Determination of Electronic Structure

Solving the Kohn-Sham Equations

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Outline

- Review
- Electronic structure methods
- Basis sets
- All-electron vs. Planewaves
- Pseudopotentials
  - General
  - Historical example: Phillips-Kleinman
- History and Types of Pseudopotentials
  - Norm Conserving
  - Ultrasoft
  - Projector Augmented Wave (PAW)
- Advantages of NC PSP
  - Optimized Norm-Conserving Vanserbilt PSP
- Generating and Testing
- Resources
- ONCVPSP tutorial

Electronic Structure

- Determine the distribution of electrons in a system
  - Geometry is a fixed parameter
  - Determine the **electronic wavefunction**
  - Gradient on each nuclei – derivative of the total energy with respect to position
- Self consist to some threshold of accuracy – energy, force, etc.
- **Series of approximations** allows for the treatment of ‘simple’ eigenvalue equation of the Hamiltonian with a **discrete set of solutions**.
  - Linear algebra calculations based on matrices and state vectors
- Resulting eigenvalues describe the **potential energy surfaces**

Solving the Kohn-Sham Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_j(\boldsymbol{r}) + [V_{ext} + V_{Hartree} + V_{xc}]\psi_j(\boldsymbol{r}) = \epsilon_j\psi_j(\boldsymbol{r})$$

$$V_{eff}$$

$$\rho(\boldsymbol{r}) = \sum_i^N |\psi_j(\boldsymbol{r})|^2$$

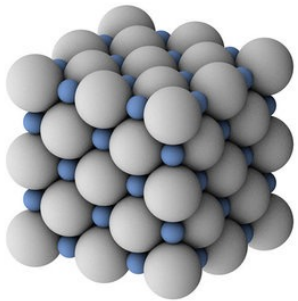
Some kind of basis set

$$\psi = \sum_\alpha C_\alpha \chi_\alpha$$

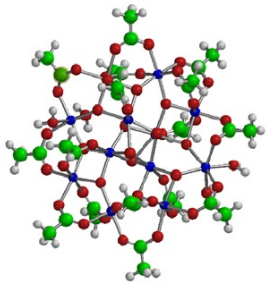
Ingredients needed:

- A form for V_{xc}
- The position and species of each atom considered (Shape of V_{ext}).
- Geometry of the problem (Boundary Conditions).

Atomic physics



Condensed Matter Physics
Materials Science



Chemistry, Large Molecules

- Physical and Chemical properties
- Total energy
- Electronic energy levels (band structure)
- Density of states
- Fermi energy
- Raman Spectra
- .....

What are we solving: The Non-Relativistic Many-Electron Problem

$$\Psi(\{r_j\},\{R_\alpha\})\left[-\sum_j^{N_e}\frac{\hbar^2}{2m}\nabla_j^2+\sum_{j<k}^{N_e}\frac{e^2}{|r_j-r_k|}-\sum_\alpha^{N_n}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2+\sum_{\alpha<\beta}^{N_n}\frac{Z_\alpha Z_\beta e^2}{|R_\alpha-R_\beta|}-\sum_j^{N_e}\sum_\alpha^{N_n}\frac{Z_\alpha e^2}{|r_j-R_\alpha|}\right]=E\,\Psi(\{r_j\},\{R_\alpha\})$$

Many-body Wave Function

Electronic Kinetic Energy

Electron-Electron Interactions

Electron Dynamics

Nuclei Kinetic Energy

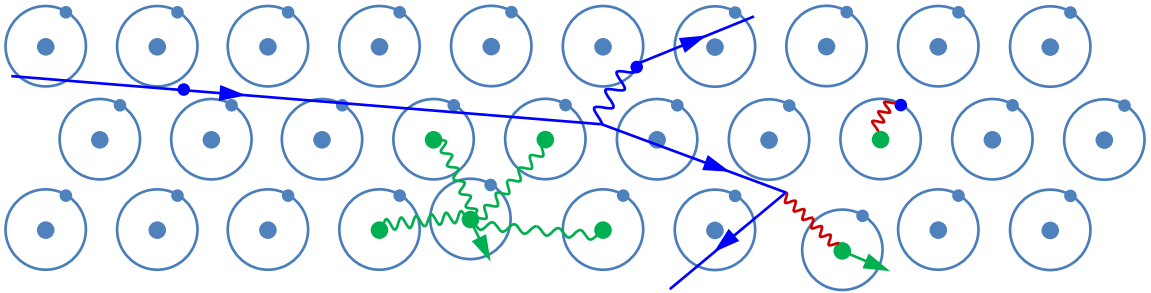
Nuclei-Nuclei Interactions

Lattice Dynamics

Electron-Nuclei Interactions

Electron-Lattice Coupling

Erwin Schrödinger



P.A.M. Dirac

Dirac (1929) "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. **It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.**"

The Non-Relativistic Many-Electron Problem

$$\Psi(\{r_j\},\{R_\alpha\})\left[-\sum_j^{N_e}\frac{\hbar^2}{2m}\nabla_j^2+\sum_{j<k}^{N_e}\frac{e^2}{|r_j-r_k|}-\sum_\alpha^{N_n}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2+\sum_{\alpha<\beta}^{N_n}\frac{Z_\alpha Z_\beta e^2}{|R_\alpha-R_\beta|}-\sum_j^{N_e}\sum_\alpha^{N_n}\frac{Z_\alpha e^2}{|r_j-R_\alpha|}\right]=E\,\Psi(\{r_j\},\{R_\alpha\})$$

Many-body Wave Function

Electronic Kinetic Energy

Electron-Electron Interactions

Electron Dynamics

Nuclei Kinetic Energy

Nuclei-Nuclei Interactions

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Electron-Lattice Coupling

Erwin Schrödinger

J. R. Oppenheimer

Born-Oppenheimer Approximation:

- We assume $\frac{m}{M} \ll 1$
- The motion of atomic nuclei and electrons can be separated, $\varphi(\{r_j\},\{R_\alpha\}) = \Psi(r_j)\theta(R_\alpha)$ where the atomic vibration can be added back in perturbatively.
- The nuclei see a consistent potential from the quick electrons $\Leftrightarrow$ Electrons see the atoms being fixed in space.

We now look for solution to the wavefunction for many electrons

$$H\Psi(r_1, r_2, .., r_{N_e}) = E\Psi(r_1, r_2, .., r_{N_e})$$

What are we solving: The Non-Relativistic Many-Electron Problem

$\Psi(x_1, x_2, \cdots, x_{N_e})$

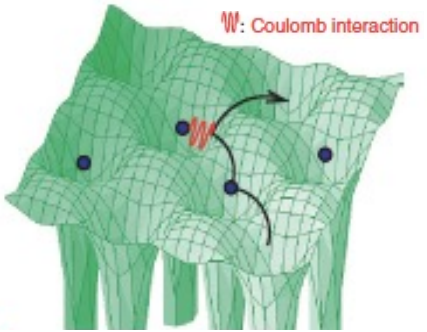
Antisymmetric N-electron wavefunction

$$\Psi(\{x_j\})\left[-\sum_j^{N_e}\frac{\hbar^2}{2m}\nabla_j^2 + \sum_{j<k}^{N_e}\frac{e^2}{|r_j - r_k|} + \sum_j^{N_e} V_{ext}(r_j)\right] = E\Psi(\{x_j\})$$

Electronic Kinetic Energy

Electron-Electron Interactions

External Potential

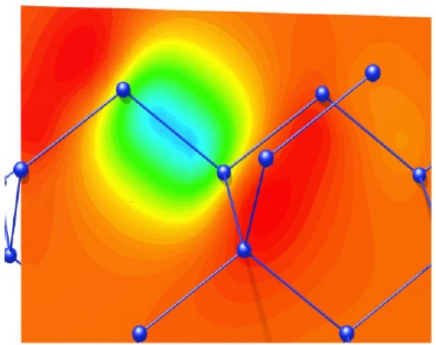


Brute Force Solution

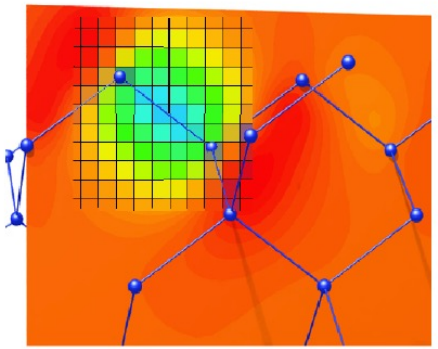
- 5 electrons in 3D space
- Number of Grid points 10x10x10
- Assuming 1 grid point takes 16 bytes of information
- Gives $16\cdot(10\text{x}10\text{x}10)^5$ bytes = 16 Petabytes!
- Or 16,000,000 DVD-RAM discs (10GB), which can be stacked up to 19.2 km in height

This approach is futile!

