Planewaves and Pseudopotentials

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The Kohn-Sham Equations

- Since pseudopotentials aid in the calculation of the potential between the nuclei and electrons, a decent place to start is by reciting the Kohn-Sham equations:[1]

$$-\frac{1}{2}\nabla^2\varphi_i(\mathbf{r}) + V_{\text{tot}}(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}),$$

$$V_{\text{tot}}(\mathbf{r}) = V_{\text{n}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$V_{\text{n}}(\mathbf{r}) = -\sum_I Z_I/|\mathbf{r} - \mathbf{R}_I|$$

$$V_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n\Big|_{n(\mathbf{r})}$$

$$\nabla^2 V_{\text{H}} = -4\pi n(\mathbf{r}); \quad n(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2 \, ;$$

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \cdots & \varphi_1(\mathbf{r}_N) \\ \vdots & \ddots & \vdots \\ \varphi_N(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix}$$

1. Note: the variables of the single-particle wavefunction are position and spin. Here, only position has been explicitly considered for simplicity. Also, $N!^{-1/2}$ is a normalization factor which ensures $\int |\Psi|^2 \, d\mathbf{r}_1 \cdots \mathbf{r}_N = 1$.

- One way of solving the Kohn-Sham equations is by representing the wavefunctions as a Fourier series and solving for the Fourier coefficients.[2]

- To justify this, consider a unit cell described by the three vectors $\mathbf{a}_1, \mathbf{a}_2$ and $\mathbf{a}_3$ with the volume given by the triple product,

$$\Omega = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|,$$

and these vectors define a lattice in *real* (*direct*) space by rigid, integral translations:

$$\mathbf{T} = N_1 \mathbf{a}_1 + N_2 \mathbf{a}_2 + N_3 \mathbf{a}_3$$

- Thus, the box used when performing a DFT calculation may be the primitive unit cell of a crystal or a supercell containing a sufficient number of independent atoms to mimic locally an amorphous solid or liquid phase.[3]

- From this, both the potential and electron density are periodic:

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r}); \quad V_{\text{tot}}(\mathbf{r} + \mathbf{T}) = V_{\text{tot}}(\mathbf{r}),$$

suggesting that the properties of the system may be described by a Fourier analysis…

2. This approach is particularly suited to periodic boundary conditions and the strategy used most often in solid-state/condensed-matter physics.
3. It is essential to make the supercells large enough to prevent the defects, surfaces or molecules in neighbouring cells from interacting appreciably with each other.

The Reciprocal Lattice

- The Fourier transforms for the density and potential in three-dimensions is:

$$n(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}\tilde{n}_{\mathbf{G}}; \quad \tilde{n}_{\mathbf{G}} = \frac{1}{\Omega}\int_{\Omega} d\mathbf{r}\, n(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}$$

$$V_{\text{tot}}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}\tilde{V}_{\text{tot}}(\mathbf{G}); \quad \tilde{V}_{\text{tot}}(\mathbf{G}) = \frac{1}{\Omega}\int_{\Omega} d\mathbf{r}\, V_{\text{tot}}(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}},$$

and the reciprocal lattice as the set of all vectors $\mathbf{G}$ given by,

$$\mathbf{G} = M_1\mathbf{b}_1 + M_2\mathbf{b}_2 + M_3\mathbf{b}_3$$

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}; \quad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}; \quad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

Bloch Theorem

- The *Bloch theorem*:

  Single-particle electronic wavefunctions in a periodic potential may be expressed as the product of a function periodic in the unit cell and a plane wave. That is,

$$\varphi_i(\mathbf{r}) \rightarrow \varphi_{i\mathbf{k}}(\mathbf{r}) = u_{i\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}},$$

$$u_{i\mathbf{k}}(\mathbf{r} + \mathbf{T}) = u_{i\mathbf{k}}(\mathbf{r})$$

  and eigenvalues corresponding to wavevectors $\mathbf{k}$ *and* $\mathbf{k} + \mathbf{G}$ *coincide.*

So, plane waves...

