From Atoms to Materials: Predictive Theory and Simulations

Week 5: Case Studies
Lecture 5.3: Density Functional Theory

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How QM works

Schrödinger-based quantum mechanics:

\[
H_{BO} (\{r\}, \{R_i\}) = \sum_{i=1}^{n} \frac{\vec{\nabla}_i^2}{2m_e} + \sum_{i<j}^{n} \frac{e^2}{|r_i - r_j|} - \sum_{i,j}^{n,N} \frac{Z_i e^2}{|r_i - R_j|} = \sum_{i=1}^{n} \frac{\vec{\nabla}_i^2}{2m_e} + \sum_{i<j}^{n} \frac{e^2}{|r_i - r_j|} + \sum_{i}^{n} V_{ext}(r_i, \{R_i\})
\]

With:

\[
V_{ext}(r_i, \{R_i\}) = -\sum_{j}^{N} \frac{Z_i e^2}{|r - R_j|}
\]

\[
V_{ext}(r_i, \{R_i\}) \rightarrow \psi(\{r\}; \{R_i\}) \text{ and } E(\{R_i\}) \rightarrow \text{Properties}
\]

Hohenberg & Kohn: ground state electron density takes the role of \(V_{ext}\)

The GS density uniquely determines the 3n-dimensional GS WF and energy

\[
n_0(r) \rightarrow \psi(\{r\}; \{R_i\}) \text{ and } E(\{R_i\}) \rightarrow \text{Properties}
\]
Electron density

\[ \psi^*({r_i}) \psi({r_i}) = |\psi({r_i})|^2 \quad \text{Probability of finding one electron at } r_1, \text{ another at } r_2, \text{ a third at } r_3, \text{ etc.} \]

\[ \times \int |\psi({r_i})|^2 \, dr_1 \, dr_2 \cdots dr_n = n \quad \text{Integrating over all variables gives the number of electrons} \]

What if I integrate over all electrons except one (it does not matter which one)

\[ \int |\psi({r_i})|^2 \, dr_2 \, dr_3 \cdots dr_n = n(r_1) \]

\[ \int n(r) \, dr = n \]
The external potential contribution to the energy expectation value depends only on electron density.

\[ H = \sum_{i=1}^{n} \frac{\mathbf{V}^2_i}{2m_e} + \sum_{i<j}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i}^{n} V_{\text{ext}}(\mathbf{r}_i; \{\mathbf{R}_i\}) \]

\[ \langle H \rangle = \langle \psi | T | \psi \rangle + \langle \psi | U | \psi \rangle + \sum_{i}^{n} \langle \psi | V_{\text{ext}}(r_i) | \psi \rangle \]

\[ \langle \psi | V_{\text{ext}}(r_k) | \psi \rangle = \int dx_1 dx_2 \cdots dx_n \psi^*(\{r_i\}) V(r_k) \psi(\{r_i\}) \]

\[ \langle \psi | V_{\text{ext}}(r_k) | \psi \rangle = \int V_{\text{ext}}(r_k) dr_k \int dx' |\psi(\{r_i\})|^2 \]

\[ \langle \psi | V_{\text{ext}}(r) | \psi \rangle = \int V_{\text{ext}}(r) n(r) dr \]
Hohenberg-Kohn theorem: proof

The ground state density uniquely determines the external potential (and consequently the wavefunction, energies, etc)

Prove by contradiction:
• Suppose there are two potentials (differing by more than a constant) with the same GS density

Potential 1 and its WF
\[ V_{\text{ext}}^{(1)} \rightarrow \psi_{0}^{(1)} \rightarrow n_{0}^{(1)}(r) \]
\[ n_{0}^{(1)}(r) = n_{0}^{(2)}(r) \]

Potential 2 and its WF
\[ V_{\text{ext}}^{(2)} \rightarrow \psi_{0}^{(2)} \rightarrow n_{0}^{(2)}(r) \]
Hohenberg-Kohn theorem: proof

Expectation value of WF 1 in Hamiltonian 1 should be lower than that of WF 2

\[ \langle \psi_0^{(1)} | H^{(1)} | \psi_0^{(1)} \rangle < \langle \psi_0^{(2)} | H^{(1)} | \psi_0^{(2)} \rangle \]

We get:

\[ \langle \psi_0^{(1)} | T | \psi_0^{(1)} \rangle + \langle \psi_0^{(1)} | U | \psi_0^{(1)} \rangle < \langle \psi_0^{(2)} | T | \psi_0^{(2)} \rangle + \langle \psi_0^{(2)} | U | \psi_0^{(2)} \rangle \]

Expectation value of WF 2 in Hamiltonian 2 should be lower than that of WF 1

\[ \langle \psi_0^{(1)} | H^{(2)} | \psi_0^{(1)} \rangle > \langle \psi_0^{(2)} | H^{(2)} | \psi_0^{(2)} \rangle \]