$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$

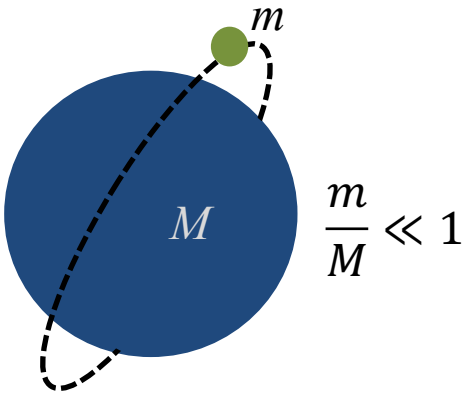


$(\#\text{grid points})^N$



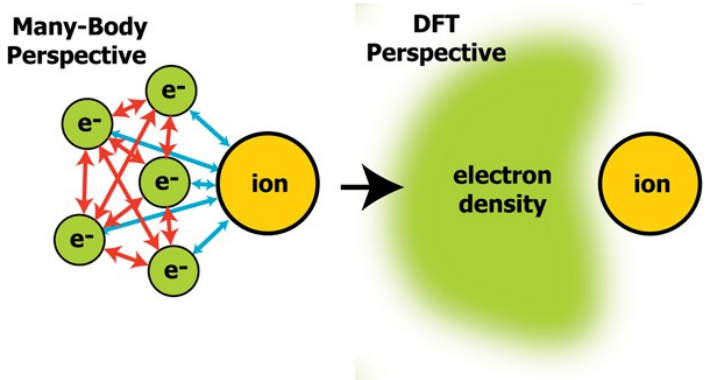
Approximations and strategies

Born-Oppenheimer Approximation

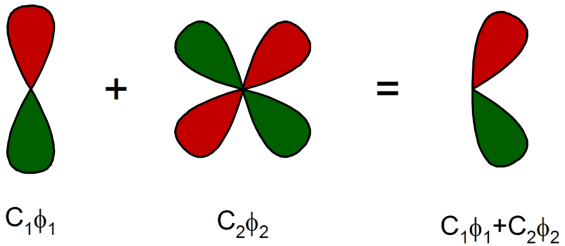


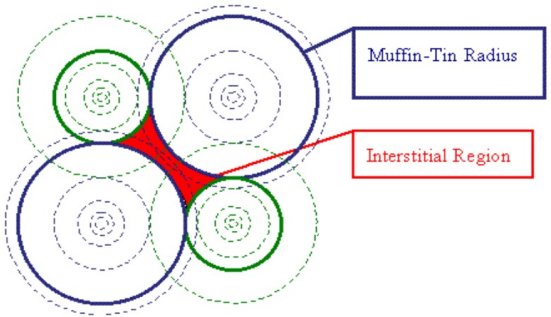
$$\frac{m}{M} \ll 1$$

Reduced quantity-based approaches



Finite Basis Sets





Approximations and strategies

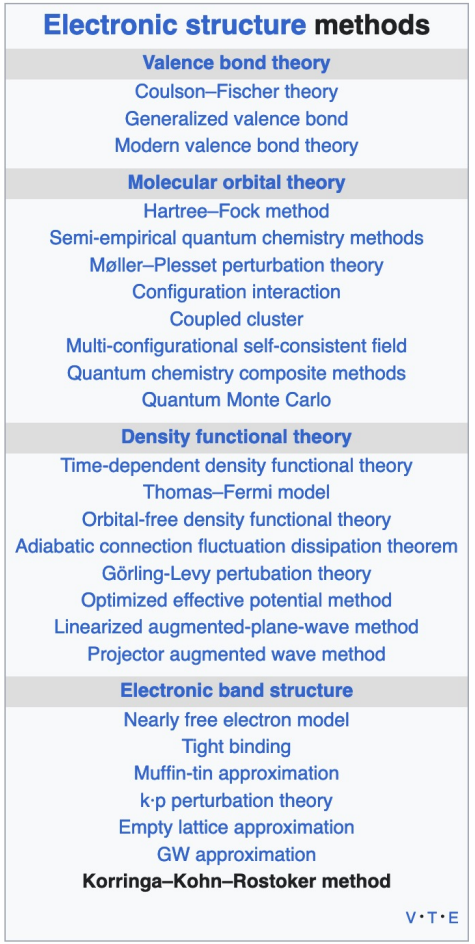
	Reduced Quantity	Difficulty in deriving approximate functionals	Numerical Effort	Best For
Particle Density	$\rho(\boldsymbol{r})$	Hard	Easy	Total Energies
Single-particle Density matrix	$\gamma(\boldsymbol{r}_1, \boldsymbol{r}_2)$	Intermediate	Intermediate	Captures orbital degeneracies intrinsically
Single-particle Green's function	$G(\boldsymbol{r}_1, \boldsymbol{r}_2)$	Easy	Hard	Spectroscopies, e.g., Photoelectron spectroscopy

	Finite-ness	Difficulty in implementing	Computational cost	Accuracy
Basis Set	$\psi = \sum_a C_a \chi_a$	Low/Intermediate	High/ Intermediate	Depends
Element	$numerical$	Hard	Intermediate	High /Intermediate
Difference	$numerical$	Easy	Low/Intermediate	Low/Intermediate

Uses and variations

- **Condensed Matter Physics** – study of electrons in materials
  - Phenomenology – quantum topological materials
  - Applications – tuning properties
  - Behavior prediction under various conditions
- **Quantum Chemistry** – study of electrons in molecules
  - Bonding mechanisms
  - Atomic/Molecular interactions
  - Applications in battery technology, critical materials recovery, pharmacology
- **Materials Science**
  - Interfaces
  - Material development and synthesis
- **Metallurgy**
  - Alloys properties and development
  - Predicting annealing effects
  - Advanced manufacturing
- **ML modeling**
  - Method efficiency
  - Interpolation applications
- **Quantum Computing**

*not comprehensive



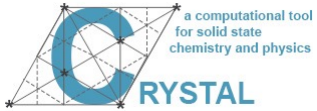
Available Codes

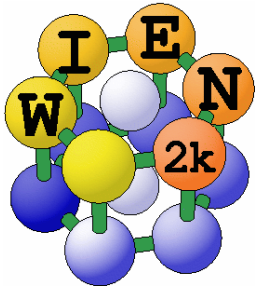
Codes Implementing Various Basis Sets:

- Gaussian Type Orbitals
  - CRYSTAL
  - Gaussian
  - TURBOMOLE
- PW
  - VASP
  - Abinit
  - CASTEP
  - YAMBO
  - Quantum Espresso
- FP-(L)APW+lo
  - WIEN2k
  - ELK
  - FLEUR
- FP-LMTO
  - MindLab
  - RSPt

:

Many more





Available Codes

Package	Basis	Periodic‡	MD	Semi-emp.	HF	TDHF	Post-HF	MP	MRCI	CC	DFT	TDDFT	GWA
ABINIT	PW	3d	Yes	No	No	Unknown	No	No	No	No	Yes	Yes	Yes Slater-type_orbital
ACES [1]	GTO	No	No	No	Yes	Unknown	Yes	Unknown	No	up to Q	Yes	Unknown	Unknown
AMS: ADF, BAND, DFTB	STO, NAO	Any	Yes	Yes	Yes	Yes	Yes	Yes	No	No	Yes	Yes	Yes
AMPAC	Unknown	Unknown	No	Yes	No	Unknown	No	Unknown	No	No	No	Unknown	Unknown
Atomistix ToolKit (QuantumATK)	NAO, EHT, PW	Any	Yes	Yes	No	Unknown	No	Unknown	No	No	Yes	Unknown	Yes
BigDFT	Wavelet	any	Yes	No	Yes	Unknown	No	Unknown	No	No	Yes	Yes	No
CADPAC	GTO	No	No	No	Yes	Unknown	Yes	Unknown	No	up to D	Yes	Unknown	Unknown
CASINO (QMC)	GTO, PW, Spline, Grid, STO	any	No	No	No	No	Yes	No	No	No	No	No	No
CASTEP	PW	3d	Yes	No	Yes	Unknown	No	Unknown	No	No	Yes	Yes	Unknown
COLUMBUS	GTO	No	No	No	Yes	No	Yes	No	Yes	No	No	No	No
CONQUEST	NAO, Spline	3d	Yes	No	Yes5	Unknown	No	Unknown	No	No	Yes	Unknown	Unknown

3 Basic Types of Basis Sets:

- Plane wave
- Localized orbitals
- Augmented functions

https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

Solving the Kohn-Sham Equation

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$$\rho(\boldsymbol{r}) = \sum_i^N |\psi_j(\boldsymbol{r})|^2$$

Some kind of basis set

$$\psi = \sum_\alpha C_\alpha \chi_\alpha$$

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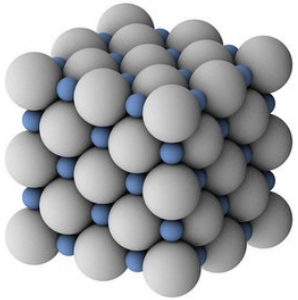
Crystal symmetry



Solving the Kohn-Sham Equation

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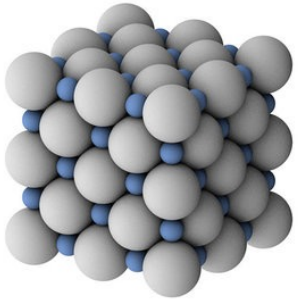
Crystal symmetry

Periodic potential



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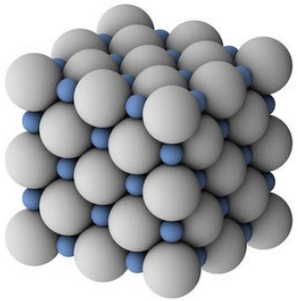


Bloch's Theorem

To the board!