- Since the function $u_{i\mathbf{k}}$ is periodic, the wavefunction may be represented as a linear combination of plane waves:

$$u_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$
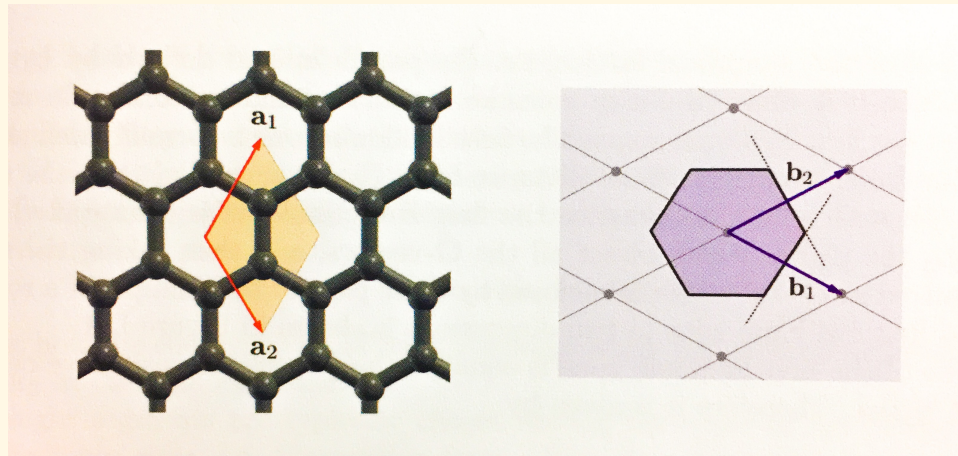
$$\implies \varphi_i = \sum_{\mathbf{G}} c_{i\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

so the energy bands in a crystal lattice are *periodic functions in reciprocal space* and we want to solve for the coefficients $c_{i\mathbf{k}}(\mathbf{G})$:[4]

$$\sum_{\mathbf{G}'} \left(\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + \tilde{V}_{\text{tot}}(\mathbf{G}-\mathbf{G}') \right) c_{i,\mathbf{k}+\mathbf{G}'} = \varepsilon_i c_{i,\mathbf{k}+\mathbf{G}}$$

4. Note that the i in $c_{i\mathbf{k}}$ represents the band index, where that in $e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$ represents the complex part of the exponential.

- Owing to this property, it is natural to study the band structure within one unit cell of the reciprocal lattice.

- In practice, $\mathbf{k}$-vectors inside a volume of reciprocal space called the *first Brillouin zone* (1BZ) is considered

  - The 1BZ is formally defined as the volume containing $\mathbf{k}$-vectors whose distance from $\mathbf{G} = 0$ is smaller than the distance from any other $\mathbf{G}$-vector.[4]
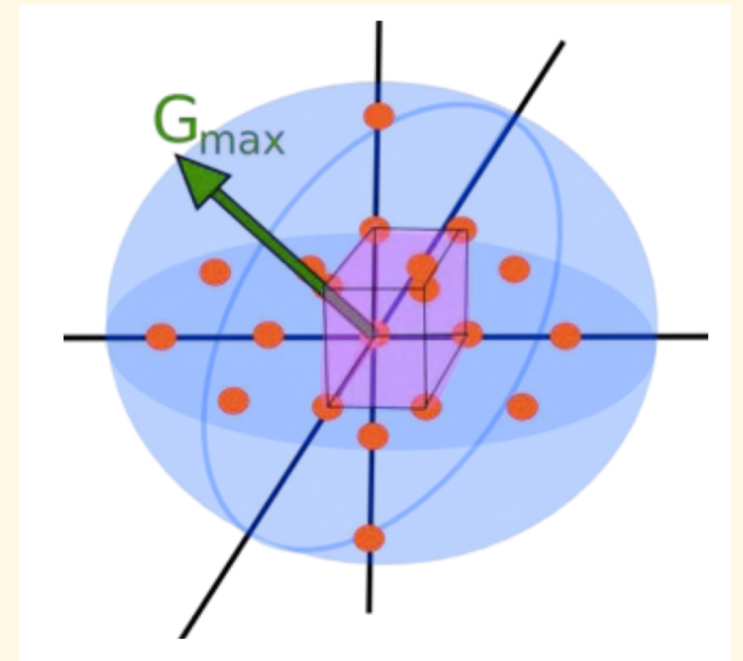

4. In practice, the 1BZ is constructed by first determining the plane waves which bisect all $\mathbf{G}$-vectors, and then taking the smallest volume centred at $\mathbf{G} = 0$ which is enclosed by these planes.

- Plane waves forming the basis set (i.e. the basis set size) are traditionally specified by one single parameter: the *kinetic energy cutoff*
  - This is the quantum mechanical kinetic energy associated with the planewave having the largest **G**-vector:

$$E_{\text{cut}} = \frac{|\mathbf{G}_{\text{max}}|^2}{2}$$

- Those reciprocal lattice vectors with a kinetic energy less than the cut-off are kept in the expansion; the remaining coefficients are set to zero.

