, USA

QUANTUM CHEMICAL MODELS

Nobel Lecture, December 8, 1998
by
JOHN A. POPLE

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA
Goal: Describe properties of matter from theoretical methods firmly rooted in fundamental equations
Goal: Describe properties of matter from theoretical methods firmly rooted in fundamental equations

Quantum Mechanics: Schrödinger equation (assuming no relativistic)

\[
-i\hbar \frac{\partial \Psi \left( \{ \vec{x}_i \}, \{ \vec{R}_\alpha \}; t \right)}{\partial t} = \hat{H} \Psi \left( \{ \vec{x}_i \}, \{ \vec{R}_\alpha \}; t \right)
\]

Coordinates of electron \( i \) \( \vec{x}_i \) comprise

\[
\begin{cases}
\text{Space coordinates} & \vec{T}_i \\
\text{Spin coordinates} & \sigma_i
\end{cases}
\]

Electromagnetism: Coulomb’s law

\[
\hat{H} = \hat{T} + \hat{V}_{\text{Coulomb}}
\]

For a pair of charged particles

\[
\hat{V}_{\text{Coulomb}} = \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}
\]
The Schrödinger equation (differential) must be solved subject to appropriate boundary conditions.

Ψ must be well behaved everywhere.

Atoms and molecules

Regular infinite solid

→ 0 at infinity

Appropriate periodic boundary conditions
The electrons are fermions, the solution must satisfy the Pauli exclusion principle

A many electron wave function must be antisymmetric with respect to the interchange of the coordinate (both space and spin) of any two electrons

\[ \Psi (\vec{x}_1, \ldots, \vec{x}_i, \ldots, \vec{x}_j, \ldots, \vec{x}_N) = -\Psi (\vec{x}_1, \ldots, \vec{x}_j, \ldots, \vec{x}_i, \ldots, \vec{x}_N) \]
Once the many-body wave function is known, we compute the expectation values of observables

\[ \langle \hat{A} \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \Psi^* \hat{A} \Psi d\vec{x}}{\int \Psi^* \Psi d\vec{x}} \]

Integration over all spatial coordinates
Summation over spin coordinates

A particular measurement gives a particular eigenvalue of \( \hat{A} \)
Many measurements average to \( \langle \hat{A} \rangle \)

The total energy is the expectation value of the Hamiltonian:

\[ E[\Psi] = \langle \hat{H} \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]

Ground state energy

\[ E_0 = \min_{\Psi} E[\Psi] \]
Minimization of the energy functional, totally equivalent to diagonalize the eigenvalue problem

Since the eigenstates of the many-body hamiltonian are stationary points (saddle points or the minimum)

\[ \delta E [\Psi] = 0 \]

The normalization condition can be imposed using Lagrange multipliers

\[ \delta \left[ \langle \Psi | \hat{H} | \Psi \rangle - E \left( \langle \Psi | \Psi \rangle - 1 \right) \right] = 0 \]

Variation of the bra from

\[ \langle \Psi | \rightarrow \langle \Psi + \delta \Psi | \]

\[ \langle \delta \Psi | \hat{H} - E | \Psi \rangle = 0 \]

This must hold for any variation in the bra, so this can be satisfied if the ket satisfies

\[ \hat{H} |\Psi\rangle = E |\Psi\rangle \]
A closer look to the hamiltonian: A difficult interacting many-body system.

\[ \hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} \]

Kinetic energy operator for the electrons
Potential acting on the electrons due to the nuclei
Electron-electron interaction
Kinetic energy operator for the nuclei
Nucleus-nucleus interaction
This hamiltonian can not be solved exactly: practical and fundamental problems

Fundamental problem:
Schrödinger’s equation is exactly solvable for
- Harmonic oscillator (analytically)
- Two particles (analytically)
- Very few particles (numerically)

Practical problem:
The number of electrons and nuclei in a pebble is of the order of $10^{23}$
A macroscopic solid contains a huge number of atoms.