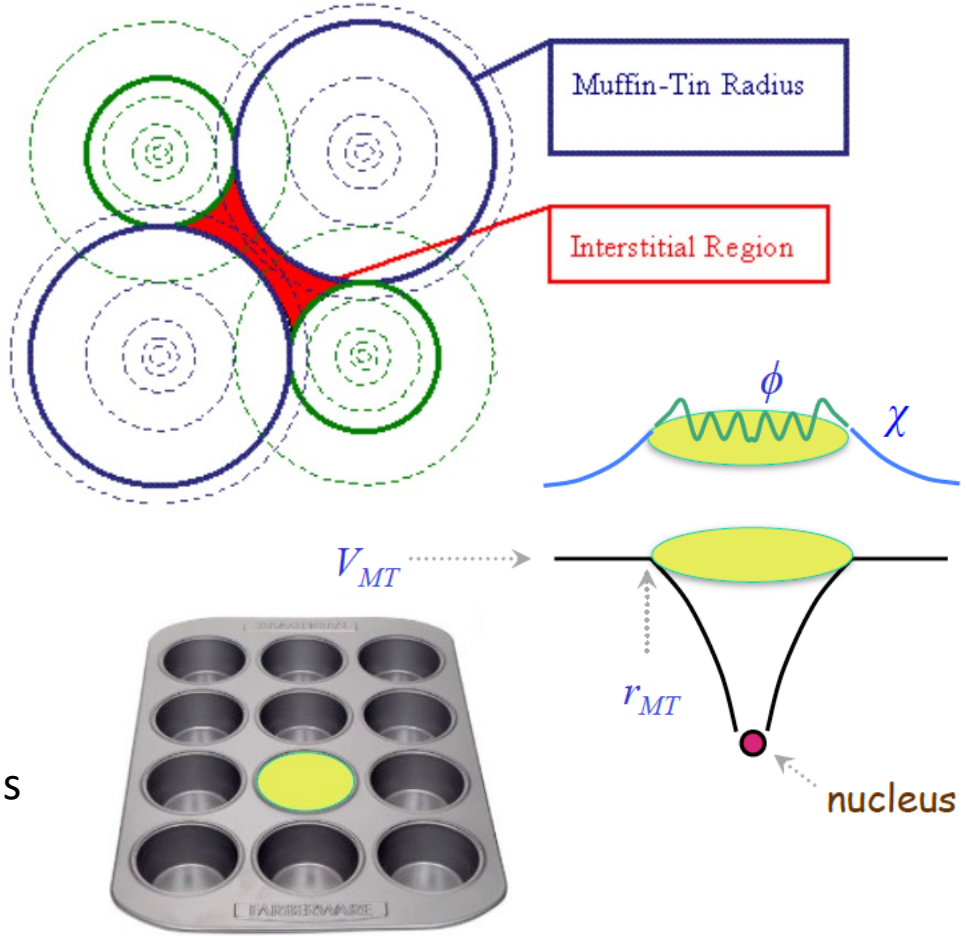
Muffin Tin Methods

MT potential: Spherically symmetric inside the 'augmentation' sphere ($r < r_{MT}$)
Constant in the interstitial space ($r > r_{MT}$)

Spherical harmonics

$$\varphi(r) = \begin{cases} \sum_{lm}^{\chi} u_l(r) Y_{lm}(\hat{r}) & r \leq r_{MT} \\ & r > r_{MT} \end{cases}$$

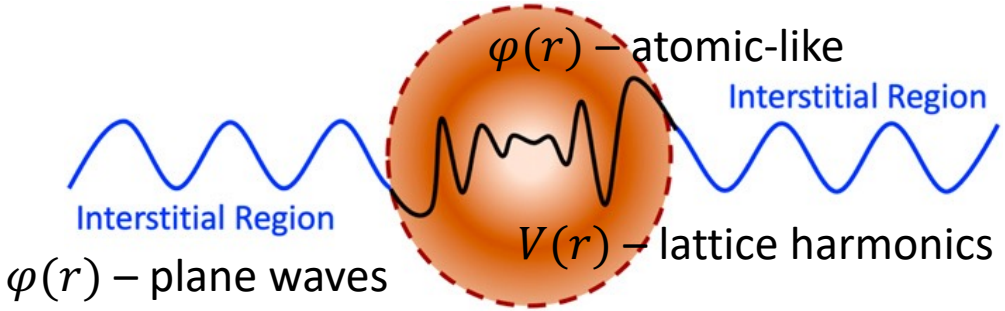
partial waves



Examples:
Korringa-Kohn-Rostoker (KKR) methods
Lineraized Muffin Tin Orbital (LMTO) methods

Augmented methods

APW potential: Spherically (nearly) symmetric inside the sphere ($r < r_{MT}$)
Plane wave potential in the interstitial space ($r > r_{MT}$)



Cell volume

$$\varphi(r) = \begin{cases} \frac{1}{\Omega^{1/2}} \sum_{\boldsymbol{G}} C_{\boldsymbol{G}} e^{i(\boldsymbol{G}+\boldsymbol{k})\cdot\boldsymbol{r}} & r > r_{MT} \\ \sum_{lm} A_{lm} u_l(r) Y_{lm}(\hat{r}) & r \le r_{MT} \end{cases}$$

$$A_{\ell m} = \frac{4\pi i^{\ell}}{\Omega^{1/2} u_{\ell}(R)} \sum_{\mathbf{G}} c_{\mathbf{G}} j_{\ell}(|\mathbf{k}+\mathbf{G}|R) Y^{*}_{\ell m}(\mathbf{k}+\mathbf{G})$$

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\ell(\ell+1)}{r^2} + V(r) - E_{\ell}\right] r u_{\ell}(r) = 0.$$

Examples:
Linearized Augmented Plane Wave (LAPW) methods
Projector Augmented Wave methods

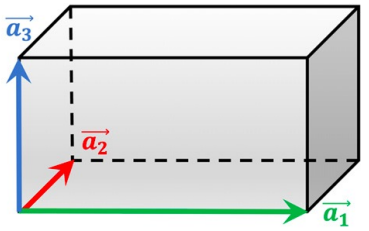
Plane Wave Basis Set

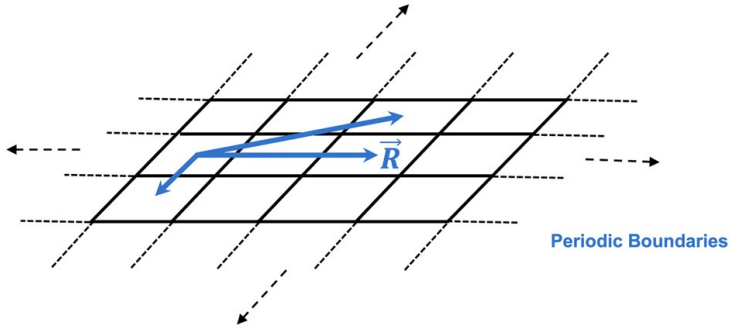
All cell-periodic functions are expanded in plane waves (Fourier analysis):

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}} \qquad u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{G}\mathbf{r}} \qquad \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}} \qquad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}}$$





Plane Wave Basis Set

All cell-periodic functions are expanded in plane waves (Fourier analysis):

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}} \qquad u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{Gr}} \qquad \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}e^{i\mathbf{Gr}} \qquad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}}e^{i\mathbf{Gr}}$$

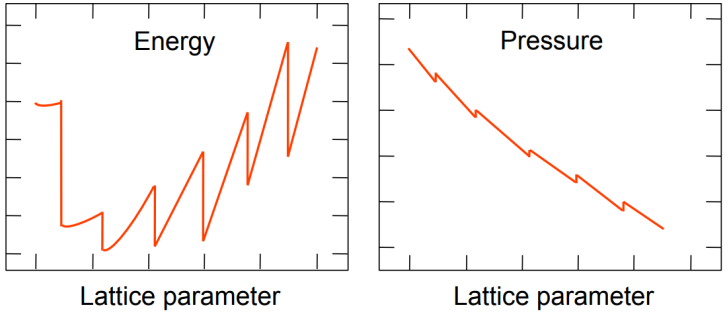
The basis set includes all plane waves for which $\frac{1}{2}|\mathbf{G}+\mathbf{k}|^2 < E_{\text{cutoff}}$

The PW basis set is complete for $E_{cutoff} \to \infty$ and orthonormal:
$\langle \boldsymbol{k}+\boldsymbol{G}|\boldsymbol{k}+\boldsymbol{G}'\rangle = \delta_{GG'}$

Transformation by means of FFT between "real" space and "reciprocal" space:

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{Gr}} \overset{\text{FFT}}{\longleftrightarrow} C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}}\sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}}e^{-i\mathbf{Gr}}$$

Number of Pain Waves (included in the basis set)= function of the kinetic cut off energy [Not Continuous!]