- The volume of the 1BZ is given by

$$\Omega_{\text{BZ}} = |\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3| = \frac{(2\pi)^3}{\Omega}$$

- The volume occupied by a single plane is the same as that of the 1BZ, and noting that the volume of the sphere containing all plane waves is,

$$V_{sphere} = \frac{4}{3}\pi|\mathbf{G}_{\text{max}}|^3$$

  we see that the number of plane waves in the basis set is,

$$N_{\text{pw}} = \frac{1}{2\pi^2}\Omega E_{\text{cut}}^{3/2}$$

- Thus, we see that the basis size depends only on the volume of the box and the kinetic energy cutoff.

Discretisation of *k*-Space

- Each electron occupies a state of definite **k**, and the infinite number of electrons in a solid gives rise to an infinite number of *k*-points.

- But, at each *k*-point only a finite number of the available energy levels will be occupied.

- So, we only need to consider a finite number of electrons at an infinite number of *k*-points…

- Also, electron wavefunctions will be very similar for values of **k** that are sufficiently close, and we may represent the wavefunctions over a region of reciprocal space by considering the wavefunction at a single *k*-point.

- Net effect while also taking into account Bloch's theorem:
  - Infinite crystal → 1BZ
  - Infinite number of electrons → finite number of electrons (only those in the 1BZ)
  - Infinite number of k-points → finite number of k-points chosen to appropriately sample the 1BZ

- Then, integrated functions may be written as sums, e.g.

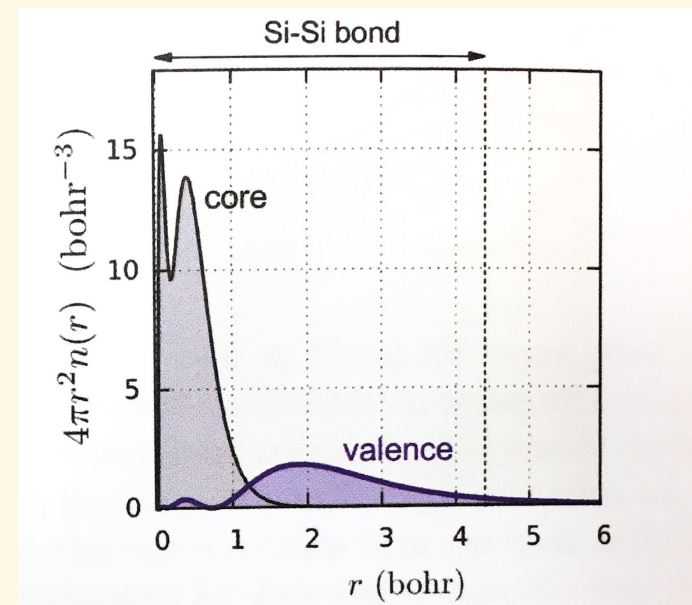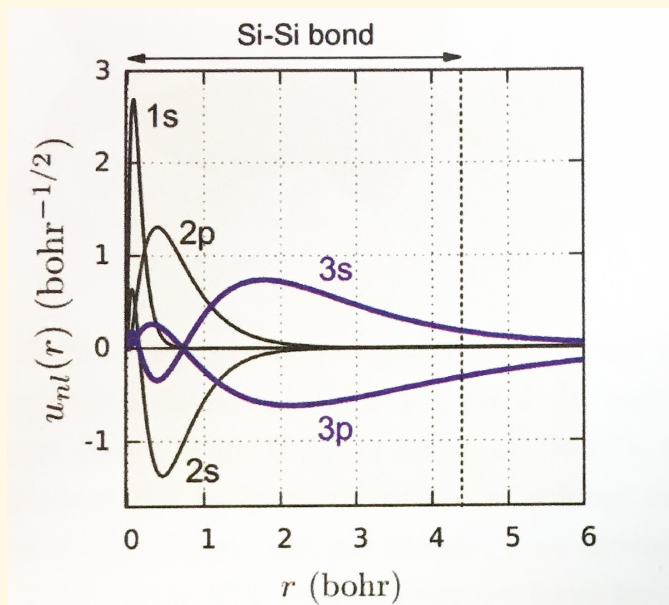$$n(\mathbf{r}) = \frac{1}{N_{kp}} \sum_{\mathbf{k},n} f(\mathbf{k},n) \left| \varphi_{\mathbf{k},n}(\mathbf{r}) \right|^2$$