Au atomic weight: 196.966569 ≈ 200

Number of moles in 1 kg of Au ≈

\[
\frac{1000 \text{ gr}}{200 \text{ gr/mol}} = 5 \text{ mol} \approx 3 \times 10^{24} \text{ atoms of gold}
\]
If the problem can not be solved exactly, how can we work it out from first-principles?

Use a set of “accepted” approximations to solve the corresponding equations on a computer.

NO EMPIRICAL INPUT

Properties
- Equilibrium structure
- Band structure
- Vibrational spectrum
- Magnetic properties
- Transport properties
- ...

IDEAL AB-INITIO CALCULATION

Chemical composition
- Number of atoms
- Type
- Position
What are the main approximations?

**Born-Oppenhaimer**
Decouple the movement of the electrons and the nuclei.

**Density Functional Theory**
Treatment of the electron — electron interactions.

**Pseudopotentials**
Treatment of the (nuclei + core) — valence.

**Basis set**
To expand the eigenstates of the hamiltonian.

**Numerical evaluation of matrix elements**
Efficient and self-consistent computations of H and S.

**Supercells**
To deal with periodic systems
What are the main approximations?

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To deal with periodic systems
Adiabatic or Born-Oppenheimer approximation decouple the electronic and nuclear degrees of freedom

\[ \frac{M_\alpha}{m_e} \gg 1 \]

\[ \Rightarrow \text{Nuclei much slower than the electrons} \]

\[ \frac{v_{\text{electron}}}{v_{\text{nucleus}}} \gg 1 \]

\[ v_{\text{electron}} \approx v_F \approx 10^8 \text{ cm/s} \]

\[ v_{\text{nucleus}} \approx 10^5 \text{ cm/s} \]

At any moment the electrons will be in their ground state for that particular instantaneous ionic configuration.

Solve electronic equations assuming fixed positions for nuclei

Move the nuclei as classical particles in the potential generated by the e-
If the nuclear positions are fixed (ignore nuclear velocities), the wave function can be decoupled

\[ \hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{\alpha} -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} \]

**Electrons**

\[ \hat{H}_{\{\vec{R}_\alpha\}}^{el} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{ext,\{\vec{R}_\alpha\}} (\{\vec{r}_i\}) \]

\[ \hat{H}_{\{\vec{R}_\alpha\}}^{el} \Psi_{n,\{\vec{R}_\alpha\}}^{el} (\{\vec{r}_i\}) = E_n^{el} \Psi_{n,\{\vec{R}_\alpha\}}^{el} (\{\vec{r}_i\}) \]

**Nuclei**

\[ \hat{H} = \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + E_n^{el} (\{\vec{R}_\alpha\}) \]

Classical displacement

\[ \vec{F}_\alpha = -\frac{\partial E_0^{el} (\{\vec{R}_\mu\})}{\partial \vec{R}_\alpha} \]
The next problem... how to solve the electronic equation

\[
\begin{align*}
\hat{H}_{\{\vec{R}_\alpha\}}^{el} &= \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{\text{ext}}^{\alpha} (\{\vec{r}_i\}) \\
\hat{H}_{\{\vec{R}_\alpha\}}^{el} \psi_{n,\{\vec{R}_\alpha\}}^{el} (\{\vec{r}_i\}) &= E_n^{el} \psi_{n,\{\vec{R}_\alpha\}}^{el} (\{\vec{r}_i\})
\end{align*}
\]

Exact solution only for one electron systems \( \Rightarrow \) H, hydrogenoid atoms, \( \mathrm{H}_2^+ \)

Main difficulty: very complicate electron-electron interactions.
What are the main approximations?

**Born-Oppenheimer**
Decouple the movement of the electrons and the nuclei.

**Density Functional Theory**
Treatment of the electron — electron interactions.

**Pseudopotentials**
Treatment of the (nuclei + core) — valence.

**Basis set**
To expand the eigenstates of the hamiltonian.

**Numerical evaluation of matrix elements**
Efficient and self-consistent computations of H and S.

**Supercells**
To deal with periodic systems.
The many-electron problem in interaction: An old and extremely hard problem.