Energy and pressure also discontinuous functions of lattice parameter at fixed kinetic energy cutoff (if not big enough to have a near complete basis).

Plain Wave Basis Set

Are planewaves a practical approach to electronic structure calculations?

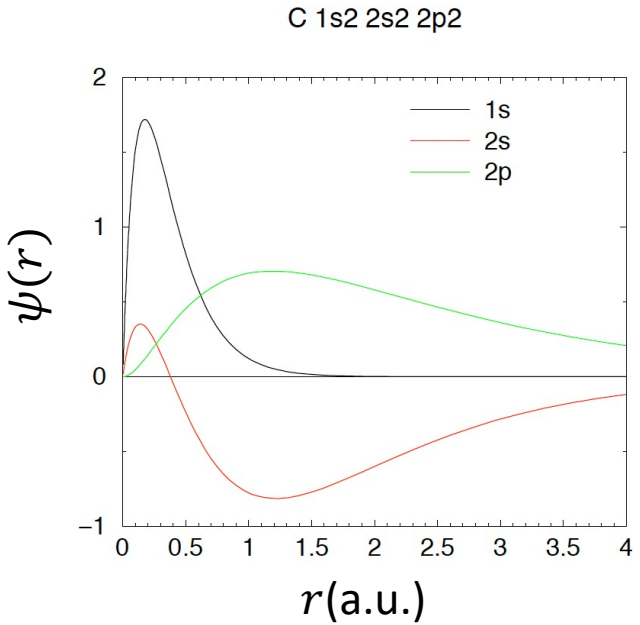
Remember: The PW basis set is complete for $E_{cutoff} \rightarrow \infty$

If we want to represent the *s* wavefunction at the length scale δ from the nucleus the reciprocal length scale is $q \sim {}^{2\pi}/_{\delta}$. For a solid we need $\sim 4\pi \, {}^{(2\pi/\delta)^3}/_{3\Omega_{BZ}}$ PWs, where $\Omega_{BZ} = 8\pi^3/\Omega$ is the volume of the Brillouin Zone.

Estimate # of plane waves need for 1s wavefunction of diamond ($a_0 = 6.74$ a.u.): for the s wavefunction $\delta \sim 0.1$ a.u., $\Omega = (2\pi)^3/(a_0^3/4) \rightarrow$ 250,000 PWs.

- Eliminate core states
- Smooth nodes close to the nucleus

Need a Pseudopotential: a smooth, weak effective potential that reproduces the effect of the nucleus plus the core electrons on the valence electrons.



All-electron vs plane waves

Full-potential, All-electron

Localized basis set

- No assumption of of spherical symmetry around atoms
- Full description of the core electrons
  - First row transition metals can readily be calculated
- Fast convergence w/respect to basis set size
- Highly accurate description of electrostatic potential
- LAPW easily adapted

- Different basis sets for molecules and solids
- Heavy computationally
- Very expensive ab initio MD
  - Difficult to calculate forces –Pulay Forces for incomplete basis set
- Difficult to improve convergence quality
- LMTO complicated to adapt

Plain Waves

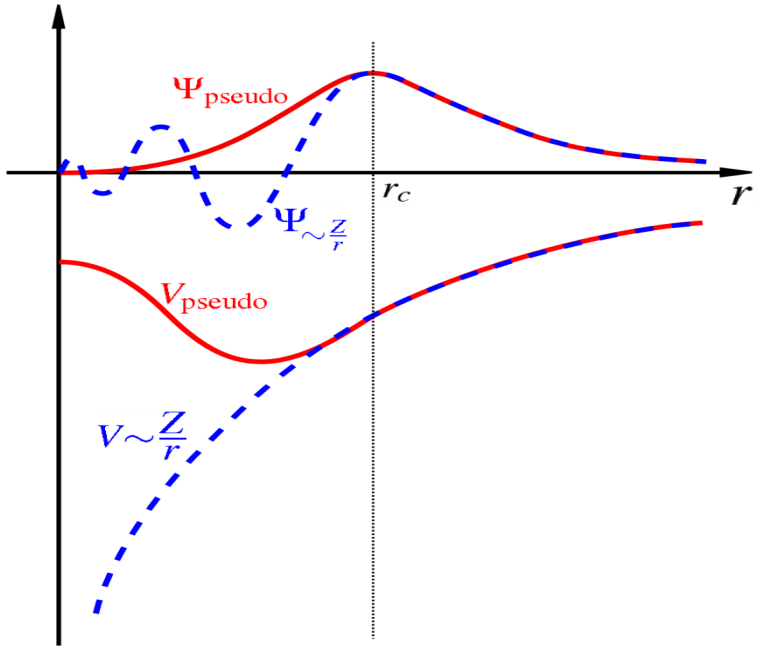
Delocalized basis set

- Very parallel efficient
- Efficient Ab Initio MD
  - Car-Parrinello
  - No Pulay forces
- Same basis set for molecules and solids
- Easy to improve convergence quality – related directly to Ecut

- Requires **pseudopotentials** to be efficient
  - Not all-electron
  - Core region not included
  - First row transition metals are difficult
- Slow convergence w/respect to basis set size

The Plane Wave Method and Pseudopotentials

- Planewave method – planewave basis set
  - Orthogonal
  - Easy to improve* – increase energy cutoff
  - Large number of basis functions needed to describe tightly bound (spatially strongly localized) states, and rapid oscillations (nodal features) of the orbitals near the nucleus exceeds any practical limit
- The common solution: Introduce the *frozen core* approximation Simplification of core electrons to limit basis – pseudopotentials (PSPs)
- Input based on atomic configuration
  - Valence and core electrons
  - Occupations
  - Cut-off radius
  - Degree of polynomial fit for the PSP



Common flavors of pseudopotentials used :

- Norm-conserving pseudopotentials
- Ultra-soft pseudopotentials
- The Projector-Augmented-Wave (PAW) method

Pseudopotential Approximation: in General

The pseudopotential approximation: the strong core potential is replaced by a pseudopotential, whose ground state wavefunction mimics the all-electron wavefunction outside a selected core radius allowing the the pseudo-wavefunction to be represented by a reasonably small number of plane waves.

Most general form for a pseudopotential

$$V_{NL} = \sum_{lm} |lm\rangle V_l \langle lm|$$

$|lm\rangle \rightarrow$ spherical harmonics

$V_l \rightarrow$ PSP for angular momentum l

When the same pseudopotential is used for each l, the PSP is the *local pseudopotential* $V_L(r)$, which is only a function of distance from the nucleus.

Scattering from the ion core is best described by a nonlocal PSP (i.e. uses a different potential for each angular momentum)

Best for meeting to goal of *transferability* – the capability to describe the scattering due to the ion in a variety of atomic environments.

Pseudopotential Approximation: Historical Example

The original PSP was constructed using the orthogonalized plane wave method (Herring, 1940).

Valence wavefunctions are expanded using a planewave basis orthogonalized to the core states:

Corresponding orthogonalized planewave

$$\phi_{OPW}(\boldsymbol{k}+\boldsymbol{G}) = \phi_{PW}(\boldsymbol{k}+\boldsymbol{G}) - \sum_{\alpha c} \langle \varphi_c | \phi_{PW}(\boldsymbol{k}+\boldsymbol{G}) \rangle \varphi_c$$

planewave

Sum over core states and atoms

A PSP related to this can be constructed: Let H be the original Hamiltonian with the core and valence wavefunctions φ_c and φ_v, respectively.