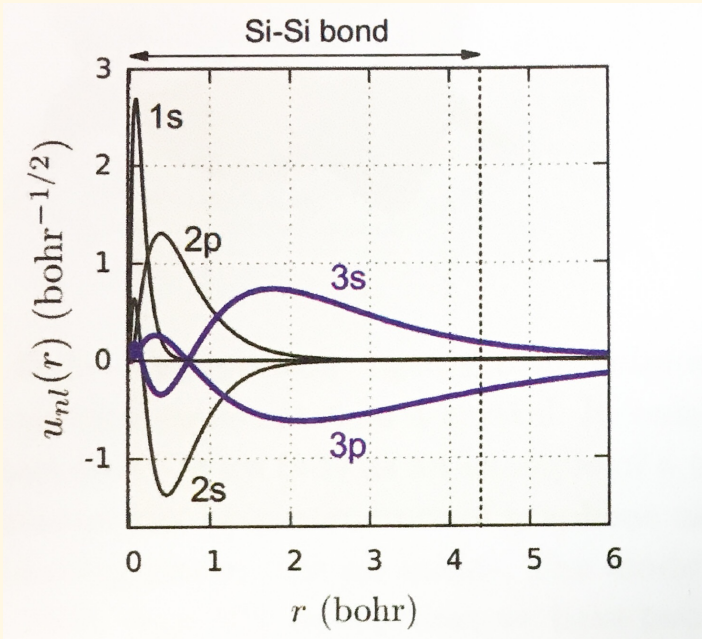No. of k-points

Occupation number

Pseudopotentials

- Valence electrons are the most sensitive to changes in chemical bonding environment, while the core electrons (located near the Coulomb singularity) will be relatively immune to such changes (we say they are *chemically inert*).

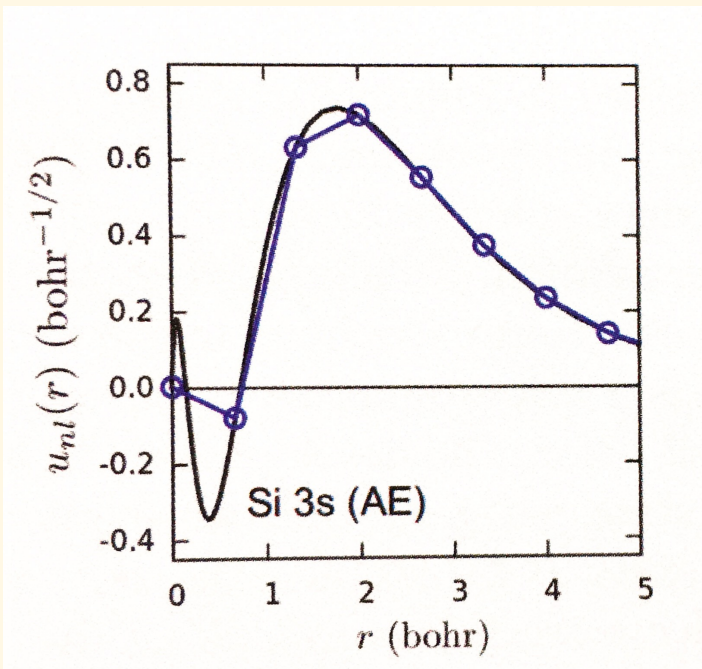- For example, consider the Kohn-Sham electron wavefunctions of an isolated Si atom…

- 1s, 2s and 2p are core states (black curves), while the 3s and 3p are valence states (purple curves).
- From the electronic densities, core electrons are tightly bound to the Si nucleus, while the valence electrons tend to localise further away.
- Also, core densities are negligible where the valence densities are large (and vice versa)

$$\psi_{nl}(\mathbf{r}) = r^{-1}u_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$$

- So, if the core is to be held frozen, there is not much point in describing the Kohn-Sham wavefunctions of these states.

- Then, we want to remove entirely the core electrons.

- This substantially reduces computational cost:
  - E.g. in the case on tungsten, only 6 valence electrons are described of the 74 total.

- But which wavefunctions are 'core' and which are 'valence' states?
  - Rule of thumb is that the 'valence' is the outermost shell of the free atom in the periodic table (tungsten $6s^25d^4$)
  - Note, however, in some cases one may need to consider more electronic states in the 'valence' electrons.
    - E.g. in bismuth, the $6s^26p^3$ and the 'semi-core' $5d^{10}$ should be considered equally.

