3.3 Pseudopotentials

An effective potentials approximation for simplifying the description of a complex system

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}} \right] \Phi_i = \epsilon_i \Phi_i \rightarrow \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}} \right] \Phi_i^{\text{pseudo}} = \epsilon_i^{\text{pseudo}} \Phi_i \]

- replace strong Coulomb potential of nucleus and effect of tightly bound core electrons by an effective ionic potential acting on the valence electrons
- pseudopotentials generated and used to compute properties of other systems as core states remain almost unchanged
Types of pseudopotentials:

1. CPW - orthogonalized plane waves
   smooth part of valence function
   plus core-like functions

2. Norm-conserving
   normalized, solutions of a model
   potential chosen to reproduce valence
   properties of an all-electron calculation.

3. ultrasoft (smaller transferability vs. hard ones)
   as smooth as possible
   + auxiliary function around each ion
   core that represents the rapidly varying
   part of the density

4. projector augmented waves (PAW)
   transforms rapidly oscillating functions
   near core into smooth wavefunctions
   and use projectors and auxiliary
   localized functions

5. spin-dependent norm-conserving
   each spin state treated independently
   total potential calculated self-consistently
   for given XC functional and configuration

Issues: Unscreening, core corrections, hardness,
        transferability

Functionals and pseudopotentials should first be
        tested.
2.4 Basis-sets

2 types of basis sets:

plane-waves: \( \phi_{mn}(r_n, \theta_n) = u_m(k) e^{i\mathbf{k} \cdot \mathbf{r}} \)

atomic-like orbitals: \( \phi_{mn}(r_n, \theta_n) = \sum_{\alpha} \Phi_{m\sigma}(r_n) Y_{\sigma\alpha} \)

- Gaussian-type: \( \psi_{n\sigma}(x, y, z) = N_n x^\alpha y^\beta z^\gamma e^{-\beta r} \)
  \( (\text{GTO}) \)
- Slater-type: \( \chi_{n\sigma}(x, y, z) = N_n x^\alpha y^\beta z^\gamma e^{-\beta r} \)
  \( (\text{STO}) \)

 contracted GTO
(\( (\text{GTO}) \))

linear combination of GTOs
(\( n \) Gaussian)

minimal basis: only one STO, GTO, or CTO for each atomic orbital

extended basis: DZ (double-zeta), TZ (triple-zeta)
(\( \text{DZ, split-valence, polarized, diffuse} \))

DZ: each atomic orbital a sum of two STOs
(each orbital treated separately)

TZ: sum of 2 STOs
split-valence calculations DZ only for valence orbitals (to decrease computational cost); the inner-shell orbitals are treated with a single STO

eg 3-21G, 4-31G, 6-31G -

notation 3-21G

number of

6

number of

GTOs for the second STO
two STO s for the inner shell orbitals

number of

6 for the first STO of DZ

split-valence
DZ 6-31G
(Pople et al.)

6 Gaussians; the core orbital is GTO made of 6 GTO s; valence described by two orbitals (one GTO made of 3 gaussians and one single gaussian)

polarized sets; when atom approaches other atoms, the orbitals overlap and are polarized; e.g., p orbitals are polarized if mixed with d orbitals

- polarized DZ (e.g., 6-31G*)
  \( \uparrow \) DZ (e.g., 6-31G**)

(with basis with angular momentum \( \ell \))

(e.g., 6-31G**)

+ p orbitals

+ both sp orbitals are polarized (e.g., 6-31+G*)

in Physics notation D2P, T2P
3.5 Time-dependent DFT (TDDFT)

DFT is a ground state method; the Kohn-Sham equations describe fictitious particles with the same density as the real system; independent particle eigenvalues which do not correspond to a true electron removal or addition energies; thus, eigenvalue differences do not correspond to excitation energies.

TDDFT extends DFT for the treatment of excitation, dynamics, and time-dependent phenomena; presence of time-dependent potentials (e.g., electric or magnetic field) → excitation energies, photoabsorption spectra, frequency-dependence response properties.

Approach similar to DFT, the time-dependent wavefunction is equivalent to the time-dependent electron density → effective potential of a fictitious non-interacting system with the same density as any interacting system.

* propagate time-dependent Kohn-Sham equations.
- Runge–Gross theorem

Simple component system in the presence of a time-dependent scalar field

\[ \hat{\mathbf{A}}(t) = \hat{T} + \hat{\mathbf{V}}_{\text{ext}}(t) + \hat{\mathbf{H}} \]

\begin{align*}
\text{kinetic} & \quad \text{external, electron-electron} \\
\text{energy} & \quad \text{potential, interaction} \\
\text{operator} & \\
\end{align*}

(\# time-dependent potential due to time-dependent magnetic or electric fields)

The time-dependent Schrödinger eq. needs to be solved to obtain the many-body wavefunction:

\[ \hat{\mathbf{A}}(t) |\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle \text{ with } |\psi(0)\rangle = |\psi\rangle \]

\( \Rightarrow \) The theorem proves that if two external potentials \( V_{\text{ext}}(\mathbf{r}, t) \) and \( V'_{\text{ext}}(\mathbf{r}, t) \) differ by more than a time-dependent constant \( c(t)^2 \), these generate different current densities.

\( \Rightarrow \) Finite systems: different current densities correspond to different electron densities.

Two regimes in TDDFT theory:

- (a) time-dependent potential weak: employ linear response theory (obtain, e.g., optical absorption spectra).

