

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

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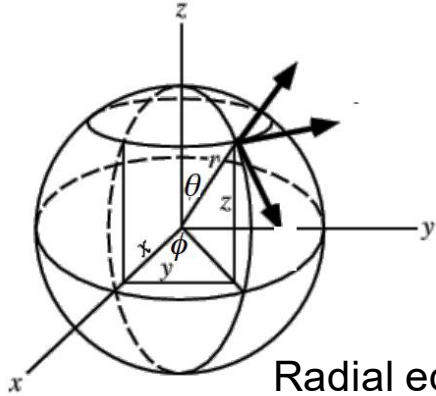
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# Solving Schrödinger equation for hydrogen atom



In spherical coordinate system

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

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

Radial equation:

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

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

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

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

Radial equation:

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

Solution of radial equation:

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

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

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

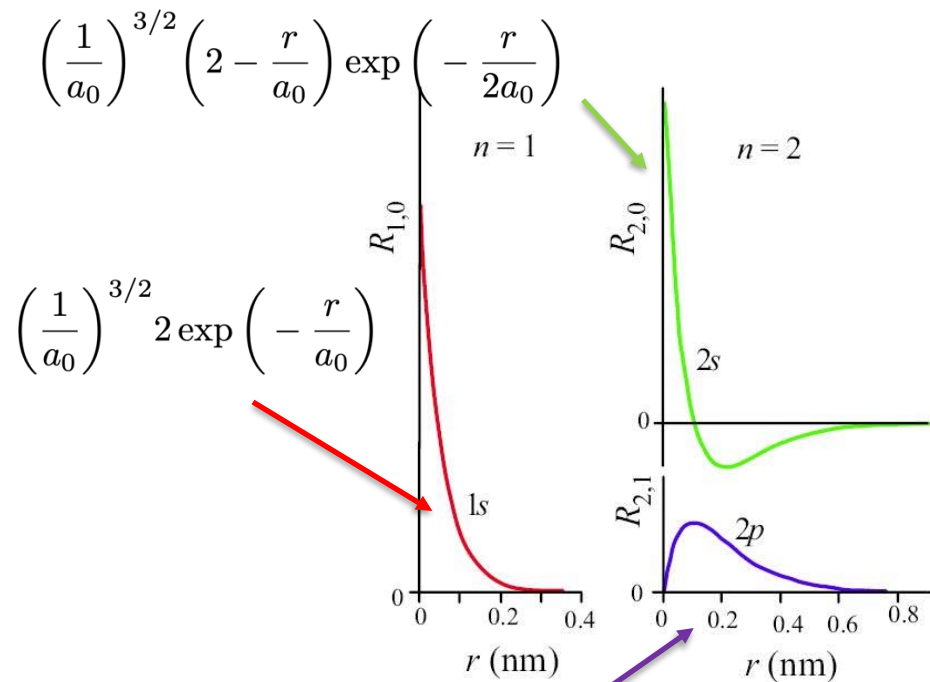
**Table 2.1** Summary of the Relationships among the Quantum Numbers  $n$ ,  $l$ ,  $m_l$  and Numbers of Orbitals and Electrons

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

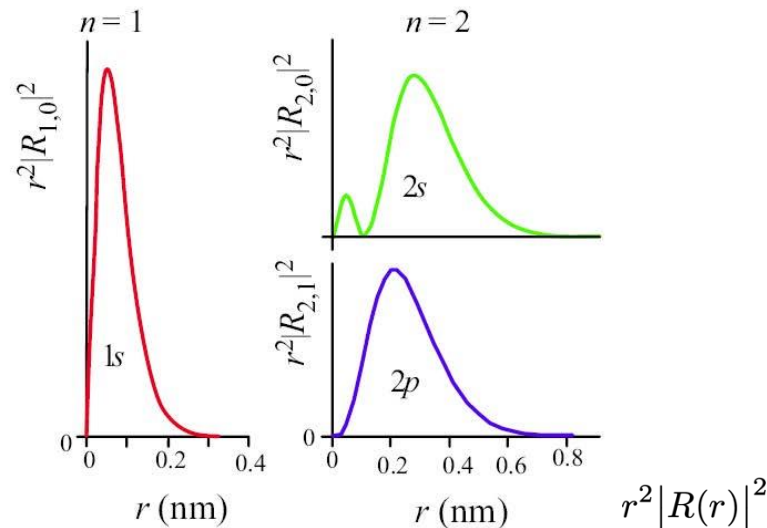
**Source:** From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.