Different approaches

• Quantum Chemistry (Hartree-Fock, CI...)
• Quantum Monte Carlo
• Perturbation theory (propagators)
• Density Functional Theory (DFT)
  Very efficient and general
  BUT implementations are approximate
  and hard to improve
  (no systematic improvement)
  (… actually running out of ideas …)
DFT: primary tool for calculation of electronic structure in condensed matter

<table>
<thead>
<tr>
<th>Many electron wave function</th>
<th>One electron density</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi (\vec{x}_1, \ldots, \vec{x}_N)$</td>
<td>$n (\vec{r})$</td>
</tr>
</tbody>
</table>

Undoubted merit: satisfies the many-electron Schrödinger equation

$$\hat{H} \Psi = E \Psi$$

Contains a huge amount of information

3N degrees of freedom for N electrons

All properties of the system can be considered as unique functionals of the ground state density

Integrates out this information

One equation for the density is remarkably simpler than the full many-body Schrödinger equation

A special role can be assigned to the density of particles in the ground-state of a quantum many-body system
First theorem of Hohenberg-Kohn

For any system of interacting particles in an external potential $V_{ext}(\vec{r})$, the potential $V_{ext}(\vec{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\vec{r})$. 

Inhomogeneous Electron Gas*

P. Hohenberg†
École Normale Superieure, Paris, France

AND

W. Kohn‡

We shall now show that conversely $v(\vec{r})$ is a unique functional of $n(\vec{r})$, apart from a trivial additive constant. The proof proceeds by reductio ad absurdum. As-
Corollary of first theorem of Hohenberg-Kohn

\[ n_0 (\vec{r}) \]

\[ \Downarrow \]

First theorem of Hohenberg-Kohn

\[ V_{\text{ext}} (\vec{r}) \]

\[ \Downarrow \]

Definition of the Hamiltonian of interacting electrons in an external potential

\[ \hat{H}_{\{\vec{r}_\alpha\}}^{\text{el}} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{\text{ext}}^{\{\vec{r}_\alpha\}} (\{\vec{r}_i\}) \]

\[ \Downarrow \]

Solving the Schrödinger equation: ground and excited many body wave functions

\[ \hat{H}_{\{\vec{r}_\alpha\}}^{\text{el}} \Psi_{n,\{\vec{r}_\alpha\}}^{\text{el}} (\{\vec{r}_i\}) = E_n^{\text{el}} \Psi_{n,\{\vec{r}_\alpha\}}^{\text{el}} (\{\vec{r}_i\}) \]

No prescription to solve this problem.

At this level we have gained nothing

All the properties of the system are completely determined given only the ground state density \( n_0 (\vec{r}) \)
A universal functional for the energy $E[n]$ in terms of the density $n(r)$ can be defined, valid for any external potential $V_{\text{ext}}(r)$. For any particular $V_{\text{ext}}(r)$, the exact ground state of the system is the global minimum value of this functional, and the density $n(r)$ that minimizes the functional is the exact ground state density $n_0(r)$. Where $F[n]$ is a universal functional, valid for any number of particles and any external potential. This functional plays a central role in the present paper. With its aid we define, for a given potential $v(r)$, the energy functional

$$E_v[n] = \int v(r)n(r)dr + F[n].$$

(10)

Clearly, for the correct $n(r)$, $E_v[n]$ equals the ground-state energy $E$. 

Second theorem of Hohenberg-Kohn
Some definitions

**Function:** rule for going from a variable $x$ to a number $f(x)$

**Functional:** rule for going from a function to a number

A function of which the variable is a function

$$E_{HK}[n] = T[n] + E_{int}[n] + \int d\vec{r} \ V_{ext}(\vec{r}) \ n(\vec{r}) + E_{II}$$

-300 eV (a value for the energy)

Universal means the same for all electron systems, independent of the external potential $V_{ext}(\vec{r})$
The kinetic energy and the interaction energy of the particles are functionals only of the density.

\[ E_{HK}[n] = T[n] + E_{int}[n] + \int d\vec{r} \ V_{ext}(\vec{r}) \ n(\vec{r}) + E_{II} \]

\[ \equiv F_{HK}[n] + \int d\vec{r} \ V_{ext}(\vec{r}) \ n(\vec{r}) + E_{II} \]

If known, minimization of \( E_{HK}[n] \) with respect variations of the density would determine the exact ground state density and energy.

