The Plane-Wave Pseudopotential Method

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The Kohn-Sham problem

- Want to solve the Kohn-Sham equations:

\[
\left( -\frac{1}{2} \nabla^2 + V_{\text{nucl}}(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{\text{XC}}[n(\mathbf{r})] \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})
\]

- Note that self-consistent solution necessary, as $H$ depends on solution:

\[
\{\psi_i\} \rightarrow n(r) \rightarrow H
\]

- Convention (most of the time, in this talk):

\[
e = \hbar = m_e = 1
\]
Kohn-Sham Equations in a Basis

- Can choose to expand wavefunctions in a basis set:

\[
\psi_i(r) = \sum_{\alpha=1}^{N_b} c_{i\alpha} f_\alpha(r)
\]

- Now obtain a matrix equation:

\[
\sum_\beta H_{\alpha\beta} c_{i\beta} = \varepsilon_i c_{i\alpha}
\]

- Solving \(\Leftrightarrow\) Have to diagonalize a matrix of size \(N_b \times N_b\)

\[\text{Size of basis}\]
Some possible basis sets

• Various possible choices of basis:
  - Plane waves $e^{iK \cdot r}$
  - Localized sets:
    e.g., Gaussians
    e.g., atomic orbitals
  - Mixed basis
  - Augmented basis

• Choose so that calculation is fast, accurate, convenient.
  - Would like $N_b$ to be small (within reason)?
  - Would like form of $f_\alpha(r)$ to be simple?
Advantages of a Plane Wave Basis

- **Simple**: Easy to take derivatives, etc. ⇒ Coding is easy!
- **Orthonormal**: No overlap integrals.
- **Independent of atomic positions** ⇒ No “Pulay forces”; easy to calculate forces for structural relaxation & molecular dynamics.
- **Unbiased**: No assumption about where charge concentrated. (But ∴ also wasteful?)
- **Easy to control convergence** w.r.t. size of basis: only one parameter $E_{\text{cut}}$ (energy cut-off for planewaves)
- **Can easily take advantage of FFT’s**: r-space ↔ k-space
Advantages of a Plane Wave Basis

Convenient use of FFTs:

\[
\tilde{f}(k) = \sum_{n=0}^{N-1} f_n e^{-2\pi i kn/N}
\]

Very practical to calculate convolutions, solve Poisson's equation, etc.

\[
V(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]

\[
\tilde{V}(\mathbf{G}) = 4\pi \frac{\tilde{n}(\mathbf{G})}{\mathbf{G}^2}
\]
Disadvantages of a Plane Wave Basis

● Often need a HUGE number of plane waves to get an adequate expansion, i.e., $N_b$ can be very large! ($\sim 10^5$ per atom) (Will discuss… solution = introduction of pseudopotentials.)

● The set of plane waves is discrete only if the system is periodic! (Will discuss solution = introduction of artificial supercell or periodic approximat.)

● Sometimes (chemical) interpretation harder.
Some popular plane wave codes

• Quantum ESPRESSO (PWscf)
• VASP
• ABINIT
• CASTEP
• CPMD

(there are others too…)

Periodic Systems

• Periodic systems are characterized by a lattice of
  - lattice vectors $\mathbf{R}$ in real (r-) space
  - reciprocal lattice vectors $\mathbf{G}$ in reciprocal (k-) space

• Spacing of $\mathbf{R}$'s inversely proportional to spacing of $\mathbf{G}$'s
Periodic Systems & Bloch’s Theorem

- For a periodic system, recall Bloch’s Theorem:
  \[ \psi_k(r) = e^{i k \cdot r} u_k(r) \]

- \( u_k(r) \) has the periodicity of the system, i.e.,
  \[ u_k(r) = u_k(r + R), \text{ where } R = \text{ lattice vector} \]

- As for all lattice-periodic functions, only certain plane waves will appear in the Fourier expansion of \( u_k(r) \):
  \[ u_k(r) = \frac{1}{\Omega} \sum_G c_{k,G} e^{i G \cdot r} \text{ where } G = \text{ reciprocal lattice vector} \]
So, for a periodic system:

\[ \psi_k(r) = \frac{1}{\Omega} \sum_G c_{k,G} e^{i(k+G) \cdot r} \]

where \( G \) = reciprocal lattice vector

The plane waves that appear in this expansion can be represented as a grid in k-space:

- Only true for periodic systems that grid is discrete.
- In principle, still need infinite number of plane waves.
Truncating the Plane Wave Expansion