**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	$\frac{1}{2}\sqrt{\frac{3}{\pi}} \cos \theta$
			1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{j\phi}$
			-1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{-j\phi}$
				$\left\{ \begin{array}{l} \propto \sin \theta \cos \phi \\ \propto \sin \theta \sin \phi \end{array} \right\}$
				Correspond to $m_\ell = -1$ and $+1$ .



(a)



(b)

Probability density in the radial direction

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

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

$l = 0, m = 0$

$l = 1$

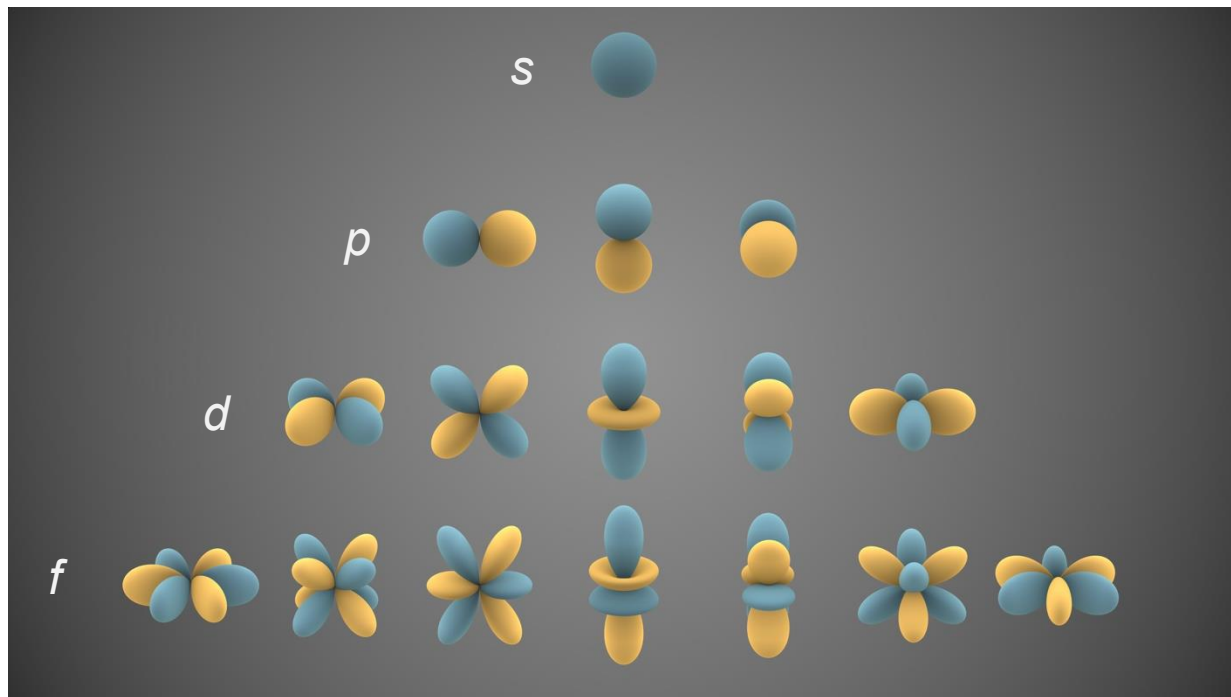
$m = -1, 0, +1$

$l = 2$

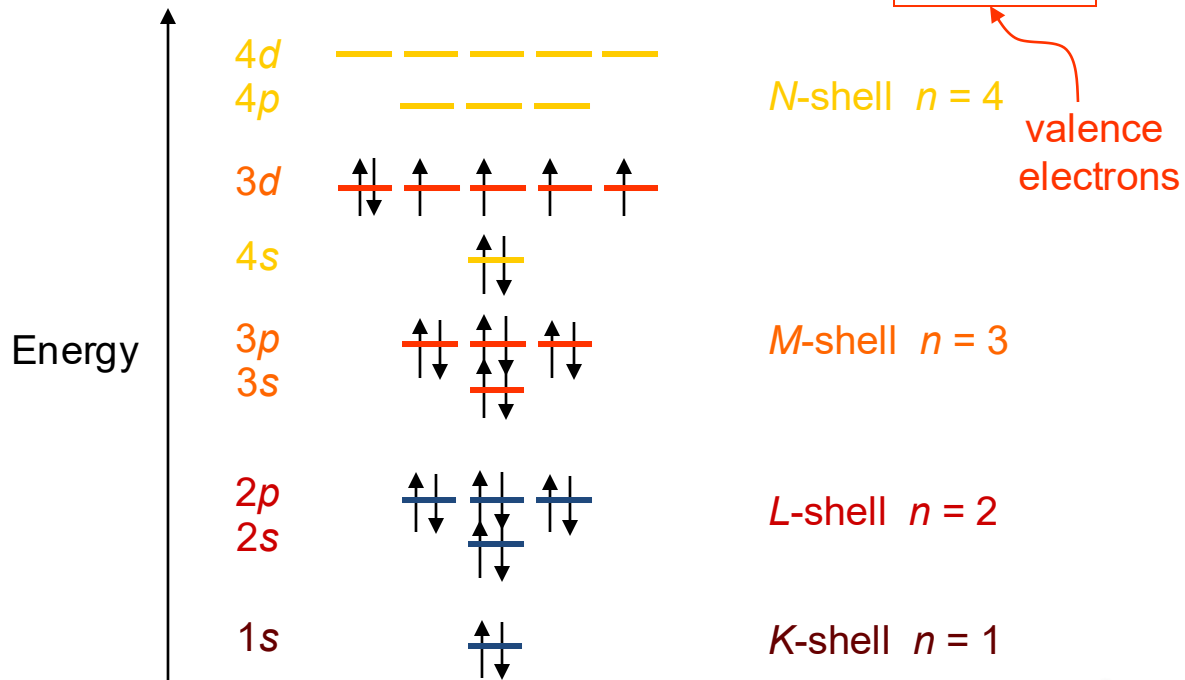
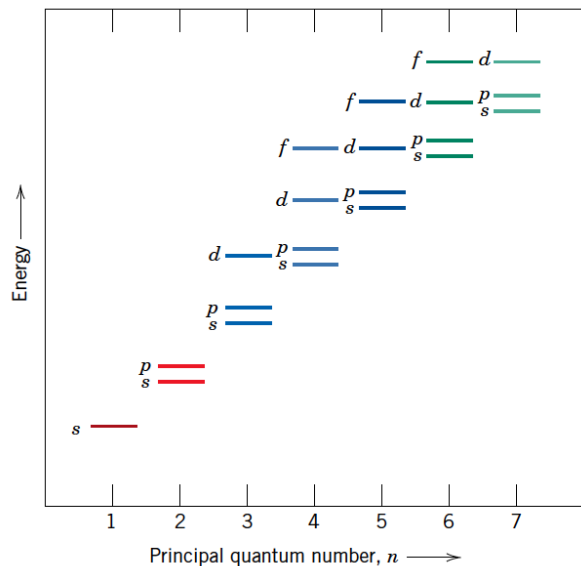
$m = -2, -1, 0, +1, +2$

$l = 3$

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



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







# Periodic Table of the Elements

1s<sup>1</sup>

1s<sup>2</sup>2s<sup>1</sup>

Group	1	2
1	1.008 1.00794 H Hydrogen [1s <sup>1</sup> ]	
2	6.94 6.941 Li Lithium [He] 2s <sup>1</sup>	9.0122 9.01218 Be Beryllium [He] 2s <sup>2</sup>
3	22.990 22.98977 Na Sodium [Ne] 3s <sup>1</sup>	24.305 24.30409 Mg Magnesium [Ne] 3s <sup>2</sup>
4	39.098 39.0983 K Potassium [Ar] 4s <sup>1</sup>	40.078 40.0784 Ca Calcium [Ar] 4s <sup>2</sup>
5	85.468 85.4678 Rb Rubidium [Kr] 5s <sup>1</sup>	87.62 87.62 Sr Strontium [Kr] 5s <sup>2</sup>
6	132.91 132.905 Cs Cesium [Xe] 6s <sup>1</sup>	137.33 137.327 Ba Barium [Xe] 6s <sup>2</sup>
7	(223) 223.018 Fr Francium [Rn] 7s <sup>1</sup>	(226) 226.025 Ra Radium [Rn] 7s <sup>2</sup>

