# Introduction to Computational Materials Science and Materials Data Science (590400)

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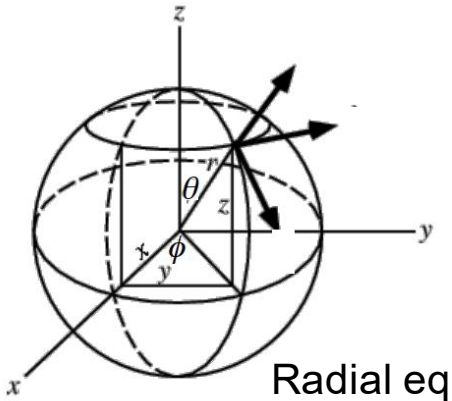
# Solving Schrödinger equation for hydrogen atom




In spherical coordinate system

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi(r,\theta,\phi)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\psi(r,\theta,\phi)+$$
$$\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi(r,\theta,\phi)-\frac{2m}{\hbar^2}\Big[V(r)-E\Big]\psi(r,\theta,\phi)=0$$

$$\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$$

Radial equation:
$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)-\frac{2mr^2}{\hbar}\Big[V(r)-E\Big]=l(l+1)$$

Angular equation:
$$\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi)=-l(l+1)$$

Azimuthal:
$$\frac{1}{g(\phi)}\frac{d^2}{dr^2}g(\phi)=-m^2$$

Polar:
$$\frac{\sin\theta}{f(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)f(\theta)+l(l+1)\sin^2\theta=m^2$$

$$Y_{l,m}(\theta,\phi)=(-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}P_{l,m}(\cos\theta)e^{im\phi}$$

https://en.wikipedia.org/wiki/Associated_Legendre_polynomials

Radial equation:

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2mr^2}{\hbar}\Big[V(r) - E\Big] = l(l+1)$$

Solution of radial equation:

$$R_{n,l}(r) = \sqrt{\left(\frac{2}{a_0 n}\right)^3 \frac{(n-l-1)!}{2n\big[(n+l)!\big]^3}} \cdot e^{-r/a_0 n}\left(\frac{2r}{a_0 n}\right)^l \cdot L_{n-l-1}^{2l+1}\left(\frac{2r}{a_o n}\right)$$

Associated Laguerre polynomials

# Quantum numbers

**Table 3.2** The quantum number $n$, $\ell$, and $m_\ell$

| | |
|---|---|
| Principal quantum number | $n = 1, 2, 3, \ldots$ |
| Orbital angular momentum quantum number | $\ell = 0, 1, 2, \ldots, (n-1) < n$ |
| Magnetic quantum number | $m_\ell = -\ell, -(\ell-1), \ldots, 0, \ldots, (\ell-1), \ell$ or $\lvert m_\ell \rvert \leq \ell$ |

**Table 2.1** Summary of the Relationships among the Quantum Numbers $n$, $l$, $m_l$ and Numbers of Orbitals and Electrons

| *Value of n* | *Value of l* | *Values of $m_l$* | *Subshell* | *Number of Orbitals* | *Number of Electrons* |
|---|---|---|---|---|---|
| 1 | 0 | 0 | 1*s* | 1 | 2 |
| 2 | 0 | 0 | 2*s* | 1 | 2 |
| | 1 | −1, 0, +1 | 2*p* | 3 | 6 |
| 3 | 0 | 0 | 3*s* | 1 | 2 |
| | 1 | −1, 0, +1 | 3*p* | 3 | 6 |
| | 2 | −2, −1, 0, +1, +2 | 3*d* | 5 | 10 |
| 4 | 0 | 0 | 4*s* | 1 | 2 |
| | 1 | −1, 0, +1 | 4*p* | 3 | 6 |
| | 2 | −2, −1, 0, +1, +2 | 4*d* | 5 | 10 |
| | 3 | −3, −2, −1, 0, +1, +2, +3 | 4*f* | 7 | 14 |

**Source:** From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes,* 4th edition. Reprinted with permission of John Wiley & Sons, Inc.