- In practice, the contribution from higher Fourier components (large $|\mathbf{k} + \mathbf{G}|$) is small.
- So truncate the expansion at some value of $|\mathbf{k} + \mathbf{G}|$.
- Traditional to express this cut-off in energy units:

$$\frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m_e} \leq E_{\text{cut}}$$
Truncating the Plane Wave Expansion

- **Beware:** charge density and orbitals have different cutoffs!

\[ n(r) = \sum_i \psi_i^*(r) \psi_i(r) \]

\[ \frac{\hbar^2 |k + G|^2}{2m_e} \leq E_{cut} \]
Truncating the Plane Wave Expansion

- **Beware:** charge density and orbitals have different cutoffs!

\[
\frac{\hbar^2 |k + G|^2}{2m_e} \leq E_{\text{cut}}
\]

\[
n(r) = \sum_i \psi_i^*(r) \psi_i(r)
\]

\[
\tilde{n}(G) = \sum_i \sum_{G'} \tilde{\psi}_i^*(G') \tilde{\psi}_i(G - G')
\]

⇒ if the orbitals are represented with a cutoff \( E_{\text{cut}} \), then the charge density is represented with a cutoff of \( 4 \ E_{\text{cut}} \).
Matrix elements of (non-)local operators

Given a general non-local operator $O(r, r')$.

Its matrix elements in the plane-wave basis read:

$$\tilde{O}(k + G, k + G') = \int dr \, dr' \, e^{i(k + G) \cdot r} \, O(r, r') \, e^{-i(k + G') \cdot r'}$$

If $O(r, r')$ is a local operator, then:

$$O(r, r') = O(r) \delta(r - r')$$

$$\tilde{O}(k + G, k + G') = \int dr \, dr' \, e^{i(k + G) \cdot r} \, O(r, r') \, e^{-i(k + G') \cdot r'}$$

$$= \int dr \, e^{i(G - G') \cdot r} \, O(r)$$

$$= \tilde{O}(G - G')$$
Kohn-Sham equations in plane wave basis

• Eigenvalue equation is now:

\[ \sum_{G'} H_{k+G,k+G'C_i,k+G'} = \varepsilon_i C_{i,k+G} \]

• Matrix elements are:

\[ \frac{1}{2}|k + G|^2 \delta_{G,G'} + V_{\text{ion}}(k + G, k + G') + V_H(G - G') + V_{\text{xc}}(G - G') \]

• Nuclear (→ ionic) potential given by:

\[ V_{\text{ion}}(G) = \sum_{\alpha} S_{\alpha}(G)v_{\alpha}(G); \quad S_{\alpha}(G) = \sum_{I} \exp(iG \cdot R_I) \]
Electrons experience a **Coulomb potential** due to the nuclei.

This has a known and simple form:

\[ V_{\text{nuc}} = -\frac{Z}{r} \]

But this leads to computational problems!
Electrons in Atoms

- Electrons in atoms are arranged in shells.

- **Quantum numbers**: $n$ [principal], $l$ [angular], $m_l$ [magnetic], $m_s$ [spin]

- **Rare gas atoms** have certain complete subshells (inert configurations):
  - He: $1s^2$  Ne: [He], $2s^2$, $2p^6$  Ar: [Ne] $3s^2$, $3p^6$
  - Kr: [Ar], $3d^{10}$, $4s^2$, $4p^6$  Xe: [Kr], $4d^{10}$, $5s^2$, $5p^6$
  - Rn: [Xe], $4f^{14}$, $5d^{10}$, $6s^2$, $6p^6$

- Can divide electrons in any atom into **core** and **valence**.

- This division is not always clear-cut, but usually **core** = rare gas configuration [+ filled d/f subshells]
Atomic Wavefunctions

• For hydrogenic atoms, recall:

\[ \psi_{lm}(r) = \psi_l(r)Y_{lm}(\theta, \phi) = r^{-\frac{1}{2}} \phi_l(r)Y_{lm}(\theta, \phi) \]

• Radial part & Angular Part.

• Being eigenfunctions of a Hermitian operator, \( \psi_{lm} \)'s are orthonormal.

• Wavefunctions with same \( n \), different \( l \) are orthogonal due to the nature of the angular part of the wavefunction.

• Wavefunctions with different \( n \), same \( l \) are orthogonal due to the nature of the radial part of the wavefunction.
Example: Wavefunctions for Ag atom

Ground state configuration: [Kr], 4d^{10}, 5s^{1}, 5p^{0}, 5d^{0}

- Core wavefunctions sharply peaked near nucleus.
- Valence wavefunctions peaked far away from nucleus, lots of wiggles near nucleus.
- 1s, 2p, 3d, 4f,… nodeless.
- Not immediately clear whether 4d should be considered core / valence?
Electrons in molecules/solids

- **Chemical bonds** between atoms are formed by sharing / transferring electrons.