standard atomic weight  
or most stable mass number

1st ionization energy  
in kJ/mol

chemical symbol

name

electron configuration

radioactive elements have  
masses in parenthesis

55.845  
762.5  
Fe  
Iron  
[Ar] 3d<sup>6</sup> 4s<sup>2</sup>

26

atomic number

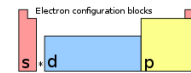
electronegativity

oxidation states  
most common are bold

1s<sup>2</sup>2s<sup>2</sup>2p<sup>1</sup>

1s<sup>2</sup>

13	14	15	16	17	18
10.81 10.811 B Boron [He] 2s <sup>2</sup> 2p <sup>1</sup>	12.011 12.011 C Carbon [He] 2s <sup>2</sup> 2p <sup>2</sup>	14.007 14.007 N Nitrogen [He] 2s <sup>2</sup> 2p <sup>3</sup>	15.999 15.999 O Oxygen [He] 2s <sup>2</sup> 2p <sup>4</sup>	18.998 18.998 F Fluorine [He] 2s <sup>2</sup> 2p <sup>5</sup>	4.0026 4.0026 He Helium [1s <sup>2</sup> ]
26.982 26.9815 Al Aluminum [Ne] 3s <sup>2</sup> 3p <sup>1</sup>	28.085 28.0855 Si Silicon [Ne] 3s <sup>2</sup> 3p <sup>2</sup>	30.974 30.9738 P Phosphorus [Ne] 3s <sup>2</sup> 3p <sup>3</sup>	32.06 32.059 S Sulfur [Ne] 3s <sup>2</sup> 3p <sup>4</sup>	35.45 35.453 Cl Chlorine [Ne] 3s <sup>2</sup> 3p <sup>5</sup>	39.948 39.948 Ar Argon [Ne] 3s <sup>2</sup> 3p <sup>6</sup>
69.723 69.723 Ga Gallium [Ar] 3d <sup>10</sup> 4s <sup>1</sup>	72.630 72.6305 Ge Germanium [Ar] 3d <sup>10</sup> 4s <sup>2</sup>	74.922 74.9216 As Arsenic [Ar] 3d <sup>10</sup> 4s <sup>2</sup>	78.971 78.9718 Se Selenium [Ar] 3d <sup>10</sup> 4s <sup>2</sup>	79.904 79.904 Br Bromine [Ar] 3d <sup>10</sup> 4s <sup>2</sup>	83.798 83.798 Kr Krypton [Ar] 3d <sup>10</sup> 4s <sup>2</sup>
114.82 114.818 Sn Tin [Kr] 4d <sup>10</sup> 5s <sup>2</sup>	121.76 121.757 Sb Antimony [Kr] 4d <sup>10</sup> 5s <sup>2</sup>	127.60 127.603 Te Tellurium [Kr] 4d <sup>10</sup> 5s <sup>2</sup>	126.90 126.905 I Iodine [Kr] 4d <sup>10</sup> 5s <sup>2</sup>	131.29 131.294 Xe Xenon [Kr] 4d <sup>10</sup> 5s <sup>2</sup>	
200.59 200.59 Hg Mercury [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	204.38 204.38 Tl Thallium [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	207.2 207.2 Pb Lead [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	208.98 208.98 Bi Bismuth [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	209 209 Po Polonium [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	210 210 At Astatine [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>
289 289 Fr Francium [Rn] 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>1</sup>	289 289 Ra Radium [Rn] 5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>	289 289 Ac Actinium [Rn] 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	289 289 Th Thorium [Rn] 5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>	289 289 Pa Protactinium [Rn] 5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>	289 289 U Uranium [Rn] 5f <sup>14</sup> 6d <sup>3</sup> 7s <sup>2</sup>



## Notes

- 1 kJ/mol = 0.0103636 eV
- all elements are implied to have an oxidation state of zero

by Robert Campion | updated 2016, 2018


- alkali metals
- alkaline earth metals
- lanthanides
- actinides
- transition metals
- unknown properties
- post-transition metals
- metalloids
- reactive nonmetals
- noble gases


