

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

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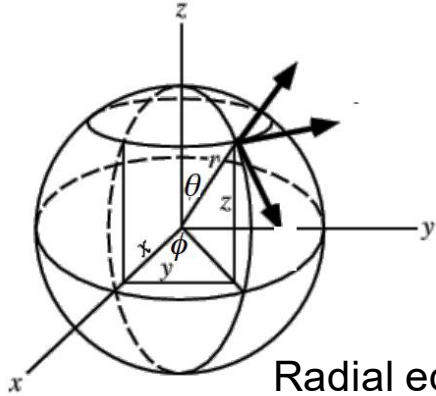
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Department of Chemical Engineering and Materials Science

Michigan State University



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 , ℓ , and m_ℓ

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$

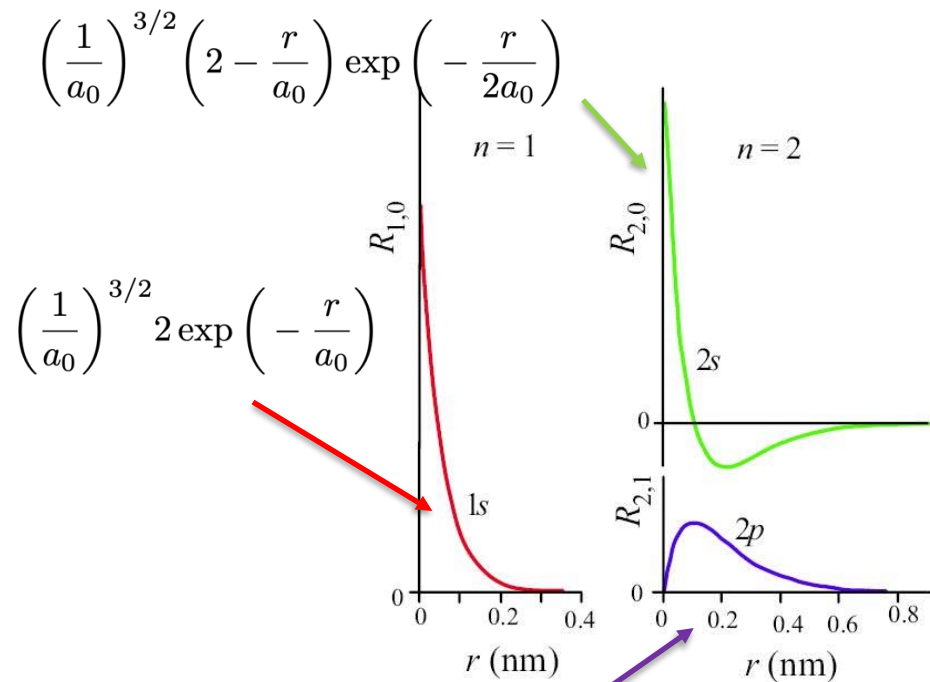
Table 2.1 Summary of the Relationships among the Quantum Numbers n , l , m_l and Numbers of Orbitals and Electrons

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
	0	0	3s	1	2
3	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

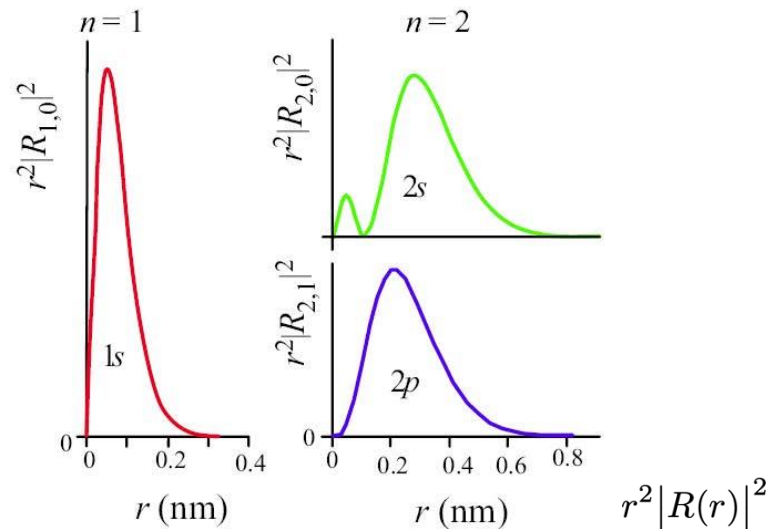
Source: From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.