- (b) time-dependent potential strong: full solution of time-dependent Kohn–Sham eq. (describe non-linear phenomena, multiphoton ionization, molecules in strong laser fields).
(6) Time-dependent Kohn-Sham System

The Kohn-Gross theorem asserts that all observables can be calculated based on the knowledge of the one-body density for a given interaction potential, the external potential uniquely determines the electron density. The external local potential $V_{ex}$ is chosen such that the density of the Kohn-Sham electrons is the same as the density of the real interacting system.

Advantage of this procedure: non-interacting systems can more easily be solved (wave function as a Slater determinant of single-particle orbitals determined by a single partial differential equation; kinetic energy expressed in terms of these orbitals).

Need to find a potential which determines a non-interacting Hamiltonian

$$H_{ks}(\Psi) = T + V_{ks}(\Psi, \tau)$$

$$H_{ks}(\Psi, \tau) | \Phi(\Psi, \tau) \rangle = i \hbar \frac{\partial}{\partial \tau} | \Phi(\Psi, \tau) \rangle, \quad | \Phi(\Psi, 0) \rangle = | \Phi \rangle$$

Use $N$ orbitals $\phi_i(\Psi, \tau)$.

$$
\left( - \frac{\hbar^2}{2m} \nabla^2 + V_{ks}(\Psi, \tau) \right) \phi_i(\Psi, \tau) = i \hbar \frac{\partial}{\partial \tau} \phi_i(\Psi, \tau), \quad \phi_i(\Psi, 0) = \phi_i(\Psi) \n$$
Define the time-dependent density:
\[
\rho_\text{ss}(\mathbf{r}, t) = \sum_{i=1}^{\text{occupied}} |\phi_i(\mathbf{r}, t)|^2
\]
which should become time independent to the density of the interacting system.

Define the current density operator:
\[
\mathbf{j}(\mathbf{r}) = \langle \Phi(\mathbf{r})/\Phi(\mathbf{r})^* \rangle /\Phi(\mathbf{r})
\]
with
\[
\frac{\partial}{\partial t} \rho_\text{ss}(\mathbf{r}, t) = - \nabla \cdot \mathbf{j}(\mathbf{r}, t)
\]

Decompose the exchange potential:
\[
V_{\text{exchange}}(\mathbf{r}, t) = V_{\text{ext}}(\mathbf{r}, t) + V_{\text{Hartree}}(\mathbf{r}, t) + V_{\text{xc}}(\mathbf{r}, t)
\]
with
\[
V_{\text{Hartree}}(\mathbf{r}, t) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}
\]

Runge-Gross theorem: define \( V_{\text{xc}}(\mathbf{r}, t) \) through a quantum mechanical action
\[
\{[\Phi] = \int dt <\Phi(\mathbf{r})/i\hbar \partial_t - H(\mathbf{r})/\Phi(\mathbf{r})^*> \]
which is treated as a density functional
\[
\{[\rho] = \{[\Phi(\mathbf{r})]\}
\]
due to the unique mapping of densities and wavefunctions.

Although in DFT \( V_{\text{xc}} \) is written as a functional derivative of the XC energy, this is not straightforward in TDFT.
Hence xc functionals \( V_{xc} \), TDDFT are at an earlier stage compared to DFT. TDDFT: Define new action functional:

\[
V_{xc}(\mathbf{r}, t) = \frac{2}{\hbar^2} \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}, t)} \Big|_{n(\mathbf{r}, t)}
\]

where \( \mathbf{r} \) a pseudo time (refer to van Leeuwen and Koldaish formalism) in the exact theory, \( V_{xc}[n(\mathbf{r}, t)] \) is a functional of \( n(\mathbf{r}, t) \) for all earlier times \( t < t' \), but it is difficult to construct functionals that include non-locality effects in time. Using approximations for the xc functionals in TDDFT is the only fundamental approximation.

### 3.5.1 XC Functionals in TDDFT

(a) Adiabatic LDA (ALDA)

\[
V_{xc}^{ALDA}(\mathbf{r}, t) = V_{xc}(n(\mathbf{r})) \Big|_{n=n(\mathbf{r}, t)}
\]

Same as LDA but applied at each time with \( n(\mathbf{r}, t) \) -- \( V_{xc} \) depends only on density at same time (functional local in time).

Problems - systems near resonance (functional should include particular states involved in transition).
- extended systems (excitation should be a functional of current density).
(b) Time-dependent optimized effective functional (alternative to orbital dependent).

\[ E_{XX} \] obtained through solution of non-local, non-linear eq. (but still local) \( F_{XX} \).

Exact exchange action \( A_x = \frac{1}{2} \sum_{i,j}^{occ} \int dt \int d^3 \mathbf{r}_i \int d^3 \mathbf{r}_j \phi_i^*(\mathbf{r}_i,t) \phi_j(\mathbf{r}_j,t) \phi_i(\mathbf{r}_i,t) \phi_j^*(\mathbf{r}_j,t) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^2} \)

(which can be rewritten based on optimize effective potentials 'KLI' (Krieger, Li, Inaba))

Simplify \( E_{XX} \) form. Both \( E_{XX} \) and KLI have the correct \( 1/r \) asymptotic behavior for neutral finite systems.

(c) Functional with memory (non-local in time)

\[ F_{xc}(\mathbf{r},t) = \frac{1}{m(\mathbf{r},t)} \int dt' \int dx_c(\mathbf{m}(\mathbf{r},t'),t,t') \]

\( x_c \) a pressure-like scalar memory function which reproduces scalar linear response of homogeneous electron gas.