- Only the **valence electrons** participate in bonding.

- **Wavefunctions of valence electrons** can change significantly once the bond is formed.

- e.g., when Ag is a constituent of a solid, the wavefunction may also acquire some $5p$ or $5d$ character?

- **Wavefunctions of core electrons** change only slightly when the bond is formed.
Problem for Plane-Wave Basis

Core wavefunctions: sharply peaked near nucleus.

Valence wavefunctions: lots of wiggles near nucleus.

High Fourier components present

i.e., need large $E_{cut}$ 😞
Solutions for Plane-Wave Basis

Core wavefunctions: sharply peaked near nucleus.

Valence wavefunctions: lots of wiggles near nucleus.

High Fourier components present
i.e., need large $E_{cut}$ 😞

Don’t solve for the core electrons!

Remove wiggles from valence electrons.
The Pseudopotential Approximation

- **Frozen core**: remove core-electron degrees of freedom i.e., NOT an “All-electron” calculation.

- Valence electrons see a *weaker potential* than the full Coulomb potential.

  \[ V_{\text{nuc}}(r) \rightarrow V_{\text{ion}}(r) \]

- Further tailor this potential so that wavefunctions behave ‘properly’ in region of interest, yet computationally cheap.
How the Pseudopotential Helps

(Numerical) Advantages when solving Kohn-Sham eqns.:

- When solving using a basis (especially plane waves), basis size drastically reduced (smaller matrices to diagonalize).
- Have to solve for fewer eigenvalues.
- No Coulomb singularity (cusp in wavefunction) at origin.

Disadvantages:

- Can lose accuracy.
An analogy!

• “Dummy cops” used by some law-enforcement agencies!

• Don’t care about internal structure as long as it works ~ right!

• But cheaper!!

• Obviously it can’t reproduce all the functions of a real cop, but should be convincing enough to produce desired results….
Wish List for a Good Pseudopotential

For accuracy:
• Should reproduce scattering properties of true potential.
• Transferable: Nice to have one pseudo-potential per element, to use in variety of chemical environments.
• Norm conserving? (will explain)
• Ab initio? (no fitting to experimental data)

For (computational) cheapness:
• Smooth / Soft: Need smaller basis set (esp. plane waves)
• ‘Separable’? (will skip!) but ‘Ghost free’ (should not introduce spurious states when making separable!)
Generating an *Ab Initio* Pseudopotential

• For the element of interest, pick a reference configuration.

• Perform an “all-electron” calculation for this reference configuration.

\[ \phi_{nl}^{AE}(r), \epsilon_{nl}^{AE} \]
All-Electron Wavefunction

all-electron wavefunction *(for some reference configuration)*

\[ \phi_l(r) \]

Pick core radius \( r_c \)
Pseudowavefunction Outside $r_c$

- Pseudowavefunction & all-electron wavefunction are identical outside cut-off radius $r_c$

\[ \phi_{l,ref}^{AE}(r) = \phi_{l,ref}^{PS}(r) \quad r \geq r_c \]
Pseudowavefunction

all-electron wavefunction

\( \phi_l(r) \)

Choose to get desired properties

\( \phi_l^{PS}(r) = f(r) \)

\( r \rightarrow \)
Norm-Conservation

- Norm conservation:
  \[ \int_{0}^{r_c} \phi^{AE}_l(r) \phi^{AE}_l(r) dr = \int_{0}^{r_c} \phi^{PS}_l(r) \phi^{PS}_l(r) dr \]

- Imposing **norm conservation** improves transferability!
  
  *(Hamann, Schlüter, Chiang, 1979)*
Pseudowavefunction $\rightarrow$ Pseudopotential

• Invert the radial Schrödinger equation to get a “screened” potential for each $l$, $V_{l}^{\text{scr}}(r)$

• This “screened” potential includes Hartree and XC contributions; “unscreen” to get pseudopotential.

\[
V_{l}^{PS}(r) = V_{l}^{\text{scr}}(r) - V_{H}[\rho^{\text{val}}(r)] - V_{XC}[\rho^{\text{val}}(r)]
\]
What does a pseudopotential look like?

Example for Mo:

- Weaker than full Coulomb potential
- No singularity at $r=0$
- Different pseudopotential for each $l$ (example of semilocal pseudopotential)
- Will be $V_{ion}$ (replacing nuclear potential)

Dealing with the non-locality

\[ V_{ps} = V_{loc} + \sum_{l} \sum_{m=-l}^{l} |lm\rangle \delta V_l \langle lm| \]

This non-local operator has \((N_{pw})^2\) matrix elements (must be avoided!)