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

n	ℓ	$R(r)$	m_ℓ	$Y(\theta, \phi)$
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

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

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

$l = 0, m = 0$

$l = 1$

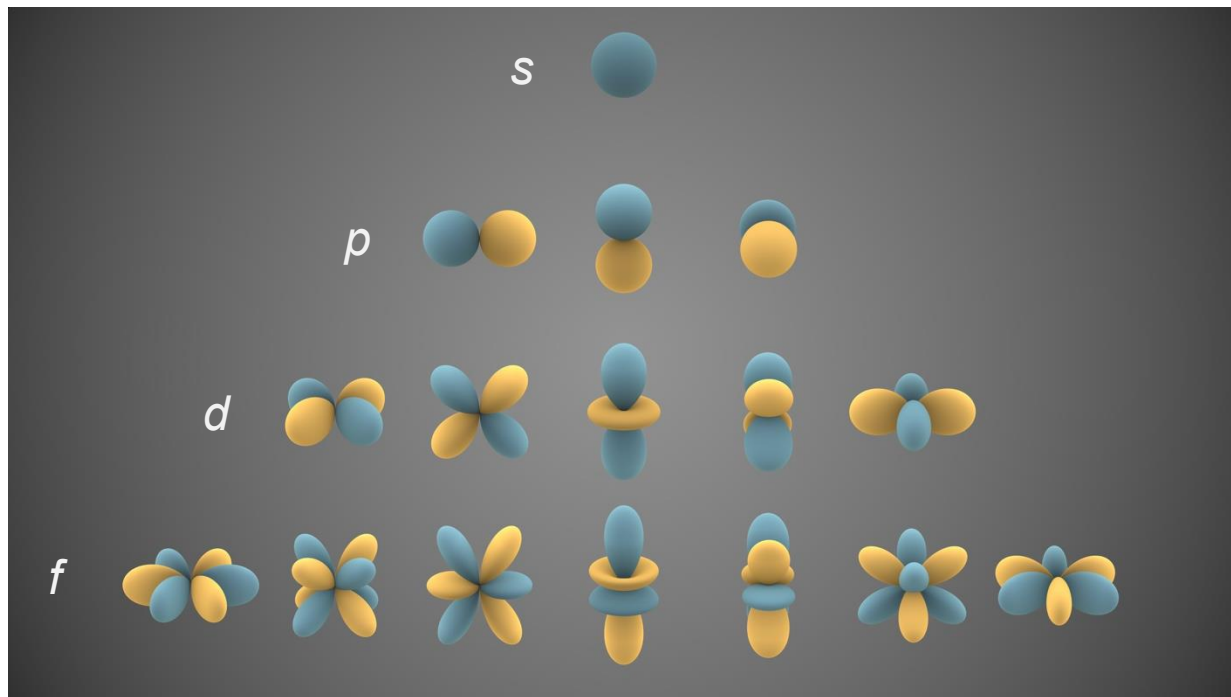
$m = -1, 0, +1$

$l = 2$

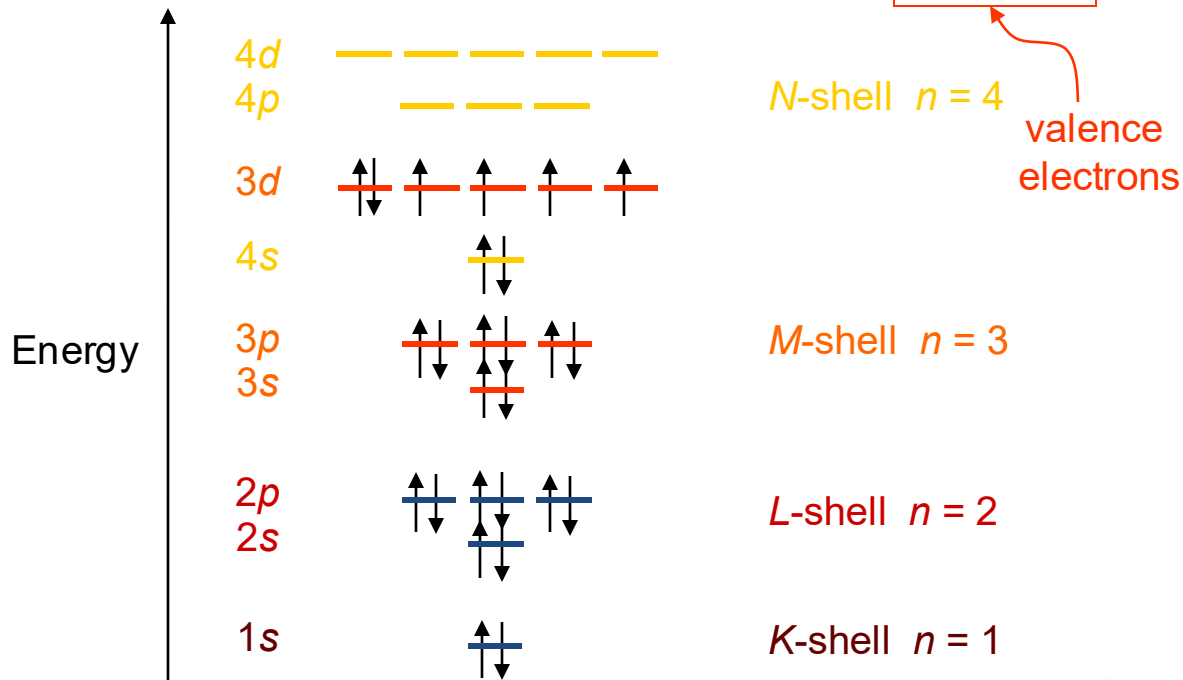
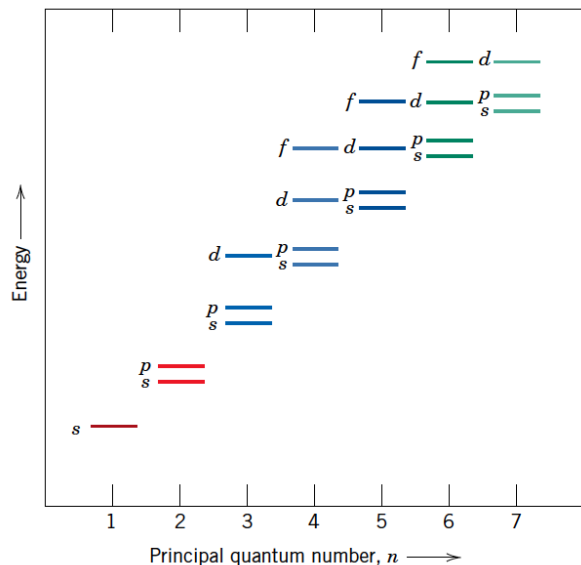
$m = -2, -1, 0, +1, +2$