**Table 3.4** The radial and spherical harmonic parts of the wavefunction in the hydrogen atom ($a_o$ = 0.0529 nm)

| $n$ | $\ell$ | $R(r)$ | $m_\ell$ | $Y(\theta, \phi)$ | |
|---|---|---|---|---|---|
| 1 | 0 | $\left(\frac{1}{a_o}\right)^{3/2} 2 \exp\left(-\frac{r}{a_o}\right)$ | 0 | $\frac{1}{2\sqrt{\pi}}$ | |
| 2 | 0 | $\left(\frac{1}{2a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$ | 0 | $\frac{1}{2\sqrt{\pi}}$ | |
| 2 | 1 | $\left(\frac{1}{2a_o}\right)^{3/2}\left(\frac{r}{\sqrt{3}a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$ | 0 | $\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$ | $\propto \sin\theta\cos\phi$ |
| | | | 1 | $\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{j\phi}$ | |
| | | | −1 | $\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-j\phi}$ | $\propto \sin\theta\sin\phi$ |

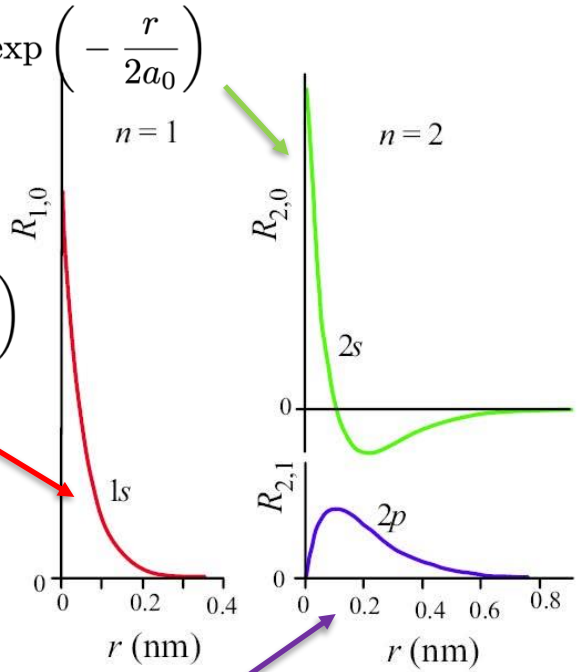
Correspond to $m_\ell = -1$ and $+1$.

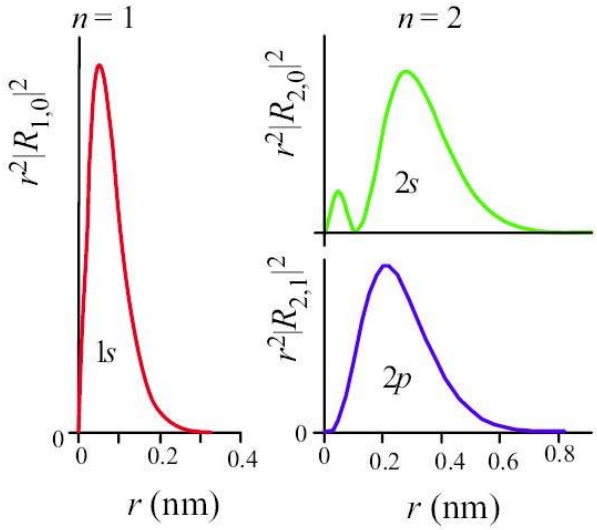
# Radial wavefunction and probability

$$\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$$

$$\left(\frac{1}{a_0}\right)^{3/2}2\exp\left(-\frac{r}{a_0}\right)$$

$$\left(\frac{1}{2a_0}\right)^{3/2}\left(\frac{r}{\sqrt{3}a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$$




$r^2|R(r)|^2$

Probability density in the radial direction

# Angular function

$$Y_{l,m}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{l,m}(\cos\theta) e^{im\phi}$$