- So, in practice, distinction between core and valence wavefunctions is not strict
  - If in doubt, consult the spatial distribution of the atomic wavefunctions as in the plots on the previous slide for Si.
  - It is possible, also, that the energy changes in bonding mean that more electrons should be considered than originally presumed. So it may be worthwhile studying spectroscopic data and/or computed MO diagrams (see the idea of *transferability* later).
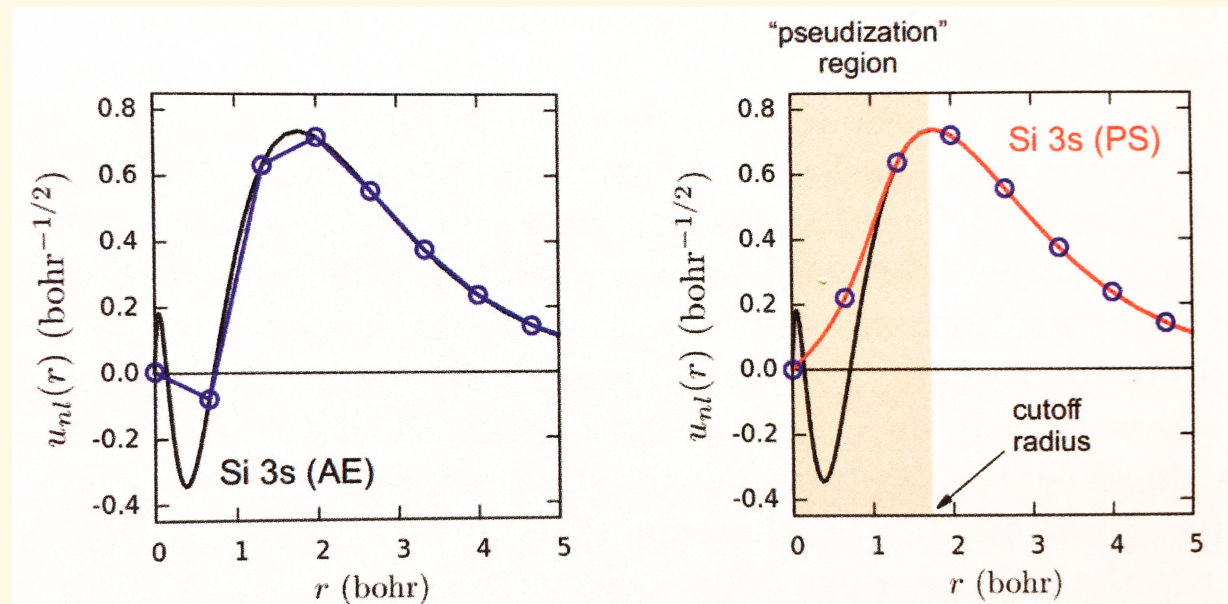
- Near the nucleus the valence electronic wavefunctions must change sign in order to be orthogonal to the core states.

- E.g. here, the 2s state has a node in the region where the 1s state is localised, and the 3s state has two nodes so that the overlap integrals with the 1s and 2s states vanish.

- So, the core states cannot simply be ignored since the valence electrons must exhibit the correct nodal behaviour near the nucleus.

- Also, even if correct oscillating features in the wavefunctions were obtained, these would be very difficult to describe using a real-space grid or a planewaves basis.

- To illustrate, here is how the nodal structure of the 3s state of Si would appear if the function was sampled only at a small number of evenly spaced points (large basis set so computationally expensive).

- Here, the description of the oscillations is very poor, reducing accuracy and numerical stability.
- Using a finer real-space grid or a higher kinetic energy cutoff would result in time-consuming calculations.
- Try removing the nodal structure altogether…
- That is, to replace the oscillating part of a valence wavefunction by a *smooth and nodeless curve*…

- To do this:

  1. Calculate the Kohn-sham 'all-electron wavefunction.'

  2. Decide on a radial cutoff, r_c; that is, the radius which sets the boundary of the region where the wavefunction is to be modified.

  3. At $r < r_c$ (the pseudisation region), replace the all-electron wavefunction by a smooth and nodeless function (e.g. a simple polynomial).

  4. This new function is chosen so as to yield the same electron density as the all-electron function for $0 < r < r_c$, and to have the same value at $r = r_c$.