Solution: Kleinman-Bylander representation

\[ V_{ps} = V_{loc} + \sum_{lm} \frac{|\delta V_l \psi_{lm}\rangle \langle \psi_{lm} \delta V_l|}{\langle \psi_{lm} | \delta V_l | \psi_{lm}\rangle} \]

\(\psi_{lm}\) is an eigenstate of the pseudo-Hamiltonian, acting as reference state.
Some Popular Pseudopotentials: BHS

• “Pseudopotentials that work: from H to Pu”
• *Ab initio, norm conserving*, so good transferability (?)
• *Semilocal* $V_l(r)$ [local in radial coordinates, nonlocal in angular coordinates]
• *Parametrized form*: chosen to give nice analytical expressions with many basis sets, 9 parameters, tabulated for all elements.
• *Non-linear fitting procedure*, caution needed!
• *Fairly hard* pseudopotentials since smoothness not built in explicitly, frequently need *high cut-off*. 
How to Make Softer?

• Increase radial cut-off $r_c$?? Softer, but transferability suffers.

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Soft / Smooth Pseudopotentials

• Want to lower $E_{cut}$ (cut-off for plane wave basis).

• Various strategies:
  - Optimize so as to minimize error in KE introduced by truncating basis (Rappe, Rabe, Kaxiras & Joannopoulos, [RRKJ] 1990)
  - Make smooth near origin (Troullier & Martins, 1991)

• Cut-offs lowered considerably, but still higher than we would like, especially for
  > first row elements (1s, 2p nodeless)
  > transition metals (3d nodeless)
  > rare-earths (4f nodeless)
Need lower $E_{\text{cut}}$ with soft pseudopotentials

e.g. Cu: localized d orbitals $\rightarrow$
high cut-off needed with BHS pseudopotential

Troullier-Martins

RRKJ

FIG. 8. The calculated total energy of fcc Cu plotted against the cutoff energy of the plane-wave basis set for the four pseudopotentials shown in Fig. 7. The total energy for all four curves are referenced to the total energy calculated at a cutoff energy of 225 Ry. The squares, circles, and triangles are the calculated data points and the curves are obtained from a spline interpolation.

FIG. 3. Atomic (solid lines) and fcc solid (dots) total energies as a function of cutoff energy for copper in the HSC and present approaches. The zero of atomic total energy for each pseudopotential was chosen to be the total atomic energy at a cutoff energy of 324 Ry. The zero of solid total energy was chosen for each pseudopotential so that the atomic and solid total energies coincide at a cutoff energy of 80 Ry.
Nodeless Wavefunctions & Norm Conservation

Cut-offs still higher than we would like, especially for
  > first row elements (1s, 2p nodeless)
  > transition metals (3d nodeless)
  > rare-earths (4f nodeless)

This is because of the constraint of norm conservation...

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Ultrasoft Pseudopotentials

- Do away with norm conservation!!
- Can make $\psi_{PS}$ extremely soft!
- Drastically reduces $E_{cut}$, especially for “difficult” elements.
- New separable form.
- Choose multiple energy references (to improve transferability).
POPULAR Pseudopotentials!


Transferability

• Condition that pseudoatom reproduces behavior of all-electron atom in wide variety of chemical environments.

• Recall, pseudopotential derived for reference config. (atom with given occ of levels), using ref eigenvalue.
• When eigenvalue changes from reference one:
  - do scattering properties of potential change correctly? (Looking at log derivatives)
• When the filling changes:
  - do eigenvalues shift correctly? (Looking at chemical hardness)
  - do scattering properties change correctly?
Transferability: log derivatives

- Log derivatives guaranteed to match at reference energy, check how log derivatives change with energy.

Log derivatives don’t match ☹

Ag

Has ghost ☹
Transferability: Occupation Changes

See how eigenvalues change with occupation

Chemical Hardness matrix: \( \eta_{ij} = \frac{1}{2} \frac{\partial \epsilon_i}{\partial f_j} \) [Teter, 1993].