$l = 0, m = 0$

$l = 1$

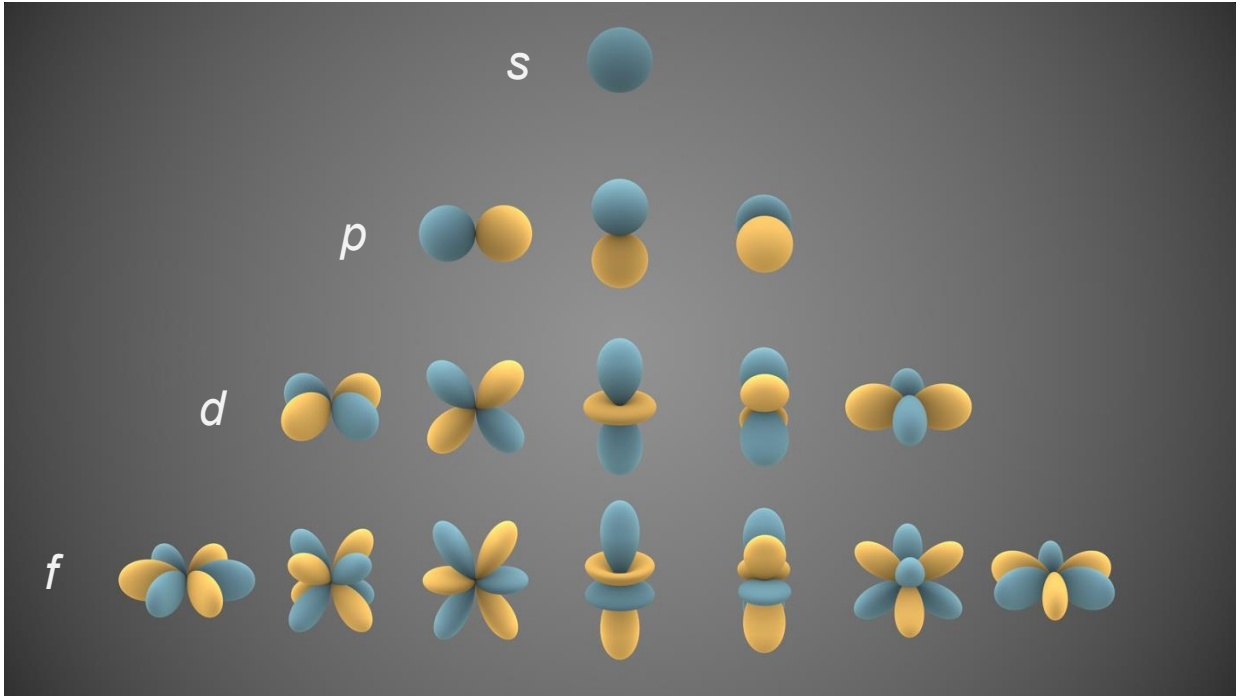
$m = -1, 0, +1$

$l = 2$

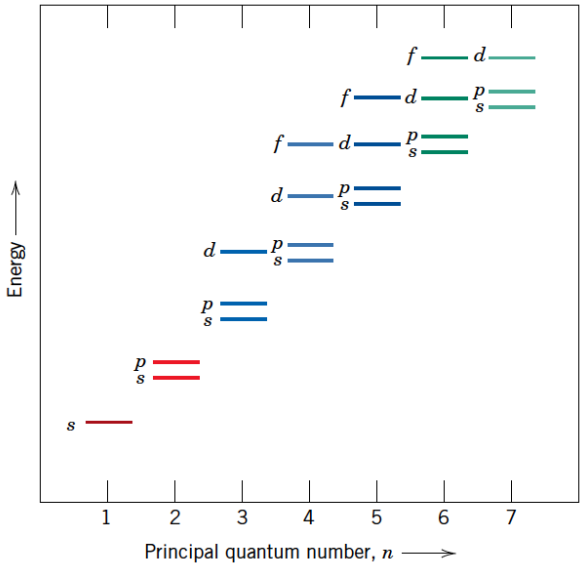
$m = -2, -1, 0, +1, +2$

$l = 3$

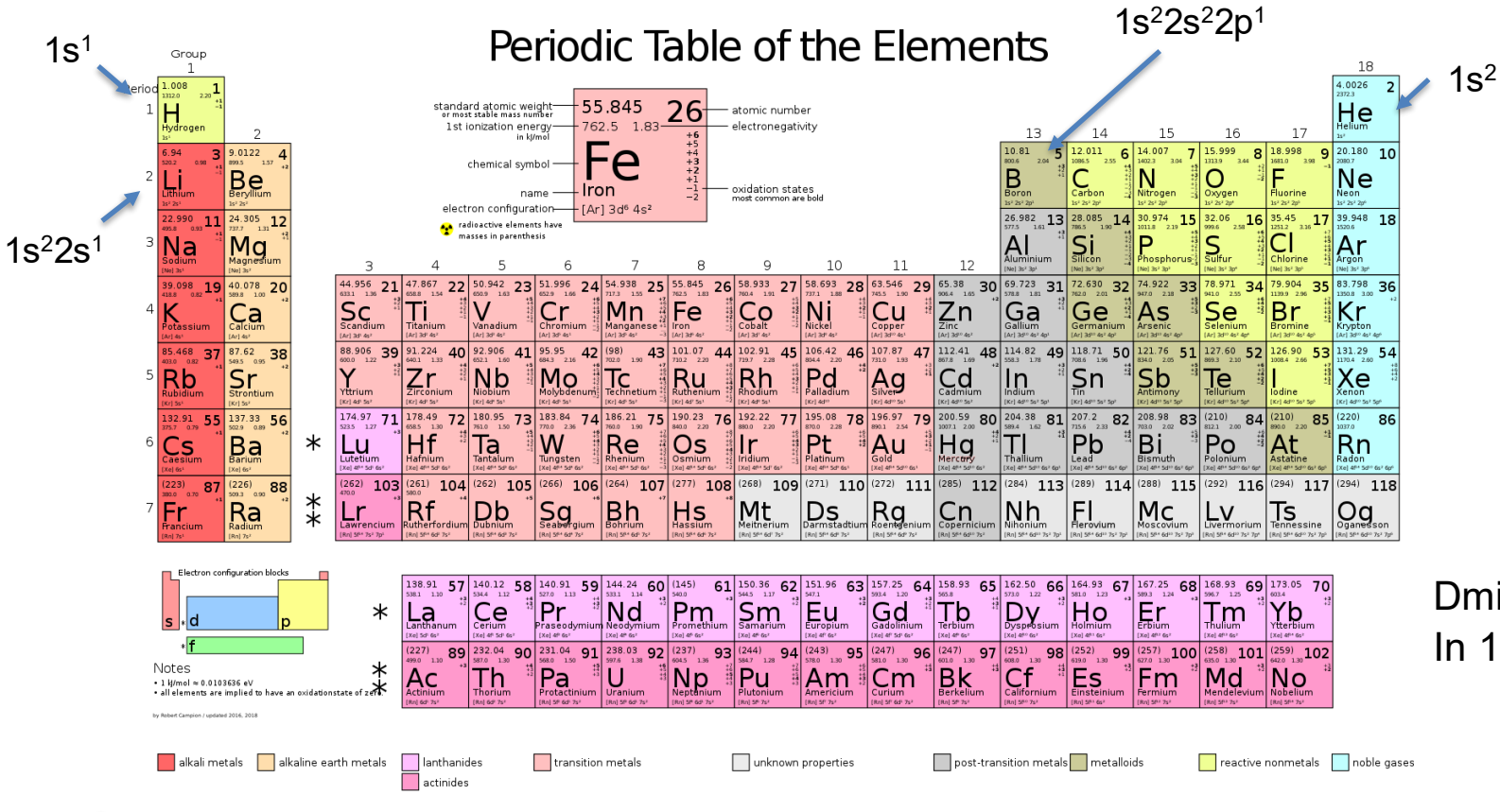
$m = -3, -2, -1, 0, +1, +2, +3$



ex: Fe - atomic # = 26 $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ $4s^2$



# Periodic Table of the Elements




Dmitri Mendeleev
In 1869

# More than one electron

Schrödinger equation

Discrete electrons

$$\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1, j\neq}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \psi(\mathbf{r}_i) = E\psi(\mathbf{r}_i)$$

Electron-ion

Electron-electron

Coulombic force

# More than one electron

Schrödinger equation

Discrete electrons

$$\left[ -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1,j\neq}^{n}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\psi(\mathbf{r}_i) = E\psi(\mathbf{r}_i)$$

Density functional theory (DFT)

$$n(\mathbf{r}) = -e\sum_{i}^{n}|\phi_i(\mathbf{r})|^2$$

Continuous electron density function

$$\left[ -\frac{\hbar}{2m}\nabla^2 + V_{ext}[n(\mathbf{r})] + V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})]\right]\phi_i = E\phi_i$$

# More than one electron

Schrödinger equation

Discrete electrons

$$\left[ -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{|\mathbf{R}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1,j\neq}^{n}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\psi(\mathbf{r}_i) = E\psi(\mathbf{r}_i)$$

Density functional theory (DFT)

$$n(\mathbf{r}) = -e\sum_{i}^{n}|\phi_i(\mathbf{r})|^2$$ ← Continuous electron density function

$$\left[ -\frac{\hbar}{2m}\nabla^2 + V_{ext}[n(\mathbf{r})] + V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})]\right]\phi_i = E\phi_i$$ ← Solution of is $\phi_i$ is obtained at the minimum of $E(\phi_i)$

$$E[\phi_i] = -\frac{\hbar^2}{2m}\sum_{i}^{n}\int \phi_i^*\nabla_i^2\phi_i d^3\mathbf{r} + \int V_{ext}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + \frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

Total energy | Kinetic | External | Classic Coulombic (Hartree) | Exchange-correlation

Ground state: the state of lowest total energy.