Excited states for the electrons must be determined by other means.

PROBLEM: Functional is unknown
The Kohn-Sham ansatz replaces the many-body problem with an independent-particle problem

All the properties of the system are completely determined given only the ground state density \( n_0 (\vec{r}) \)

But no prescription to solve the difficult interacting many-body hamiltonian

\[
\hat{H}^{el}_{\{\vec{R}_\alpha\}} \Psi^{el}_{n,\{\vec{R}_\alpha\}} (\{\vec{r}_i\}) = E^{el}_n \Psi^{el}_{n,\{\vec{R}_\alpha\}} (\{\vec{r}_i\})
\]

Ground state density of the many-body interacting system = Density of an auxiliary non-interacting independent particle system

Kohn-Sham ansatz (never proven in general)
One electron or independent particle model

We assume that each electron moves independently in a potential created by the nuclei and the rest of the electrons.

Actual calculations performed on the auxiliary independent-particle system

\[ \hat{H}_{\text{aux}}^\sigma = -\frac{1}{2} \nabla^2 + V_{\text{eff}}^\sigma (\vec{r}) \]
The independent-particle kinetic energy is given explicitly as a functional of the orbitals

$$T_s = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_\sigma} \langle \psi_i^\sigma | \nabla^2 | \psi_i^\sigma \rangle = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_\sigma} | \nabla \psi_i^\sigma |^2$$

They rewrote the functional as

$$E_{KS}[n] = T_s[n] + \int d\vec{r} \ V_{ext}(\vec{r}) \ n(\vec{r}) + E_{Hartree}[n] + E_{xc}[n]$$

Equivalent to independent particles under the potential

$$V_{KS}^\sigma(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_{xc}^\sigma(\vec{r})$$
The one-particle eigenstates are filled following the “Aufbau” principle: from lower to higher energies.

\[ n^\sigma (\vec{r}) = \sum_i f_i^\sigma |\psi_i^\sigma (\vec{r})|^2 \]

Occupation numbers

The ground state has one (or two if spin independent) in each of the orbitals with the lowest eigenvalues.
The Kohn-Sham equations must be solved self-consistently. The potential (input) depends on the density (output).

1. **Initial guess**: 
   \[ n^\uparrow (\mathbf{r}), n^\downarrow (\mathbf{r}) \]

2. **Calculate effective potential**:
   \[ V_{\text{eff}}^\sigma (\mathbf{r}) = V_{\text{ext}}^\sigma (\mathbf{r}) + V_{\text{Hartree}}[n] + V_{\text{xc}}[n^\uparrow, n^\downarrow] \]

3. **Solve the KS equation**:
   \[ \left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}^\sigma (\mathbf{r}) \right] \psi_i^\sigma (\mathbf{r}) = \epsilon_i^\sigma \psi_i^\sigma (\mathbf{r}) \]

4. **Compute electron density**:
   \[ n^\sigma (\mathbf{r}) = \sum_i f_i^\sigma |\psi_i^\sigma (\mathbf{r})|^2 \]

5. **Self-consistent?**
   - Yes: Output quantities: Energy, forces, stresses ...
   - No: Go back to the initial guess and repeat the process.
Density functional theory is the most widely used method today for electronic structure calculations because of the approach proposed by Kohn and Sham.
Local Density Approximation (LDA)

Solids can be often considered as close to the limit of the homogeneous electron gas.
In this limit, effects of exchange and correlation are local in character.

\[ V_{xc} [n] \approx V_{xc} [n (\vec{r})] \]

Exchange-correlation energy of the homogeneous electron gas a function of density.