Consider a pseudostate that is a combination of the valence wavefunction and a summation of the core states:

pseudostates

$$\varphi_v^{PS} = \varphi_v + \sum_{\alpha c} a_{vc} \varphi_c$$

$$a_{vc} = \langle \varphi_c | \varphi_v^{PS} \rangle$$

Pseudopotential Approximation: Phillips-Kleinman

Applying the Hamiltonian we have:

$$H|\varphi_v^{PS}\rangle = \epsilon_v|\varphi_v\rangle + \sum_{\alpha c} a_{vc}\epsilon_c|\varphi_c\rangle$$

$$= \epsilon_v|\varphi_v^{PS}\rangle + \sum_{\alpha c} a_{vc}(\epsilon_c - \epsilon_v)\,|\varphi_c\rangle$$

The pseudostates satisfy and Schrodinger-like equation with an additional contribution V^R

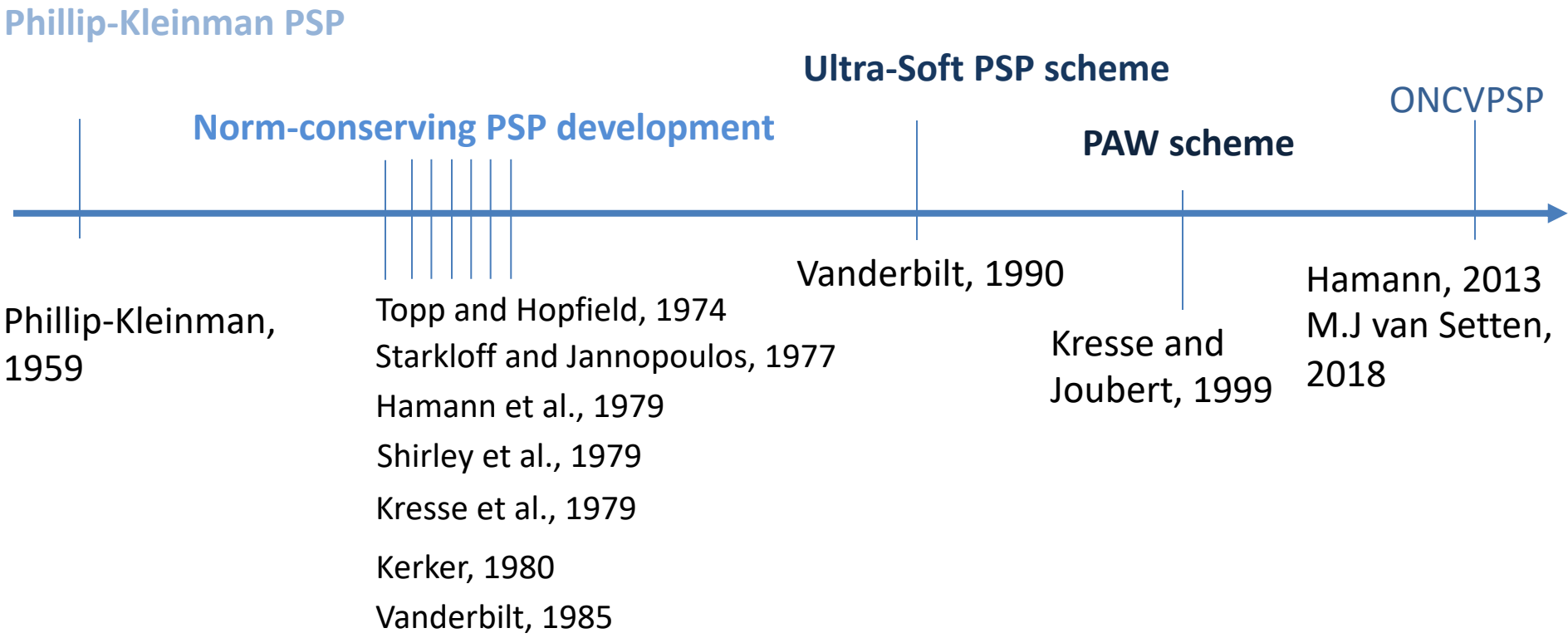
$$\left[H + \sum_{\alpha c} (\epsilon_v - \epsilon_c)\,|\varphi_c\rangle\langle\varphi_c|\right]\varphi_v^{PS} = \epsilon_v^{PS}\varphi_v^{PS}$$

$$V^R = \sum_{\alpha c} (\epsilon_v - \epsilon_c)\,|\varphi_c\rangle\langle\varphi_c|$$

Differs from a normal potential term in that it is energy dependent (ϵ_v). Adding V^R to the original V in the Hamiltonian give the Phillips-Kleinman pseudopotential (Philips and Kleinman, 1959).

$$V^{PK} = V + V^R$$

History and Types of PSP



Pseudopotential: Goals

Evolution of PSPs is motivated by the following goals:

1) Soft as possible: allow for the expansion of the valence pseudo-wavefunctions using as few planewaves as possible
2) Transferable: the capability to describe the scattering due to the ion in a variety of atomic environments.
3) Charge density match: the pseudo-charge density should reproduce the valence charge density as accurately as possible.

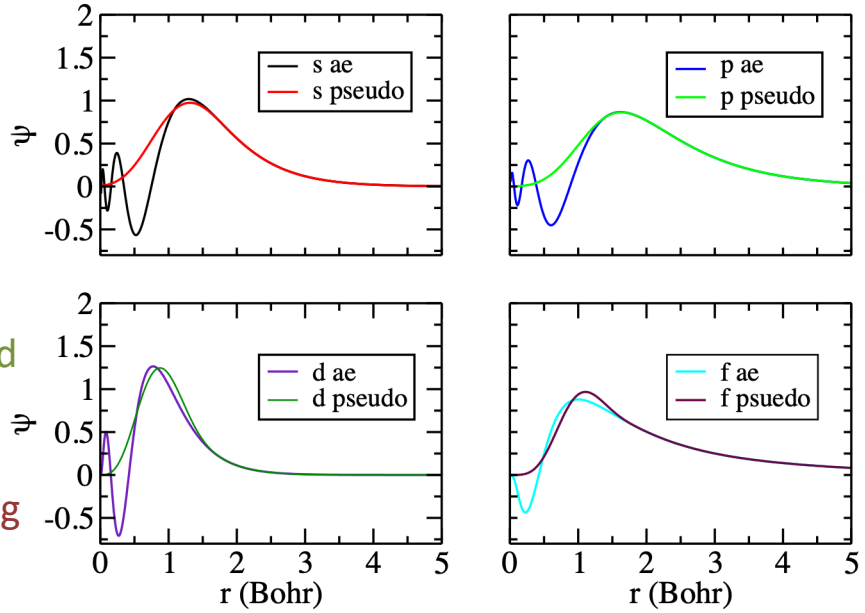
Norm Conserving

Norm-conserving PSPs: the pseudo-wavefunctions and potential are constructed to be equal to the actual valence wavefunctions and potential outside of some core radius r_c.

Inside r_c the pseudo wavefunctions differ from the true wavefunctions, but the norm is constrained to be the same.

$$\int_0^{r_c} dr\, r^2 \varphi^{PS*}(r)\, \varphi^{PS}(r) = \int_0^{r_c} dr\, r^2 \varphi^{*}(r)\, \varphi(r)$$

- Simple to make and use: universally implemented in PW codes (usually)
- They are relatively hard: r_c cannot exceed the outermost valence orbital by much without losing transferability – lead to high Ecut in transition metals and heavy elements



Ultrasoft

Ultrasoft PSPs use a pseudized (smoothed) augmentation function, $Q_{lm}(r)$. The augmentation function and pseudized augmentation are calculated on a FFT grid.

- Because of the augmentation the Ultrasoft PSP can be made soft without loss of transferability. The core radius can be pushed pushed out even for 3d and 4d elements.

- Difficult to generate: pseudization of the augmentation charges is challenging
- Introduced several additional terms in the formalism which are not implemented in all components of some PW codes

- Even less core information is available.

Vanderbilt, 1990

PAW

In the Projector-Augmented Wave (PAW) scheme, augmentation functions are calculated and stored on a radial grid, centered at each atom. The charge density is made up of a “smooth” term expanded into the plane waves and an augmentation term calculated on the radial grid.

- PAW are the most transferable with accuracy comparable to all-electron techniques
- There is much more information about the orbitals close to the nucleus

- At least as difficult to generate at Ultrasoft PSPs

- Introduce more terms into the formalism: implementation into PW codes is complicated and limited (so far)

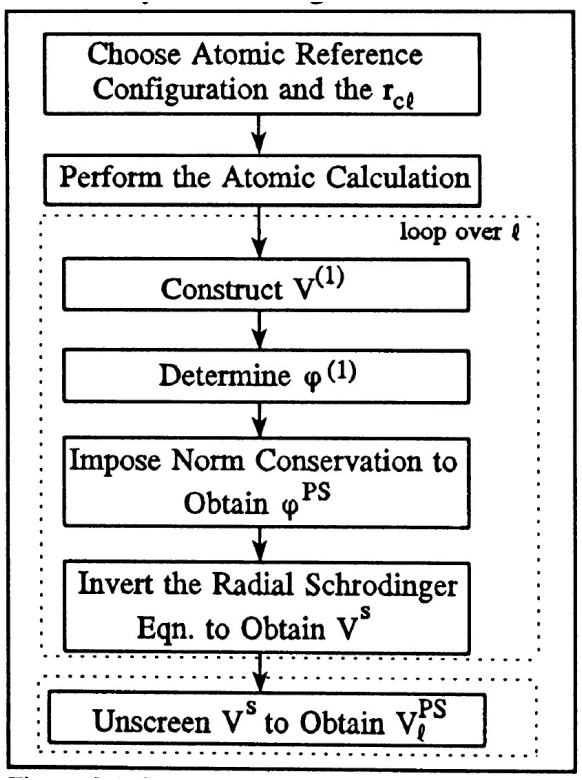
Kresse and Joubert, 1999

Advantages of NC PSPs

- Norm-conserving computations use a simple, robust formalism with easily transferable formats that are used in most plane wave DFT software
  - Especially important for more complex calculations such as DFPT, GW, BES, QMC
  - Example: DFPT and related capabilities are most widely available with NC PSPs
- Can be made with many exchange-correlation (XC) flavors and with or without spin-orbit coupling

Places to get NCPSPs:
http://www.pseudo-dojo.org/
http://nninc.cnf.cornell.edu/index.php

*Personal tip: Don't start from scratch



Bachelet, Hamann, and Schluter procedure for generating norm-conserving pseudopotentials.