We get:

\[ \langle \psi_0^{(1)} | T | \psi_0^{(1)} \rangle + \langle \psi_0^{(1)} | U | \psi_0^{(1)} \rangle > \langle \psi_0^{(2)} | T | \psi_0^{(2)} \rangle + \langle \psi_0^{(2)} | U | \psi_0^{(2)} \rangle \]
Hohenberg-Kohn theorem

Expectation value of WF 1 in Hamiltonian 1 should be lower than that of WF2

We get:

$$\left\langle \psi^{(1)}_0 | T | \psi^{(1)}_0 \right\rangle + \left\langle \psi^{(1)}_0 | U | \psi^{(1)}_0 \right\rangle < \left\langle \psi^{(2)}_0 | T | \psi^{(2)}_0 \right\rangle + \left\langle \psi^{(2)}_0 | U | \psi^{(2)}_0 \right\rangle$$

Expectation value of WF 2 in Hamiltonian 2 should be lower than that of WF1

We get:

$$\left\langle \psi^{(1)}_0 | T | \psi^{(1)}_0 \right\rangle + \left\langle \psi^{(1)}_0 | U | \psi^{(1)}_0 \right\rangle > \left\langle \psi^{(2)}_0 | T | \psi^{(2)}_0 \right\rangle + \left\langle \psi^{(2)}_0 | U | \psi^{(2)}_0 \right\rangle$$

Absurd

Two different potentials cannot lead to identical ground state densities

The ground state density uniquely determines the external potential (and consequently the wavefunction, energies, etc)
Hohenberg and Kohn (1964)

• Ground state (GS) wave function $\Psi_0(x_1, x_2 \ldots x_n)$ is a functional of GS electronic density $n_0(r)$

  • Electronic density: $n(r) = \int ds_1 d^3 x_2, d^3 x_3, \ldots, d^3 x_n |\psi(r, s_1, x_2, \ldots, x_n)|^2$

  • Ground state energy is also a functional of density:

\[
E_0 = \langle \Psi_0[n_0] | H | \Psi_0[n_0] \rangle = E[n_0]
\]

• Variational property: the electron density that minimizes the energy functional is the ground state density

\[
E[n_0] \leq E[n]
\]
DFT: Kohn-Sham equations

\[ E[n] = F[n] + V_{\text{ext}}[n] = F[n] + \int v_{\text{ext}}(r)n(r)\,d^3r \]

Kohn and Sham (1965) bring single electronic orbitals back into play:
Consider a set of non-interacting electrons with the density \( n(r) \) with orbitals: \( \phi(r) \)

\[
T[n] = -\frac{\hbar^2}{2m} \sum_i^n \int \phi_i(r) \nabla^2 \phi_i(r)\,d^3r + T_c[n(r)] = T_{SP}[n(r)] + T_c[n(r)]
\]

\[
U[n] = e^2 \sum_{i<j} \int \frac{\phi_i(r)^2\phi_j(r')^2}{|r-r'|}\,d^3r\,d^3r' + U_{xc}[n(r)] = U_H[n(r)] + U_{xc}[n(r)]
\]

The functional can be written as:

\[
E[n] = T_{SP}[n] + U_H[n] + V_{\text{ext}}[n] + V_{xc}[n]
\]
Kohn-Sham equations

\[ E[n] = T_{SP}[n] + U_H[n] + V_{ext}[n] + E_{xc}[n] \]

Just like the Hartree equation but with \( V_{ext} \rightarrow V_{ext} + V_{xc} \)

And the solution is:

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(r) + v_H(r) + v_{xc}(r) \right] \phi_i = \varepsilon_i \phi_i \]

With:

\[ n(r) = \sum |\phi_i(r)|^2 \]

Remaining issues:

- Exchange and correlation functional
- Numerical issues:
  - Basis sets and pseudopotentials
Exchange and correlation functionals

• Local density approximation (LDA)

**Exchange**: can be calculated exactly for a non-interacting homogeneous electron gas:

\[
E_x^{\text{Hom}}(n) = -\frac{3q^2}{4} \left( \frac{3}{\pi} \right)^{1/3} n^{4/3}
\]

**Correlation**: no analytical solution. Alder and Ceperley (1980) performed Quantum Monte Carlo simulations

Various fits: Perdew-Zunger (PZ), Perdew-Wang (PW)

• Generalized Gradient Approximation (GGA)

\[
E_{xc}^{GGA}[n(r)] = \int d^3r \, e_{xc}^{GGA}(n(r), \nabla n(r))
\]

PBE: Perdew, Burke, Ernzerhof (1996)
BLYP: Becke’s exchange + Lee, Yang and Parr (1988)
B3LYP: mix 30% of exact exchange (HF) (hyper-GGA)
Additional reading


- The ABC of DFT, Kieron Burke
From density functional theory to defect level in silicon: Does the “band gap problem” matter?

By Peter A. Schultz

Sandia National Laboratories, Albuquerque, NM

Modeling the electrical effects of radiation damage in semiconductor devices requires a detailed description of the properties of point defects generated during and subsequent to irradiation. Such modeling requires physical parameters, such as ...

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