Dmitri Mendeleev  
In 1869

Schrödinger equation

Discrete electrons

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

  
Electron-ion

  
Electron-electron

Coulombic force



Schrödinger equation

Discrete electrons

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

Density functional theory (DFT)

$$n(\mathbf{r}) = -e \sum_i^n |\phi_i(\mathbf{r})|^2 \quad \leftarrow \text{Continuous electron density function}$$

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



Schrödinger equation

Discrete electrons

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

Density functional theory (DFT)

$$n(\mathbf{r}) = -e \sum_i^n |\phi_i(\mathbf{r})|^2 \quad \longleftarrow \quad \text{Continuous electron density function}$$

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

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

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

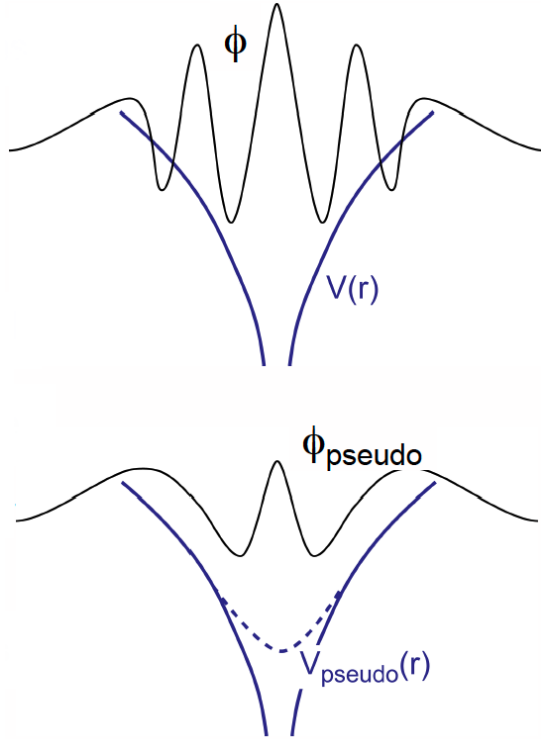
$$E[\phi_i] = -\frac{\hbar^2}{2m} \sum_i^n \int \phi_i^* \nabla_i^2 \phi_i d^3\mathbf{r} + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

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.

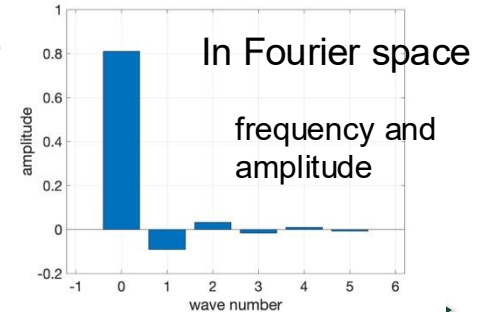
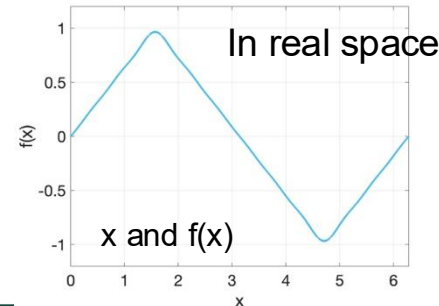
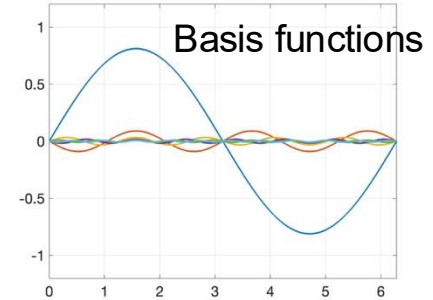
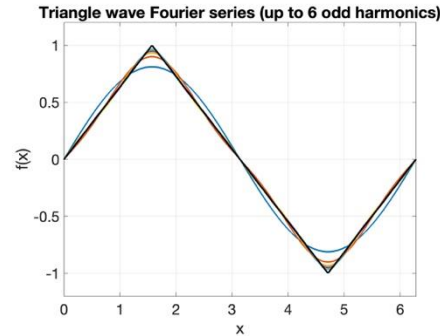
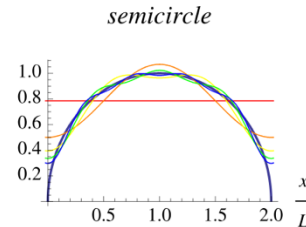
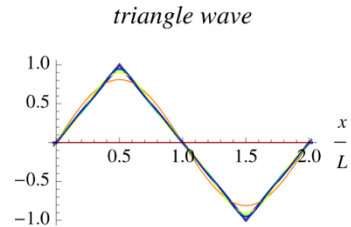
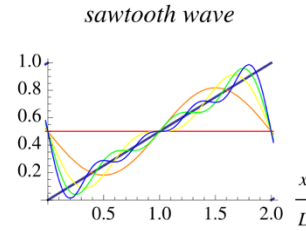
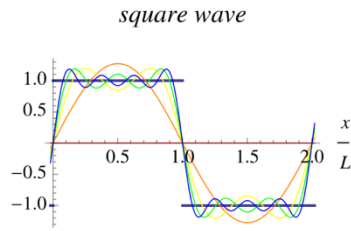