Optimized Norm-Conserving Vanderbilt Pseudopotential

- ONCVPSP formalism
- Based on the use of two projectors and generalized norm conservation

Construct several radial pseudo-wavefunctions (φ_i) at energies ε_i and angular momentum l, which agree with all-electron (AE) wavefunctions (ψ_i) outside a core radius r_c.

Start with simplified kinetic energy operator: $T = \left[-{}^{d^2}/_{dr^2} + {}^{\ell(\ell+1)}/_{r^2}\right]/2$

Introduce the projectors

$$|\chi_i\rangle = (\varepsilon_i - T - V_{loc})|\varphi_i\rangle$$

The non-local PSP will be

$$V_{NL} = \sum_{i,j} |\chi_i\rangle\,(B^{-1})_{ij}\,\langle\chi_j|$$

Where $B_{ij} = \langle\varphi_i|\chi_j\rangle$ and $B_{ij} \neq B_{ji}$. After performing integration by parts

$$B_{ij} = \int_0^{r_c} \varphi_i \left[\varepsilon_j + \frac{1}{2}\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{2r^2} - V_{loc}\right]\varphi_j$$

B_{ij} will be symmetric matrix if the generalized norm-conservation condition

$$\langle\varphi_i|\varphi_j\rangle_{r_c} = \langle\psi_i|\psi_j\rangle_{r_c}$$

is satisfied for the cut off radius r_c.

Optimized Norm-Conserving Vanderbilt Pseudopotential

For ease of integration with PW codes –normalize χ_i, rescale B_{ij} (diagonalize it and form linear combinations of the projectors, χ_i, using the resulting eigenvectors).

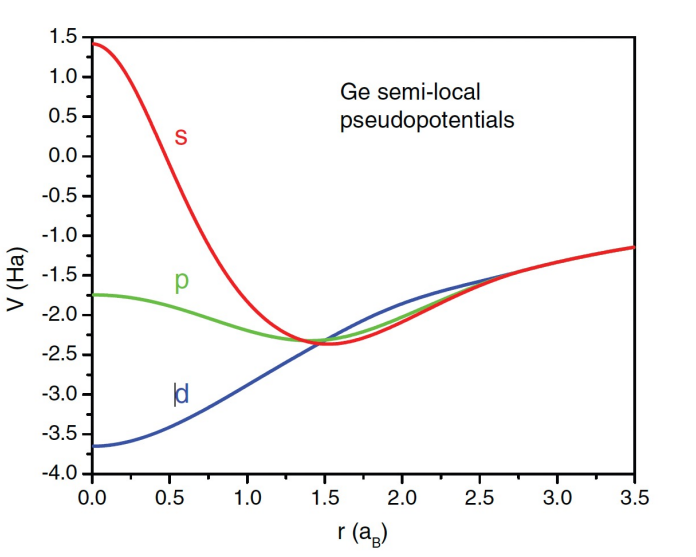
Final non-local operator is

$$V_{NL} = \sum_{i,j} |\tilde{\chi}_i\rangle \frac{1}{\tilde{b}_i} \langle \tilde{\chi}_j |$$

b_i are the eigenvalues of the rescaled B_{ij}.

Non-local radial Schrodinger equation: solutions will agree with AE solutions for $r \geq r_c$

$$(T + V_{loc} + V_{NL})\varphi = \varepsilon\varphi$$



M.J. van Setten, et al., Comp. Phys. Comm. 226, 39-54 (2018).
D. R. Hamann, Phys. Rev. B 88, 085117 (2013)

D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
A. Rappeet al., Phys. Rev. B 41, 1227 (1990).

Optimized Norm-Conserving Vanderbilt Pseudopotential

- Scalar relativistic (SR) and fully relativistic (FR)implementations:
  - SR is the default algorithm
- FR non-local PSPs are generated as sums over the total angular momenta

$$V(\mathbf{r},\mathbf{r}') = V_{\text{loc}} + \sum_{\ell}\left[V_{\ell}^{\text{SR}}(\mathbf{r},\mathbf{r}') + \mathbf{L}\cdot\mathbf{S}V_{\ell}^{\text{SO}}(\mathbf{r},\mathbf{r}')\right]$$

$$V_{\ell}^{\text{SR}} = \frac{(\ell+1)V_{\ell+1/2}^{\text{Rel}} + \ell V_{\ell-1/2}^{\text{Rel}}}{2\ell+1}, \quad V_{\ell}^{\text{SO}} = \frac{2\left(V_{\ell+1/2}^{\text{Rel}} - V_{\ell-1/2}^{\text{Rel}}\right)}{2\ell+1}$$

- ONCVPSP code forms projectors based on the selection of SR or spin-orobit SO (i.e. FR)

M.J. van Setten, et al., Comp. Phys. Comm. 226, 39-54 (2018).

Generating and Testing

Codes:

ATOMPAW – generating PAW potentials – formats for Abinit and Quantum Espresso
ONCVPSP – norm-conserving PSP – formats for Abinit, Quantum Espresso, and SIESTA (psml)
OPIUM – norm-conserving PSPs
APE – norm-conserving PSPs - Abinit, Quantum Espresso, and SIESTA (psf)
USPP – ultrasoft PSPs QE and Abinit
ld1 – internal QE generator – mostly verified for PAW

PSPs should be tested for:

Ghost states: unphysical states in the region of the valence energies or near them.

Poor transferability – check for reasonable recreation of ground state characteristics

- Lattice constants, volume
- Convergence of Ecut
- Convergence of k point grid

Resources

General information

David J. Singh, *Planewaves, Pseudopotentials, and the LAPW Method.* Springer Science (1994).
M.C Payne *et al*., Reviews of Modern Physics, **64** (1992).

Norm conserving PSPs

M.J. van Setten, et al., Comp. Phys. Comm. 226, 39-54 (2018).
D. R. Hamann, Phys. Rev. B 88, 085117 (2013)

D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
A. Rappeet al., Phys. Rev. B 41, 1227 (1990).

Ultra Soft PSPs

David Vanderbilt. Phys. Rev. B 41, 7892(R) (1990).
USPP code: https://www.physics.rutgers.edu/~dhv/uspp/

PAW

G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
ATOMPAW code: http://users.wfu.edu/natalie/papers/pwpaw/man.html

PSP tables:
http://pseudopotentials.quantum-espresso.org/legacy_tables

https://www.abinit.org/psp-tables

http://www.pseudo-dojo.org/

http://nninc.cnf.cornell.edu/index.php

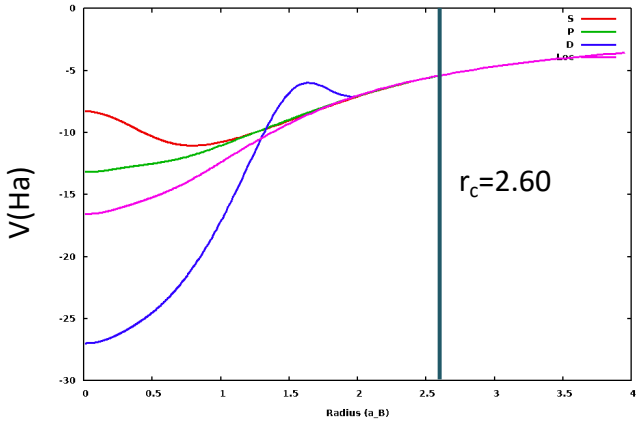
Always test PSPs you get from a table!