- Then we get the 'pseudo-wavefunction'
- Now, how do we obtain this smooth pseudo-wavefunction by solving the KS equations?...

- The pseudopotential method is based on the strategy that a modified nuclear potential is constructed, which obeys the conditions:

    1. Outside the pseudisation region, the modified potential coincides with the original KS potential (from an all-electron calculation).

    2. When $r < r_c$, the potential is modified in such a way that the solution of the KS equation yields the pseudo-wavefunction.

- As a simplified example, consider the Si 3s wavefunction, which we will denote $\psi_{3s}^{\text{AE}}(\mathbf{r})$ (spherical coordinate system):

$$\psi_{3s}^{\text{AE}}(\mathbf{r}) = \frac{1}{r} u_{3s}^{\text{AE}}(r) Y_{00}(\hat{\mathbf{r}})$$

1. Find u_{3s}^{AE}:

Total potential felt
by KS electrons

Solution of the radial
KS equation

$$-\frac{1}{2}\frac{d^2}{dr^2}u_{3s}^{AE}(r) + V^{AE}(r)u_{3s}^{AE}(r) = E_{3s}u_{3s}^{AE}(r)$$
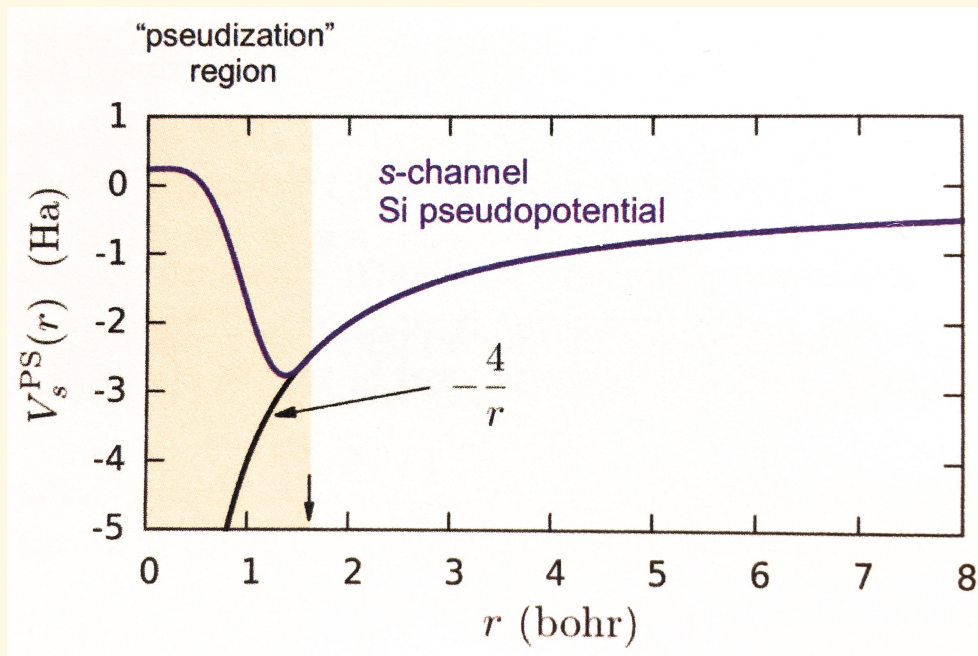
2. Find pseuopotential (pseudo-wavefunction known by smoothing u_{3s}^{AE} at $r < r_c$):

$$-\frac{1}{2}\frac{d^2}{dr^2}u_{3s}^{PS}(r) + V_{3s}^{PS}(r)u_{3s}^{PS}(r) = E_{3s}u_{3s}^{PS}(r)$$

$$\Rightarrow V_{3s}^{PS} = E_{3s} + \frac{1}{2u_{3s}^{PS}}\frac{d^2u_{3s}^{PS}}{dr^2}$$

- Using this pseudopotential gives a pseudo-wavefunction which is smoothed at $r < r_c$ and gives the same KS eigenvalue as in the original all-electron wavefunction.

- Note that for $r > r_c$, we have $u_{3s}^{PS} = u_{3s}^{AE}$ and $V_{3s}^{PS} = V_{3s}^{AE}$

- Usually, in actual calculations, more than just the 3s state must be considered since these will also be involved in bonding.
- That is, the pseudopotential must be *transferable*.
  - Achieved by removing by removing the electronic contributions from V_H and V_{xc}, which are specific to particular electronic configurations, while keeping the modified nuclear potential.
  - This gives the *ionic pseudopotential*…

$$V^{PS}(r) = -\frac{Z_v}{r} \qquad (r > r_c)$$

- Note, Z_v is the number of valence electrons and not the nuclear charge.