See how 'tail norms' \( N_i = \int_{r_c}^{\infty} |\phi_i|^2 dr \) change with occupation: \( \frac{\partial N_i}{\partial f_j} \) should be reproduced

e.g.: check transferability of a pseudopotential for Ag with 4d in core:
Non-Linear Core Correction

Working only with $\rho^{\text{val}}$ corresponds to linearizing the XC potential, but $V_{XC}(\rho^{\text{val}}+\rho^{\text{core}}) \neq V_{XC}(\rho^{\text{val}})+V_{xc}(\rho^{\text{core}})$

This is particularly a problem when there is significant overlap between $\rho^{\text{val}}$ and $\rho^{\text{core}}$


- When unscreening, subtract out $V_{H}(\rho^{\text{val}})$ and $V_{XC}(\rho^{\text{val}}+\rho^{\text{core}})$
- Store $\rho^{\text{core}}$ from atomic calculation
- Use $V_{XC}(\rho^{\text{val}}+\rho^{\text{core}})$ in all calculations
- Okay to just use partial $\rho^{\text{core}}$ (in region of overlap)
Recall (from a quantum mechanics course?):

- Scattering properties of a potential described by phase shift $\eta_l$.
- Related to logarithmic derivatives: [see, e.g. Eq. J.6, Martin]

$$D_i(\epsilon, r) = r \frac{d}{dr} \ln \psi_l(\epsilon, r) = r \frac{d}{dr} \ln \left( \frac{\phi_l(\epsilon, r)}{r} \right)$$

- Weaker potentials will have fewer bound states.
- In the pseudopotential approximation: want to make the potential weak enough that the valence electron is the lowest bound state (with that $l$), while reproducing log derivatives to the extent possible....
Extra Stuff: Norm Conservation & Transferability

• By construction, log derivatives satisfy:

\[ D_l^{AE}(\epsilon, r_c) = D_l^{PS}(\epsilon, r_c) \]

• In addition, if we impose norm conservation:

\[ \int_0^{r_c} \phi^{*AE}(r)\phi^{AE}(r)dr = \int_0^{r_c} \phi^{*PS}(r)\phi^{PS}(r)dr \]

then from the identity (see e.g. pg. 214 of Martin for derivation):

\[ \frac{\partial}{\partial \epsilon} D_l(\epsilon, r_c) = -\frac{r_c}{|\phi_l(r_c)|^2} \int_0^{r_c} dr |\phi_l(r_c)|^2 \]

we have*

\[ \frac{\partial}{\partial \epsilon} D_l^{AE}(\epsilon, r_c) = \frac{\partial}{\partial \epsilon} D_l^{PS}(\epsilon, r_c) \]

i.e., if energy is shifted slightly from that of reference eigenvalue, log derivatives ~ unchanged →

improved transferability!

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* Hamann, Schlüter, & Chiang, PRL 43, 1494 (1979)
Terminology: Local, Semilocal, Separable, etc.

Local PSP

\[ \hat{V}_{ps} = V_{ps}(r) \quad \text{(local in } r, \theta, \phi) \]

Semilocal PSP

\[ \hat{V}_{ps} = \sum_{l} V^{(l)}_{ps}(r) \hat{P}_l \quad \text{(local in } r, \text{ nonlocal in } \theta, \phi) \]

Nonlocal separable PSP (e.g., Kleinman-Bylander)

\[ \hat{V}_{ps} = V^\text{loc}_{ps}(r) + \sum_{l,m} D_l \left| \beta_{lm} \right\rangle \left\langle \beta_{lm} \right| \]

General nonlocal separable PSP

\[ \hat{V}_{ps} = V^\text{loc}_{ps}(r) + \sum_{\tau} \sum_{l,m} D_{\tau \tau'} \left| \beta_{\tau lm} \right\rangle \left\langle \beta_{\tau' l} \right| \]

(Note: All are spherically symmetric.)

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Extra Stuff: Relativistic Pseudopotentials

- Do all-electron calculation on free atom using Dirac equation
- Obtain $\psi_{nlj}(r)$ for $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$
- Invert Schrödinger equation to get $V_{lj}^{ps}(r)$
- For “scalar relativistic” target calc., use $j$-averaged PSPs:
  \[
  V_{l}^{ps}(r) = \frac{1}{2l + 1} \left[ (l + 1) V_{l,l+\frac{1}{2}}^{ps} + l V_{l,l-\frac{1}{2}}^{ps} \right]
  \]
- For spin-orbit interactions, keep also
  \[
  V_{l}^{so}(r) = \frac{1}{2l + 1} \left[ V_{l,l+\frac{1}{2}}^{ps} - V_{l,l-\frac{1}{2}}^{ps} \right]
  \]
  and use, schematically speaking,
  \[
  \hat{V}_p = \sum_l |l\rangle \left[ V_{l}^{ps}(r) + V_{l}^{so}(r) \mathbf{L} \cdot \mathbf{S} \right] \langle l |
  \]

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