Functional is a function of function. We will work on that when learning phase field methods

$$E[\phi_i] = -\frac{\hbar^2}{2m}\sum_i^n \int \phi_i^* \nabla_i^2 \phi_i d^3\mathbf{r} + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

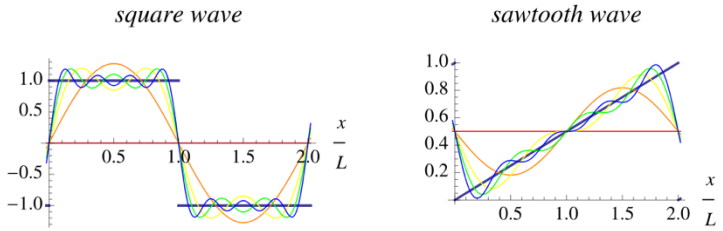
Local density approximation (LDA): $E_{xc}[n(\mathbf{r})]$ is a function of $n(\mathbf{r})$

Generalized gradient approximation (GGA): $E_{xc}$ is a function of $n(\mathbf{r})$ and the gradient of $n(\mathbf{r})$, i.e., $E_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$

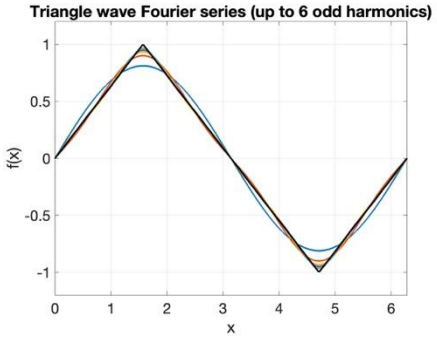
There are many exchange-correlation functionals have been proposed and used.

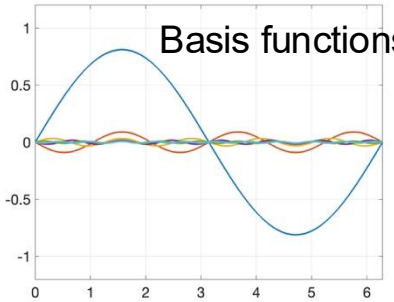
# Additional technique: Fourier spectrum method

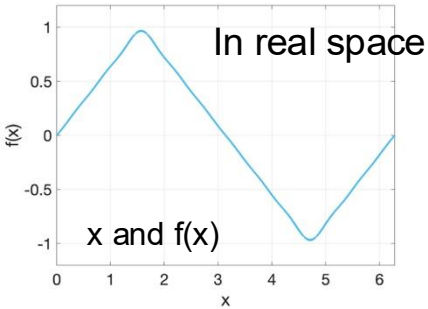
- Fourier transformation: any function can be represented by a series of sin and cos .
- Solving differential equation in Fourier space is much faster.
- For periodic lattice structure in solids, wave-functions are solved using Fourier spectrum method, which is much faster than classical solving methods.

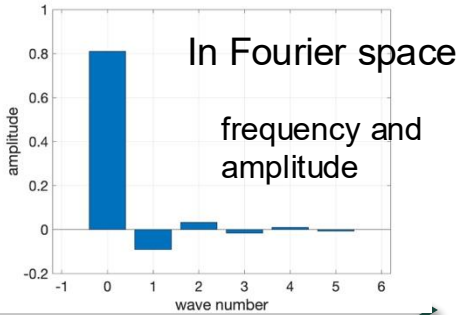



$$f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx)$$

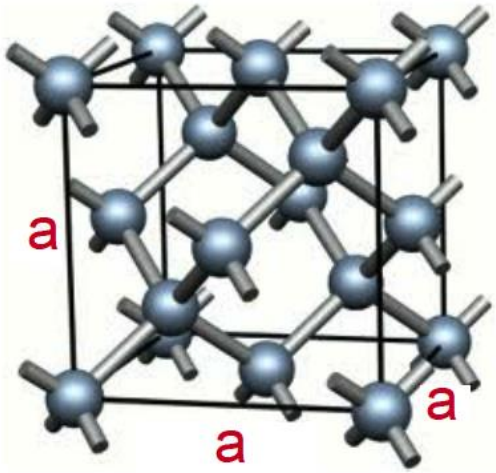


Example: Si of diamond structure




Primitive fcc cell vectors

(0, ½, ½) (½, 0, ½) (½, ½, 0)