- Now, the singularity at $r = 0$ is removed and the potential resembles that of a potential well in the pseudisation region.

Norm-Conservation

- To begin, let's list the requirements for a "good" *ab initio* pseudopotential:

   1. All-electron and pseudo-wavefunctions eigenvalues agree for the chosen atomic reference configuration.

   2. All-electron and pseudo-wavefunctions agree beyond a chosen core radius, r_c.

   3. The logarithmic derivatives of the all-electron and pseudo-wavefunctions agree at r_c.

   4. The integrated charge inside r_c for each wavefunction agrees (**norm-conservation**).

   5. The *first energy derivative* of the logarithmic derivatives of the all-electron and pseudo-wavefunction agree at r_c.

- Points 1 and 2 have already been considered.
- Point 3 follows since the wavefunction $\psi_l(r)$ and its radial derivative $\psi_l'(r)$ are continuous at r_c for any smooth potential.
  - The dimensionless logarithmic derivative is defined by:

$$D_l(r) \equiv r\, u_l'(r)/u_l(r) = r\frac{\mathrm{d}}{\mathrm{d}r}\ln u_l(r)$$

- For $r < r_c$ the pseudopotential and pseudo-wavefunction differ from their all-electron counterparts.

  - However, point 4 requires that the integrated charge,

$$Q_l = \int_0^{r_c} \mathrm{d}r\, r^2 \left|u_l^{\mathrm{PS}}(r)\right|^2 = \int_0^{r_c} \mathrm{d}r\, r^2 \left|u_l^{\mathrm{AE}}(r)\right|^2$$

  is the same for u_l^{PS} as for the all-electron radial orbital u_l^{AE} for a valence state in the core region.

  - This conservation of Q_l ensures that the total charge in the core region is correct, and the normalized pseudo-wavefunction equals the true orbital at $r > r_c$.

- Applied to a molecule or solid, these conditions ensure that the normalized pseudo-wavefunction and potential are correct in the region $r > r_c$, where bonding occurs.

5. The *first energy derivative* of the logarithmic derivatives of the all-electron and pseudo-wavefunction agree at r_c.

- This is the crucial point which greatly increases the transferability of the pseudopotential
- This reproduces the changes in eigenvalue to linear first-order
- It was shown by Hamann *et al.* (1979)[5] that point 4 (norm-conservation) implies point 5.
- The final relation is,

$$2\pi \left[r u_l^2(r) \frac{\partial}{\partial \varepsilon} D_l(\varepsilon, r) \right]_{r=r_c} = 4\pi \int_0^{r_c} dr \, r^2 u_l^2(r)$$

- So, if u_l^{PS} has the same magnitude as u_l^{AE} at r_c and obeys norm-conservation, then the first energy derivative of the logarithmic derivative is the same for the pseudo- and all-electron wavefunction.

5. D. R. Hamann, M. Schülter, and C. Chiang, "Norm-conserving pseudopotentials," *Phys. Rev. Lett.* 43:1494–1497, 1979.
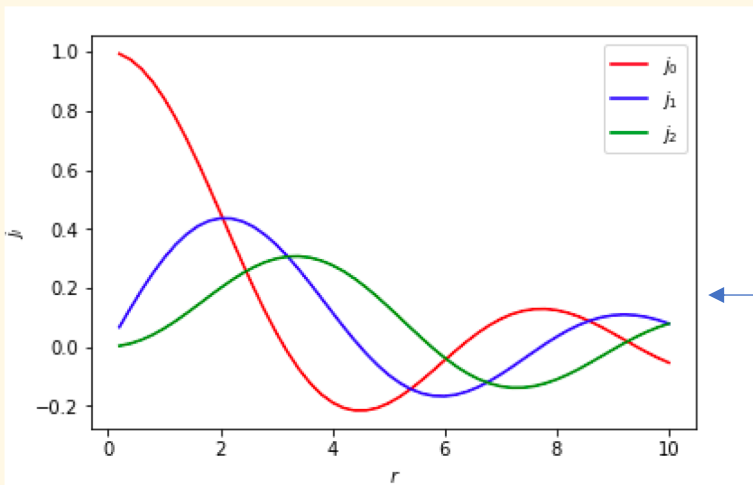
So?...