$l = 3$

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



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





Periodic Table of the Elements

1s¹

1s²2s¹

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

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] 3d⁶ 4s²

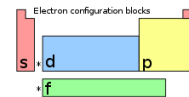
26

atomic number

electronegativity

oxidation states
most common are bold

3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
44.956 44.95591 Sc Scandium [Ar] 3d ¹ 4s ²	47.867 47.867 Ti Titanium [Ar] 3d ² 4s ²	50.942 50.9415 V Vanadium [Ar] 3d ³ 4s ²	51.996 51.9961 Cr Chromium [Ar] 3d ⁵ 4s ¹	54.938 54.937025 Mn Manganese [Ar] 3d ⁵ 4s ²	55.845 55.845 Fe Iron [Ar] 3d ⁶ 4s ²	58.933 58.933195 Co Cobalt [Ar] 3d ⁷ 4s ²	58.693 58.6934 Ni Nickel [Ar] 3d ⁸ 4s ²	63.546 63.54688 Cu Copper [Ar] 3d ¹⁰ 4s ¹	65.38 65.38 Zn Zinc [Ar] 3d ¹⁰ 4s ²	69.723 69.7231 Ga Gallium [Ar] 3d ¹⁰ 4s ² 4p ¹	72.630 72.6305 Ge Germanium [Ar] 3d ¹⁰ 4s ² 4p ²	74.922 74.9216 As Arsenic [Ar] 3d ¹⁰ 4s ² 4p ³	78.971 78.9718 Se Selenium [Ar] 3d ¹⁰ 4s ² 4p ⁴	79.904 79.904 Br Bromine [Ar] 3d ¹⁰ 4s ² 4p ⁵	83.798 83.798 Kr Krypton [Ar] 3d ¹⁰ 4s ² 4p ⁶
88.906 88.90584 Y Yttrium [Kr] 4d ¹ 5s ²	91.224 91.224 Zr Zirconium [Kr] 4d ² 5s ²	92.906 92.90638 Nb Niobium [Kr] 4d ⁴ 5s ¹	95.95 95.94 Mo Molybdenum [Kr] 4d ⁵ 5s ¹	(98) 98.00 Tc Technetium [Kr] 4d ⁵ 5s ²	101.07 101.07 Ru Ruthenium [Kr] 4d ⁷ 5s ¹	102.91 102.9055 Rh Rhodium [Kr] 4d ⁸ 5s ¹	106.42 106.42 Pd Palladium [Kr] 4d ¹⁰	107.87 107.8682 Ag Silver [Kr] 4d ¹⁰ 5s ¹	112.41 112.411 Cd Cadmium [Kr] 4d ¹⁰ 5s ²	114.82 114.818 In Indium [Kr] 4d ¹⁰ 5s ² 5p ¹	118.71 118.710 Sn Tin [Kr] 4d ¹⁰ 5s ² 5p ²	121.76 121.757 Sb Antimony [Kr] 4d ¹⁰ 5s ² 5p ³	127.60 127.603 Te Tellurium [Kr] 4d ¹⁰ 5s ² 5p ⁴	126.90 126.905 I Iodine [Kr] 4d ¹⁰ 5s ² 5p ⁵	131.29 131.294 Xe Xenon [Kr] 4d ¹⁰ 5s ² 5p ⁶
174.97 174.967 Lu Lutetium [Xe] 4f ¹⁴ 5d ¹ 6s ²	178.49 178.49 Hf Hafnium [Xe] 4f ¹⁴ 5d ² 6s ²	180.95 180.94788 Ta Tantalum [Xe] 4f ¹⁴ 5d ³ 6s ²	183.84 183.84 W Tungsten [Xe] 4f ¹⁴ 5d ⁴ 6s ²	186.21 186.207 Re Rhenium [Xe] 4f ¹⁴ 5d ⁵ 6s ²	190.23 190.23 Os Osmium [Xe] 4f ¹⁴ 5d ⁶ 6s ²	192.22 192.22 Ir Iridium [Xe] 4f ¹⁴ 5d ⁷ 6s ²	195.08 195.083 Pt Platinum [Xe] 4f ¹⁴ 5d ⁹ 6s ¹	196.97 196.96655 Au Gold [Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹	200.59 200.59 Hg Mercury [Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	204.38 204.38 Tl Thallium [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	207.2 207.2 Pb Lead [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	208.98 208.98 Bi Bismuth [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	209 209 Po Polonium [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	210 210 At Astatine [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	220 220 Rn Radon [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
(262) 262 Lr Lawrencium [Og] 5f ¹⁴ 6d ¹ 7s ²	(261) 261 Rf Rutherfordium [Og] 5f ¹⁴ 6d ² 7s ²	(262) 262 Db Dubnium [Og] 5f ¹⁴ 6d ³ 7s ²	(266) 266 Sg Seaborgium [Og] 5f ¹⁴ 6d ⁴ 7s ²	(264) 264 Bo Bohrium [Og] 5f ¹⁴ 6d ⁵ 7s ²	(277) 277 Hs Hassium [Og] 5f ¹⁴ 6d ⁶ 7s ²	(268) 268 Mt Meitnerium [Og] 5f ¹⁴ 6d ⁷ 7s ²	(271) 271 Ds Darmstadtium [Og] 5f ¹⁴ 6d ⁸ 7s ²	(272) 272 111 Roentgenium [Og] 5f ¹⁴ 6d ⁹ 7s ²	(285) 285 112 Copernicium [Og] 5f ¹⁴ 6d ¹⁰ 7s ²	(284) 284 Nh Nihonium [Og] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	(289) 289 Fl Flerovium [Og] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	(288) 288 115 Moscovium [Og] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	(292) 292 Lv Livermorium [Og] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	(294) 294 Ts Tennessine [Og] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	(294) 294 Og Oganesson [Og] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶



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

1s²2s²2p¹


1s²

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)