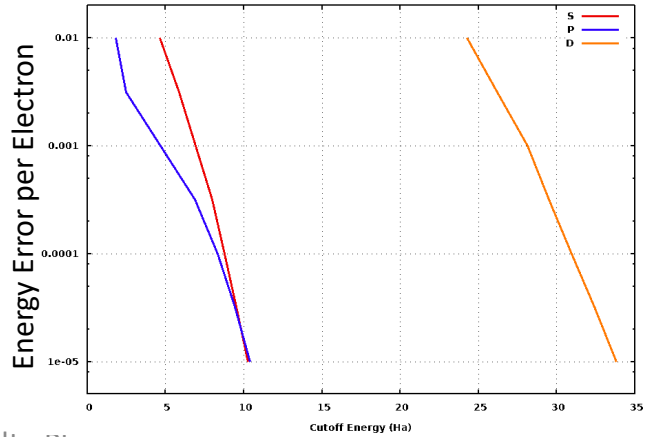
Tutorial:Norm-conserving Pseudopotentials

LA-UR-22-27189

Pseudopotentials and the planewave method

- Planewave method – planewave basis set
  - Orthogonal
  - Easy to improve* – increase energy cutoff
  - Large number of basis functions needed
- Simplification of core electrons to limit basis – pseudopotentials (PSPs)
- Input based on atomic configuration
  - Valence and core electrons
  - Occupations
  - Cut-off radius
  - Degree of polynomial fit for the PSP





ONCVPSP Tutorial

- Ge - $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^2$
- Input file format – Ge.dat

```
# ATOM AND REFERENCE CONFIGURATION
#
# atsym,   z,    nc, nv, iexc   psfile
   Ge    32.0  5   3    3     psp8
#
#
# n,  l,    f
  1   0   2.0
  2   0   2.0
  2   1   6.0
  3   0   2.0
  3   1   6.0
  3   2  10.0
  4   0   2.0
  4   1   2.0
```

core

valence

atsym - atomic symbol
z - atomic number
nc - number of core states
nv - number of valence states
iexc - exchange-correlation functional: 1-Wigner, 2-Hedin-Lundquist, 3-Perdew-Zunger-Ceperly-Alder, 4-Perdew-Burke-Enzerhof
psfile - format of pseudopotential file, psp8 for ABINIT, upf for PWSCF, or both
#
n - principal quantum number
l - angular momentum
f - occupancy (MUST be >0)

```
# PSEUDOPOTENTIAL AND OPTIMIZATION
# lmax
   2
#
#
#
#   l,    rc,      ep,    ncon, nbas, qcut
    0    2.60    -0.00     4       8     5.00
    1    2.60    -0.00     4       8     5.20
    2    2.00     0.00     4       9     8.40
```

*Choosing qcut is a compromise. While a smaller qcut will typically give better convergence up to the corresponding energy, the "foot" of the convergence curve will have an earlier onset and be flatter.
The cutoff convergence profiles in the output can guide you. Increasing qcut by a small amount, say ~0.5, can usually give more uniform convergence at only a small sacrifice of low-cutoff convergence.

lmax - maximum angular momentum for which psp is calculated (<=3)

l - angular momentum (l's must be in order)
rc - core radius for this l
ep - energy at which psp is generated (eigenvalue inserted for occupied state in reference configuration, positive energy must be specified for barrier-confined "scattering" state for unoccupied l <=lmax
A small positive energy is usually good (0.1-0.25 Ha).
ncon - number of constraints for pseudo wave function to match all-electron wave function at rc, value + ncon-1 derivatives, must be between 3 and 5
nbas - number of basis functions. Must be between ncon+2 and ncon+5
qcut - wave vector defining "residual energy" in the RRKJ method

Rappe A., Rabe K., Kaxiras E., Joannopoulos J., “Optimized pseudopotentials”
Phys. Rev. B, 41 (2) (1990), pp. 1227-1230

```
# LOCAL POTENTIAL
#
# lloc, lpopt, rc(5), dvloc0
   4      5      2.0     0.0
```

lloc - angular momentum whose semi-local psp is taken as local. lloc=4 denotes a smooth polynomial continuation of the all-electron potential. If lloc<=lmax, remaining data are ignored, but must be there (zeros are OK). The rc corresponding to lloc MUST BE THE MINIMUM rc for lloc<=lmax, or <= the minumum for lloc=4 (usually the best choice)

lpopt - type of polynomial continuation for lloc=4. values 1-5 permitted.

1) match 2 derivatives, r^0,2,4
2) match 2 derivatives, r^0,4,6
3) match 3 derivatives, r^0,4,5,6
4) match 3 derivatives, r^0,4,6,8
5) match 3 derivatives, r^0,2,4,6

rc(5) - minimum rc from pseudopotential

dvloc0 - shift of r=0 potential from basic continuation for lloc=4 depends on lpopt above as follows, with x=(r/rc)

1) dvloc0*(1-x^2)^3
2) dvloc0*(1-x^4)^3
3-5) dvloc0*(1-x^4)^4

*When an eigenvalue of the B matrix is close to zero, very large coefficients can be carried through transformation to the orthonormal projectors, and produce deeply-bound ghost states. A well-tested and benchmarked psp can be close to having such a zero, and an inconsequential change could push the eigenvalue enough towards that zero to make a ghost.

The recommended fix is a small change in the local potential, which in principal should have no effect on the quality of the psp.
dvloc0 shifts as small as +/- 0.5 or even 0.25 Ha can eliminate a ghost.

```
# VANDERBILT-KLEINMAN-BYLANDER PROJECTORs
#  l, nproj, debl
   0   2     1.50
   1   2     1.50
   2   2     1.50
```

l - angular momentum
nproj - number of projectors, 1 or 2. automatically set to 0 for l=lloc
debl - energy added to basic psp
energy ep for 2nd projector automatically reset to match 2nd projector with 2nd bound state at this l when it is occupied (ie., the psp is generated for a corresponding-l shallow core state)

```
# MODEL CORE CHARGE
# icmod, fcfact, (rcfact)
   0         0.25,   (added for icmod=3)
```

icmod - 0: no non-linear core correction charge.
1: smooth monotonic polynomial model core charge fit at "matching" rc
2,3: Teter function (see doc/core_correction.txt)
4: The "blended" Teter function
fcfact - radius for above determined by rho_core(r)=fcfact*rho_pseudo_valence(r) values 0.25-0.5 are usually good.
For icmod = 3, fcfact has a different meaning and a third artument rcfact is added (see core_correction.txt)
For icmod = 4, fcfact is ignored but must be present (0.0 OK)

```
# LOG DERIVATIVE ANALYSIS
# epsh1, epsh2, depsh
  -2.0      2.0     0.02
```

epsh1 - lower energy limit for "phase-shift-like" log-derivative plots should be below the nearest core level for this l to make sure there are no ghosts, but -2.0 Ha usually is OK
When semi-cores are treated as valence, this should be below the lowest core energy

epsh2 - upper energy limit, 2.0 usually good

depsh - energy mesh interval for plot, 0.02 usually good enough

```
# OUTPUT GRID
# rlmax, drl
   4.0    0.01
```

rlmax - maximum radius for Abinit psp code 8 format output. Must be greater than maximum rc (including lloc=4 rc), but also determines range of diagnostic plots, so ~2-3*rcmax is usually good

drl - mesh spacing of linear radial mesh for Abinit output. 0.02 is good for "softer" psps, 0.01 is probably better with 1st row, 3d's, or semi-core psps.

```
# TEST CONFIGURATIONS
# ncnf
  4
#  n   l   f
  3                #nvcnf
  3   2  10.00
  4   0   1.00
  4   1   2.00
#
  3
  3   2  10.00
  4   0   2.00
  4   1   1.00
#
  3
  3   2  10.00
  4   0   1.00
  4   1   1.00
#
  3
  3   2  10.00
  4   0   1.00
  4   2   1.00
```

ncnf - number of test configurations (<=4) The reference config is always run first as a consistency check. Core always is the reference core configuration. The excitation energy of the configuration for the pseudo-atom will be compared with the all-electron result.
n - principal quantum number for all-electron atom
l - angular momentum
f - occupancy
nvcnf - (repeated ncnf times) number of valence states in this test configuration

```
*REFERENCE CONFIGURATION
# n   l   f
  3   2  10.0
  4   0   2.0
  4   1   2.0
```

Generate PSP

- Using executable
  - oncvpspnr.x – non-relativistic
  - oncvpsp.x – scalar relativistic
  - oncvpspr.x – fully relativistic
- To generate plots and psp files use utility scripts:
    - run_nr.sh, run.sh, or run_r.sh
    - **./run.sh Ge**
    - **./extract.sh Ge** – prints psp file

Appendix

The Non-Relativistic Many-Electron Problem

$\Psi(x_1, x_2, \cdots, x_{N_e})$

Antisymmetric N-electron wavefunction

$$\Psi(\{x_j\})\left[-\sum_j^{N_e}\frac{\hbar^2}{2m}\nabla_j^2 + \sum_{j<k}^{N_e}\frac{e^2}{|r_j - r_k|} + \sum_j^{N_e} V_{ext}(r_j)\right] = E\Psi(\{x_j\})$$

Electronic Kinetic Energy

Electron-Electron Interactions

External Potential

Wavefunction Methods

Hartree-Fock (HF)

- No Correlation

Beyond HF Approaches

- Configuration interaction (CI)
- Methods building off of CI:
  - Coupled Cluster (CC),
  - Multi-configurational self-consistent field (MCSCF),
  - Multireference CI (MRCI), …