**Exchange:**
- analytic form

**Correlation:**
calculated to great accuracy with Monte Carlo methods.
GGA follows LDA

DFT thanks to Claudia Ambrosch (Graz)
All the unknown terms below a carpet: the exchange-correlation functional

\[ V_{xc}^\sigma (\vec{r}) \equiv \frac{\delta E_{xc}}{\delta n (\vec{r}, \sigma)} \]

Local Density Approximation (LDA)

Solids can be often considered as close to the limit of the homogeneous electron gas. In this limit, effects of exchange and correlation are local in character.

\[ V_{xc} [n] \approx V_{xc} [n (\vec{r})] \]

Exchange-correlation energy of the homogeneous electron gas a function of density

- **Exchange:**
  - analytic form

- **Correlation:**
  - calculated to great accuracy with Monte Carlo methods

Generalized Gradient Approximation (GGA)

\[ V_{xc} [n] \approx V_{xc} [n (\vec{r}), \nabla n (\vec{r})] \]

Provide required accuracy for DFT to be adopted by the Chemistry Community.

Problem: does not lead to consistent improvement over the LSDA.
### Accuracy of the xc functionals in the structural and electronic properties

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>-1%, -3%</td>
<td>+1%</td>
</tr>
<tr>
<td>$B$</td>
<td>+10, +40%</td>
<td>-20%, +10%</td>
</tr>
<tr>
<td>$E_c$</td>
<td>+15%</td>
<td>-5%</td>
</tr>
<tr>
<td>$E_{gap}$</td>
<td>-50%</td>
<td>-50%</td>
</tr>
</tbody>
</table>

**LDA:** crude approximation but sometimes is accurate enough (structural properties, …).

**GGA:** usually tends to overcompensate LDA results, not always better than LDA.
In some cases, GGA is a must: DFT ground state of iron

Results obtained with Wien2k.

Courtesy of Karl H. Schwartz
Kohn-Sham fails in strongly correlated systems

CoO
- in NaCl structure
- antiferromagnetic: AF II
- insulator
- $t_{2g}$ splits into $a_{1g}$ and $e_g'$
- Both LDA and GGA find them to be metals (although GGA almost splits the bands)

Results obtained with Wien2k.

Courtesy of Karl H. Schwartz
The number of citations allow us to gauge the importance of the works on DFT

11 papers published in APS journals since 1893 with >1000 citations in APS journals (~5 times as many references in all science journals)

Table 1. Physical Review Articles with more than 1000 Citations Through June 2003

<table>
<thead>
<tr>
<th>Publication</th>
<th># cites</th>
<th>Av. age</th>
<th>Title</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR 140, A1133 (1965)</td>
<td>3227</td>
<td>26.7</td>
<td>Self-Consistent Equations Including Exchange and Correlation Effects</td>
<td>W. Kohn, L. J. Sham</td>
</tr>
<tr>
<td>PR 136, B864 (1964)</td>
<td>2460</td>
<td>28.7</td>
<td>Inhomogeneous Electron Gas</td>
<td>P. Hohenberg, W. Kohn</td>
</tr>
<tr>
<td>PR 108, 1175 (1957)</td>
<td>1364</td>
<td>20.2</td>
<td>Theory of Superconductivity</td>
<td>J. Bardeen, L. N. Cooper, J. R. Schrieffer</td>
</tr>
<tr>
<td>PRL 19, 1264 (1967)</td>
<td>1306</td>
<td>15.5</td>
<td>A Model of Leptons</td>
<td>S. Weinberg</td>
</tr>
<tr>
<td>PRB 12, 3060 (1975)</td>
<td>1259</td>
<td>18.4</td>
<td>Linear Methods in Band Theory</td>
<td>O. K. Anderson</td>
</tr>
<tr>
<td>PR 124, 1866 (1961)</td>
<td>1178</td>
<td>28.0</td>
<td>Effects of Configuration Interaction of Intensities and Phase Shifts</td>
<td>U. Fano</td>
</tr>
<tr>
<td>PRB 13, 5188 (1976)</td>
<td>1023</td>
<td>20.8</td>
<td>Special Points for Brillouin-Zone Integrations</td>
<td>H. J. Monkhorst, J. D. Pack</td>
</tr>
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What are the main approximations?