Basis atomic positions

(0, 0, 0) (1/4 ,1/4, 1/4)

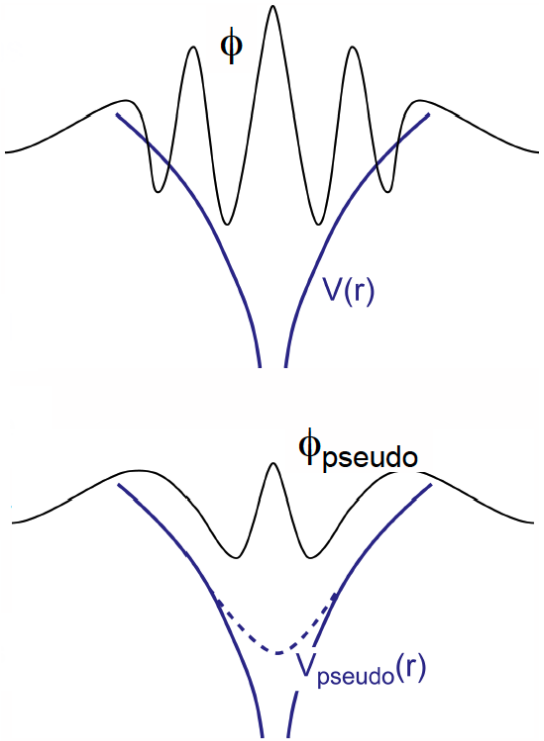
All atoms can be found at the multiple of

(0, 0, 0) (0, ½, ½) (½, 0, ½) (½, ½, 0)

(1/4 ,1/4, 1/4) (1/4 ,3/4, 3/4)

(3/4 ,1/4, 3/4) (3/4 ,3/4, 1/4)

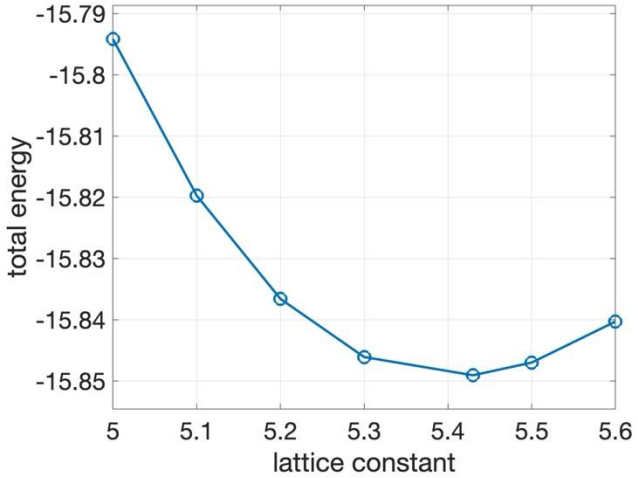
# Additional technique: pseudo-potential




- $V_{ext}$ potential at nucleus is singular
- Very hard to solve for the wave function, $\phi$
- Use a smooth, nonsingular pseudopotential to replace $V_{ext}$
- Much easier to solve
- Need to keep the result of $\phi_{pseudo}$ close to the true one in the region away for the core
- Solve wave functions of only the valence electrons

Adopted from Prof M Asta's (UC Berkeley ) course materials

- Log in to nanohub
- Search “quantum”
- Find DFT calculations with Quantum ESPRESSO
- Try different lattice constants




Volume $V = a^3$

Pressure $P = -\frac{\partial E}{\partial V}$

Bulk modulus $B = -V\frac{\partial P}{\partial V} = -V\frac{\partial^2 E}{\partial V^2}$

- VASP (http://cms.mpi.univie.ac.at/vasp/)
  - Commercial, Plane-Wave Basis, Pseudopotentials and PAW
- PWSCF (http://www.quantum-espresso.org/)
  - Free (and available to run on nanohub), Plane-Wave Basis, Pseudopotentials and PAW
- CASTEP (http://ccpforge.cse.rl.ac.uk/gf/project/castep/)
  - Free in UK, licensed by Accelrys elsewhere, Plane-Wave Basis, Pseudopotentials
- ABINIT (http://www.abinit.org/)
  - Free (and available to run on nanohub), plane-wave basis, pseudopotentials and PAW
- WIEN2K (http://www.wien2k.at/)
  - Commercial (modest license fee), all-electron augmented wave method

## Materials Project

https://next-gen.materialsproject.org/

- Log in
- Try making some phase diagram by selecting elements
- Explore crystal structures and properties of relevant compounds