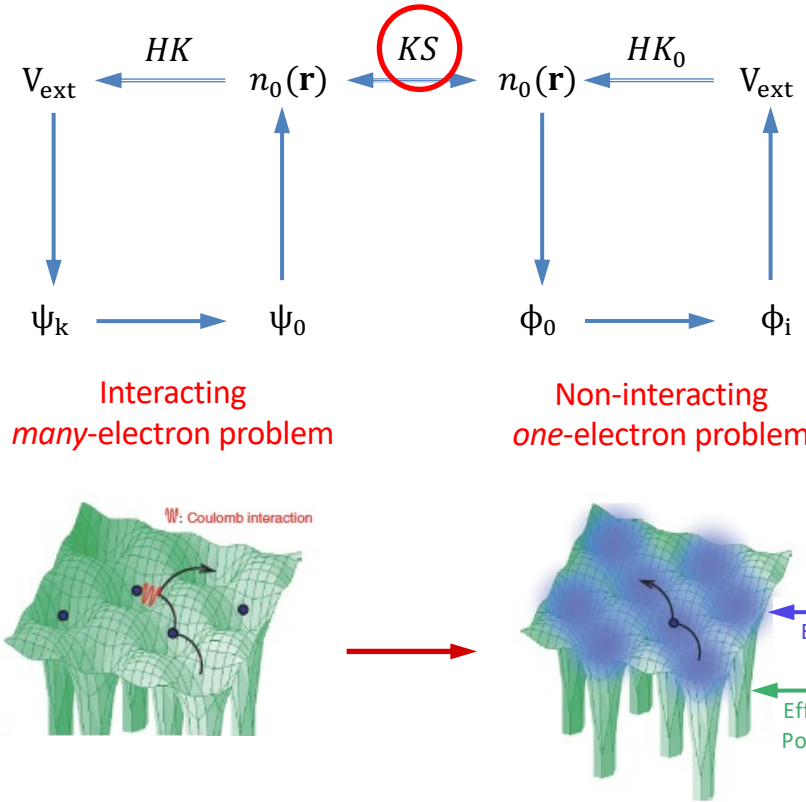
- Problem with wavefunction methods
  - 3N Dimensional Function
  - Computationally very expensive
  - Limited to ~100 electrons

Kohn-Sham Auxiliary System

To move forward, we replace one problem with another…

- The *ansatz* of Kohn and Sham assumes that the ground state density of the original *interacting* system is equal to that of a chosen *non-interacting* system.
- The non-interacting system leads to an independent particle picture which is exactly solvable (numerically)
- Its solution gives the ground state energy and density.
- *The main problem: What is the potential that generates the corresponding interacting electron density?*

  → Exchange-correlation Functional



W. Kohn and L. J. Sham Phys. Rev. 140, A1133 (1965)
P. Hohenberg and W. Kohn Phys. Rev. 136, B864 (1964)

Diagonalization of the KS Hamiltonian: Basis Sets

Solving the KS Hamiltonian, $H_{KS}\psi = \epsilon\psi$, at a fixed potential is the hard part – how to proceed?

- Expand ψ into some suitable basis set $\{\phi_i\}$ as

$$\psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r})$$

- For and orthonormal basis set, we solve the secular equations

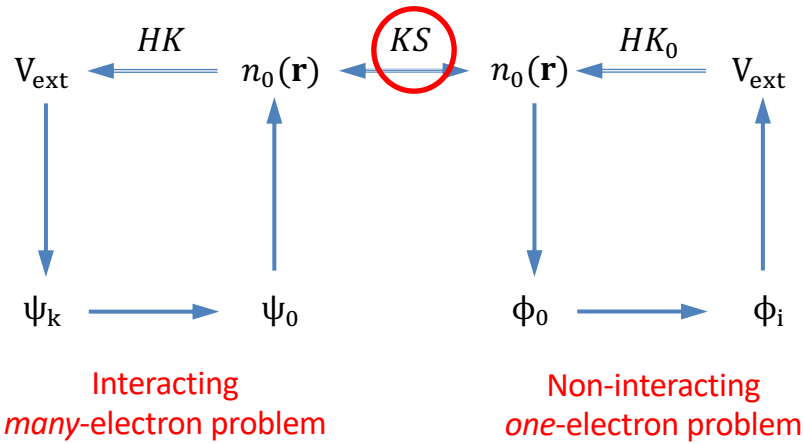
$$\sum_j (H_{ij} - \epsilon\delta_{ij})c_j = 0$$

- Where $H_{ij} = \langle\phi_i|H_{KS}|\phi_j\rangle$ are the matrix elements of the Hamiltonian. For a non-orthonormal basis set, we solve

$$\sum_j (H_{ij} - \epsilon S_{ij})c_j = 0$$

- Where $S_{ij} = \langle\phi_i|\phi_j\rangle$

- *Diagonalization algorithms are well known in linear algebra – in practice we use iterative algorithms so we don't have to store massive matrices.*



Exchange-Correlation Energy

$$E_{KS}[n] = \sum_{i}^{occupied} \int d\boldsymbol{r}\, \psi_i^*(\boldsymbol{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 \right] \psi_i(\boldsymbol{r}) + \int d\boldsymbol{r}\, n(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) + \frac{1}{2}\int d\boldsymbol{r} \int d\boldsymbol{r}' \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + E_{xc}[n]$$

Non-interacting kinetic energy

External Potential

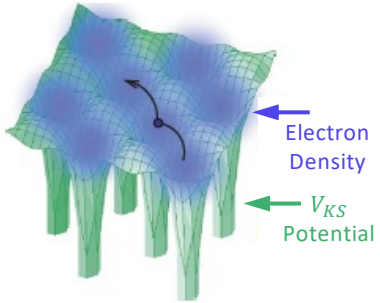
Hartree electrostatic self-repulsion

Exchange-correlation Energy

Need to approximate

E_{XC} Encodes the many-body information

$$E_{xc}[n] = F[n] - T_s - E_{Hartree}$$
$$= \langle \hat{T} \rangle - \hat{T}_s + \langle \hat{V}_{e-e} \rangle - E_{Hartree}$$



Varying E_{KS} with respect to ψ_i^*

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i + \left[\frac{\delta E_{ext}}{\delta n(r)} + \frac{\delta E_{Hartree}}{\delta n(r)} + \frac{\delta E_{xc}}{\delta n(r)}\right]\psi_j = -\frac{\hbar^2}{2m}\nabla^2\psi_i + V_{KS} = \epsilon_j \psi_j$$

Effective one-body potential

$$V_{KS}(r) = V_{ext} + V_{Hartree} + V_{xc}$$
$$= \frac{\delta E_{ext}}{\delta n(r)} + \frac{\delta E_{Hartree}}{\delta n(r)} + \frac{\delta E_{xc}}{\delta n(r)}$$

Total energy and electronic structure is obtained by solving an effective Schrödinger Equation

$$H_{KS}\psi_i = \epsilon_i \psi_i$$

W. Kohn and L. J. Sham Phys. Rev. 140, A1133 (1965)
P. Hohenberg and W. Kohn Phys. Rev. 136, B864 (1964)

Development of Exchange-Correlation Approximations

(1964, HK)

(1965, KS; LDA: n)

GGA: $n, \nabla n$

1968 (MB)

1980s
(LM, PW86, B88, LYP, …)

1991 (PW91)

1996 (PBE)

2000s
(WC, AM05, PBEsol, SOGGA, …)

Efficient semilocal approximations

$$E_{xc}^{sl}[n] = \int d\boldsymbol{r}\, n(\boldsymbol{r})\varepsilon_{xc}(n, \nabla n, \tau)$$

$$n = \sum_{i}^{occup} |\phi_i|^2 \qquad \tau = \frac{1}{2}\sum_{i}^{occup} |\nabla\phi_i|^2$$

ϕ are the KS orbitals

meta-GGA: $n, \nabla n, \tau$

1975 (CS)

1989 (BR)

1990s
(BC95, VS, PKZB,…)

2000s
(TPSS, M06L,…)

2010s
(MS, M11L, …)

2015 (SCAN)

hybrid GGA

1993 (B3PW91)

1994 (B3LYP)

1999 (PBE0)

2003 (HSE)

2000s
(O3LYP, X3LYP, wB97,…)

hybrid meta-GGA

1996 (B88B95)

2000 – current
(TPSSh, MS2h,…)

Hybrid Functionals

$$E_{xc}^{hyb}[n] = \alpha E_x^{sl}[n] + (1-\alpha)E_x^{exact} + E_c^{sl}$$

$$E_x^{exact} = -\frac{1}{2}\sum_{\sigma}\sum_{i,j}^{N_\sigma}\int d\boldsymbol{r}\int d\boldsymbol{r}'\,\frac{\phi_{i\sigma}^*(\boldsymbol{r})\phi_{j\sigma}(\boldsymbol{r}')\phi_{i\sigma}(\boldsymbol{r}')\phi_{j\sigma}^*(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}$$