- So, we know from scattering theory that an incoming plane wave with wave vector $\mathbf{k}$ to be scattered from a spherically symmetric potential (within a radius r_c and centred at the origin) may be decomposed into partial waves with the identity:

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y_{lm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}})$$
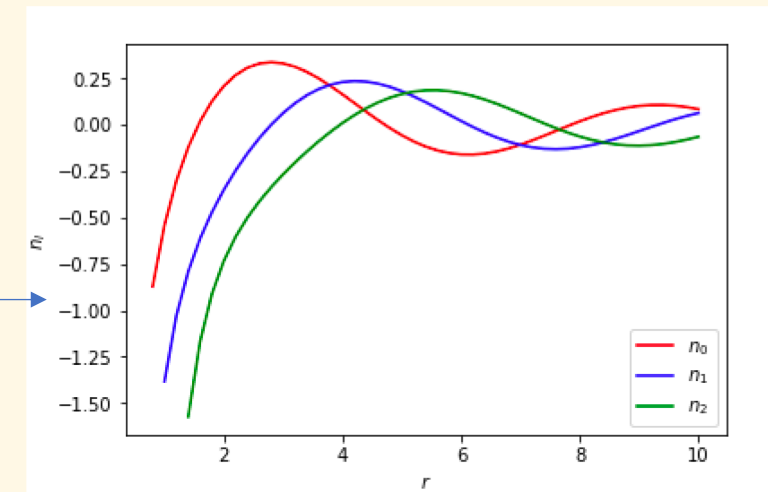
- These spherical waves are then elastically scattered by the potential, introducing a phase-shift δ_l, related to $D_l(r)$ by:

$$\frac{u_l'(r_c)}{u_l(r_c)} = k \frac{j_l'(kr_c) - \tan(\delta_l) n_l'(kr_c)}{j_l(kr_c) - \tan(\delta_l) n_l(kr_c)} = \frac{1}{r_c} D_l(r_c)$$

Spherical Bessel function

von Neumann function

- Then, if the pseudopotential is norm-conserving and $u_l^{\mathrm{PS}} = u_l^{\mathrm{AE}}$ at $r = r_c$,

  - The first energy derivative of the log derivative is the same for both wavefunctions,

  - The norm-conserving pseudopotential has the same scattering phase shifts as the all-electron atom to linear order in energy around the chosen energy ε_l,

  - And, therefore, u_l^{PS} has the same scattering properties as u_l^{AE}.

And finally...

- Define the reduced phase-shift η_l by,

$$\delta_l = n_l \pi + \eta_l$$

- The scattering amplitude is dependent on $\exp(2i\delta_l)$, so the factors of π in δ_l have no effect
- n_l fixed by requiring η_l to be in the interval $0 \leq \eta_l \leq \pi$
- n_l counts the number of radial nodes in $u_l(r)$ (equal to the number of core states with angular momentum l)
- The pseudopotential is then defined as the potential whose complete phase shifts are the reduced phase shifts, so the radial pseudo-wavefunction has no nodes and, thus, the potential has no core states.
  - The scattering effect of this potential is the same as for the original potential.
- Note again the energy-dependence of the phase-shifts.
  - Necessary to match the phase-shifts to first-order in the energy over a range of energies (good transferability)

```
[KBdesign]
s     # local orbital
1     # number of boxes
au 0.1 1.60   0.001
```

Kleinman-Bylander representation (see later talks)

```
[loginfo]
0
1.90 −10 5
END COMMENT
 3 5
        100.00000000
        127.9972203478   −289394.1894188060    −72252.5832274149
     −32041.2147029790    −17967.2829763957    −11453.1149536131
      −7914.6094510304     −5781.0593706204     −4396.3621045706
      −3447.0782846965     −2768.1222081501     −2265.8333287659
      −1883.8638873322     −1586.6647698582     −1350.9096675068
      −1160.7780658273     −1005.2330762906      −876.3851339492
       −768.4733324577      −677.2116447282      −599.3579546141
       −532.4231603314      −474.4706369804      −423.9753484236
       −379.7231605049      −340.7377608060      −306.2268614457
       −275.5420818611      −248.1486757241      −223.6024350737
       −201.5318908719      −181.6244660302      −163.6156087826
       −147.2801952234      −132.4256752049      −118.8865689874
       −106.5200187767       −95.2021702404       −84.8252116372
```

Configuration no. used to plot log. derivatives (0 means reference state)

Radius, min energy, max energy

Thank you.