- $V_{ext}$  potential at nucleus is singular
- Very hard to solve for the wave function,  $\phi$
- Use a smooth, nonsingular pseudopotential to replace  $V_{ext}$
- Much easier to solve
- Need to keep the result of  $\phi_{pseudo}$  close to the true one in the region away from the core
- Solve wave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

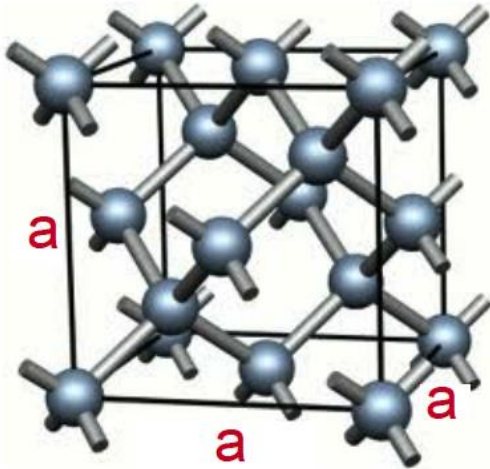


- Fourier transformation: any function can be represented by a series of sin and cos .
- Solving differential equation in Fourier space is much faster.
- For periodic lattice structure in solids, wave-functions are solved using Fourier spectrum method, which is much faster than classical solving methods.



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

Example: Si of diamond structure



Primitive fcc cell vectors

$$(0, \frac{1}{2}, \frac{1}{2}) \quad (\frac{1}{2}, 0, \frac{1}{2}) \quad (\frac{1}{2}, \frac{1}{2}, 0)$$

Basis atomic positions

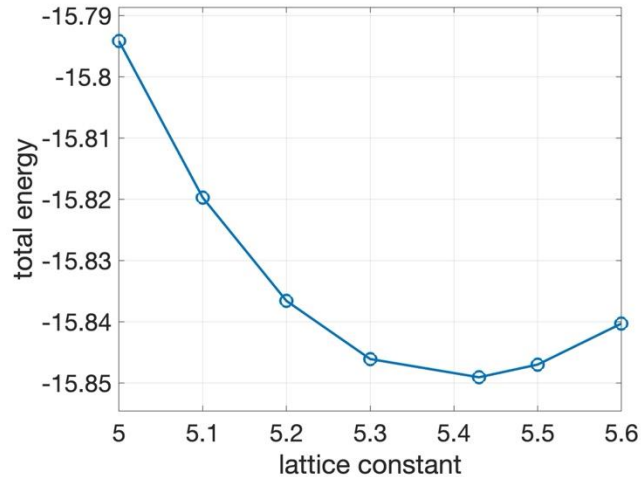
$$(0, 0, 0) \quad (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$$

All atoms can be found at the multiple of

$$\begin{aligned} &(0, 0, 0) \quad (0, \frac{1}{2}, \frac{1}{2}) \quad (\frac{1}{2}, 0, \frac{1}{2}) \quad (\frac{1}{2}, \frac{1}{2}, 0) \\ &(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \quad (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}) \\ &(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}) \quad (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}) \end{aligned}$$



- Log in to [nanohub](https://nanohub.org)
- 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/)

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

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