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Decouple the movement of the electrons and the nuclei.

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Treatment of the electron — electron interactions.

**Pseudopotentials**

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**Basis set**

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**Numerical evaluation of matrix elements**

Efficient and self-consistent computations of H and S.

**Supercells**

To deal with periodic systems.
Treatment of the boundary conditions

**Isolated objects** (atoms, molecules, clusters)
- open boundary conditions
- (defined at infinity)

**3D periodic objects** (crystals)
- periodic boundary conditions
- (might be considered as the repetition of a building block, the unit cell)

**Mixed boundary conditions**
- 1D periodic (chains)
- 2D periodic (slabs and interfaces)
Periodic systems are idealizations of real systems
Conceptual problems

NO exactly periodic systems in Nature
(periodicity broken at the boundary)

BUT

The great majority of the physical quantities are unaffected by the existence of a border
Periodic systems are idealizations of real systems
Computational problems

1. In a periodic solid:
   \[ \infty \text{ Number of atoms} \]
   \[ \infty \text{ Number and electrons} \]
   \[ \Downarrow \]
   \[ \infty \text{ Number of wave functions ??} \]

2. Wave function will be extended over the entire solid (\(\infty\))

Bloch theorem will rescue us!!
A periodic potential commensurate with the lattice. The Bloch theorem

**Bloch Theorem**: The eigenstates of the one-electron Hamiltonian in a periodic potential can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice.

\[ V(\vec{r}) = V(\vec{r} + \vec{R}) \]

\[ \psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n,\vec{k}}(\vec{r}) \]

\[ u_{n,\vec{k}}(\vec{r} + \vec{R}) = u_{n,\vec{k}}(\vec{r}) \]

Periodicity in reciprocal space

\[ \psi_{n,\vec{k} + \vec{k}'}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r}) \]

\[ \varepsilon_{n,\vec{k} + \vec{k}'} = \varepsilon_{n,\vec{k}} \]
The wave vector $k$ and the band index $n$ allow us to label each electron (good quantum numbers).

The Bloch theorem changes the problem

Instead of computing an infinite number of electronic wave functions, there is a finite number of wave functions at an infinite number of $k$-points.

In practice: electronic wave functions at $k$-points that are very close together will be almost identical ⇒

It is possible to represent electronic wave functions over a region of $k$-space by the wave function at a single $k$-point.

\[
\int d\vec{k} \rightarrow \sum \Delta \vec{k}
\]
Systems with open and mixed periodic boundary conditions are made artificially periodic: supercells

M. C. Payne et al., Rev. Mod. Phys., 64, 1045 (1992)
Recap

Born-Oppenheimer approximation

Electron nuclear decoupling

Many electron problem treated within DFT (LDA, GGA)

One electron problem in effective self-consistent potential (iterate)

Extended crystals: periodic boundary conditions + k-sampling
Supplementary information
Length and time scales:
More suitable methods for a particular problem

K. Reuter, C. Stampfl, and M. Scheffler, cond-mat/0404510
A classical view of the Born-Oppenheimer approximation

In equilibrium

Atomic positions
\[ x_1 = x_0 \]
\[ x_2 = 2x_0 \]
Length of the springs
\[ l_1 = x_0 \]
\[ l_2 = x_0 \]

Out of equilibrium

Atomic displacements
\[ u_1 = x_1 - x_0 \]
\[ u_2 = x_2 - 2x_0 \]
Spring’s elongation
\[ \Delta l_1 = x_1 - x_0 \]
\[ \Delta l_2 = x_2 - x_1 - x_0 \]

The potential energy of the system equals:
\[ V = \frac{1}{2} K (x_1 - x_0)^2 + \frac{1}{2} K (x_2 - x_1 - x_0)^2 \quad ; K > 0 \]

And the equation of motion of the two particles:
\[ M \ddot{x}_1 = -K (x_1 - x_0) + K (x_2 - x_1 - x_0) \]
\[ m \ddot{x}_2 = -K (x_2 - x_1 - x_0) \]
\[ \ddot{u}_1 = -\omega_N^2 u_1 + \omega_N^2 (u_2 - u_1) \quad \omega_N = \sqrt{\frac{K}{M}} \]
\[ \ddot{u}_2 = -\omega_e^2 (u_2 - u_1) \quad \omega_e = \sqrt{\frac{K}{m}} \]
Making the change of variables $u \equiv u_2 - u_1$

$\ddot{u}_1 = -\omega_N^2 u_1 + \omega_N^2 (u_2 - u_1)$  \hspace{1cm} $\omega_N = \sqrt{\frac{K}{M}}$

$\ddot{u}_2 = -\omega_e^2 (u_2 - u_1)$  \hspace{1cm} $\omega_e = \sqrt{\frac{K}{m}}$

Seek stationary solutions of the kind:

$u_1 = \Re(\alpha e^{i\omega t})$  \hspace{1cm} $u = \Re(\beta e^{i\omega t})$

$\begin{pmatrix}
\omega_N^2 - \omega^2 & -\omega_N^2 \\
-\omega_N^2 & \omega_e^2 + \omega_N^2 - \omega^2
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix} =
\begin{pmatrix}
0 \\
0
\end{pmatrix}$

Solving this equation, we find two solutions for $\omega$, $\omega_1$ and $\omega_2$, each with the corresponding eigenvector (normal between them)

$\omega_1^2 \rightarrow \{\alpha_1, \beta_1\}$  \hspace{1cm} $\omega_2^2 \rightarrow \{\alpha_2, \beta_2\}$  \hspace{1cm} $\alpha_1 \alpha_2 + \beta_1 \beta_2 = 0$
The equation
\[
\begin{pmatrix}
\omega_N^2 - \omega^2 & -\omega_N^2 \\
-\omega_N^2 & \omega_e^2 + \omega_N^2 - \omega^2
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
= 
\begin{pmatrix}
0 \\
0
\end{pmatrix}
\]
has non trivial solutions if and only if
\[
\det[H - \omega^2 I] = 0,
\quad
H = \begin{pmatrix}
\omega_N^2 & -\omega_N^2 \\
-\omega_N^2 & \omega_e^2 + \omega_N^2
\end{pmatrix},
\quad
I = \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
\]
Assuming that \( M \gg m \Rightarrow \omega_N^2 \ll \omega_e^2 \), so we can decompose
\[
H = H_0 + H',
\quad
H_0 = \begin{pmatrix}
0 & 0 \\
0 & \omega_e^2
\end{pmatrix},
\quad
H' = \begin{pmatrix}
\omega_N^2 & -\omega_N^2 \\
-\omega_N^2 & \omega_N^2
\end{pmatrix}
\]
Then, \( H' \) is just a perturbation of \( H_0 \)

Then, at first order, the only thing we have to do is find the eigenvalue of \( H_0 \)
A classical view of the Born-Oppenheimer approximation

Solution at first-order:

\[
\text{det} \begin{bmatrix} H_0 - \omega^2 I \end{bmatrix} = \begin{vmatrix} -\omega^2 & 0 \\ 0 & \omega_e^2 - \omega^2 \end{vmatrix} = 0
\]

Mode 1

\[
\omega_1^2 = 0 \quad \Rightarrow \quad \ket{N} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}
\]

\[
u(t) = u_2(t) - u_1(t) = 0 \quad \Rightarrow \quad u_1(t) = u_2(t)
\]

Mode 2

\[
\omega_2^2 = \omega_e^2 \quad \Rightarrow \quad \ket{e} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\]

\[
u_1(t) = 0
\]

\[
u(t) = u_2(t) - u_1(t) = u_2(t) = \Re(e^{i\omega_e t})
\]