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

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



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 $n(\mathbf{r})$

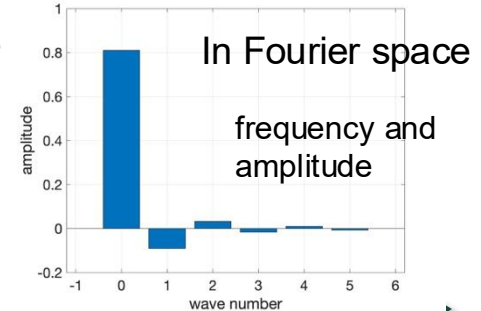
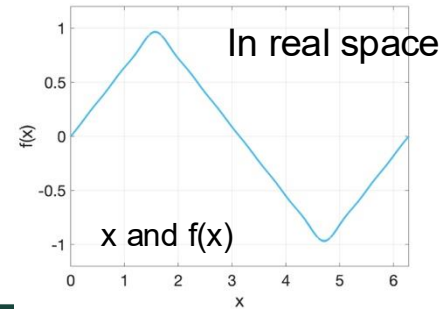
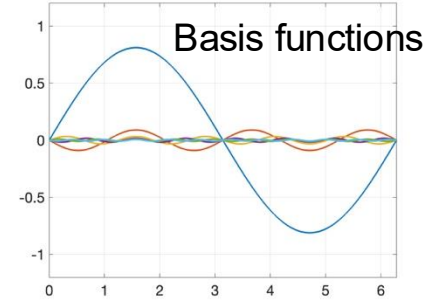
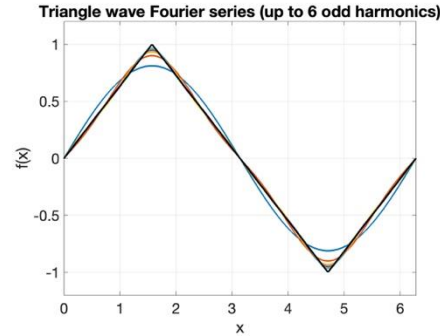
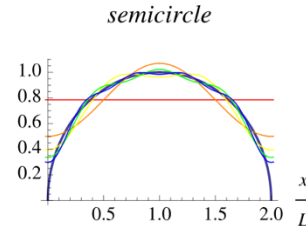
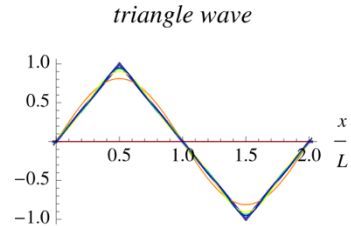
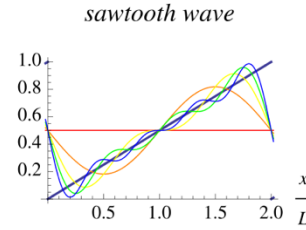
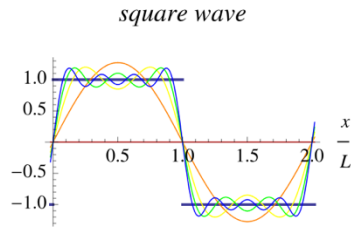
Generalized gradient approximation (GGA): E_{xc} is a function of $n(\mathbf{r})$ and the gradient of $n(\mathbf{r})$, i.e., $E_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$

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



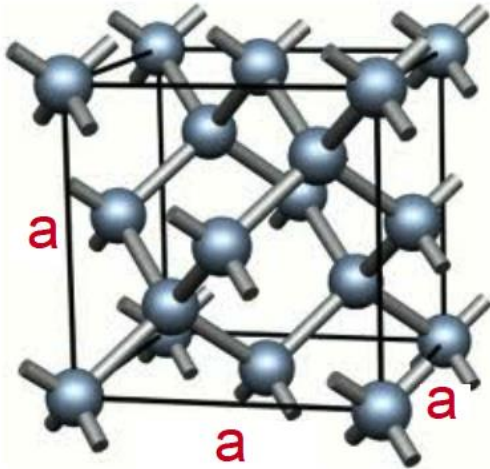


- Fourier transformation: any function can be represented by a series of sin and cos .
- Solving differential equation in Fourier space is much faster.
- For periodic lattice structure in solids, wave-functions are solved using Fourier spectrum method, which is much faster than classical solving methods.



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

Example: Si of diamond structure



Primitive fcc cell vectors

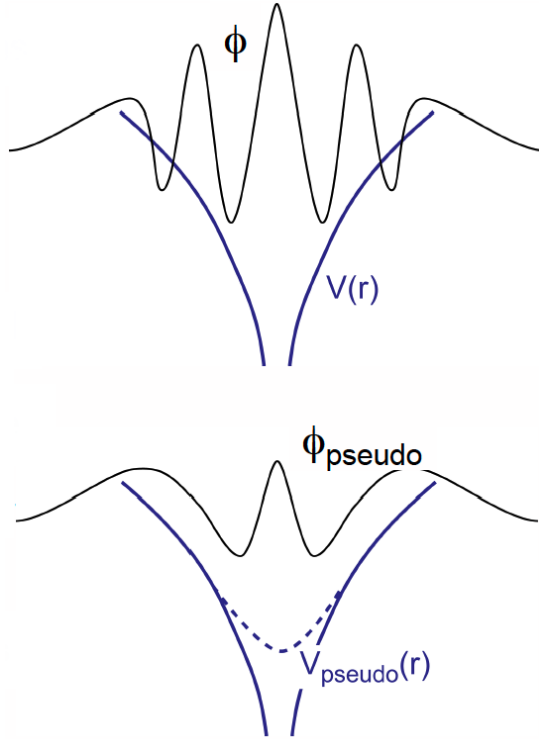
$$(0, \frac{1}{2}, \frac{1}{2}) \quad (\frac{1}{2}, 0, \frac{1}{2}) \quad (\frac{1}{2}, \frac{1}{2}, 0)$$

Basis atomic positions

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

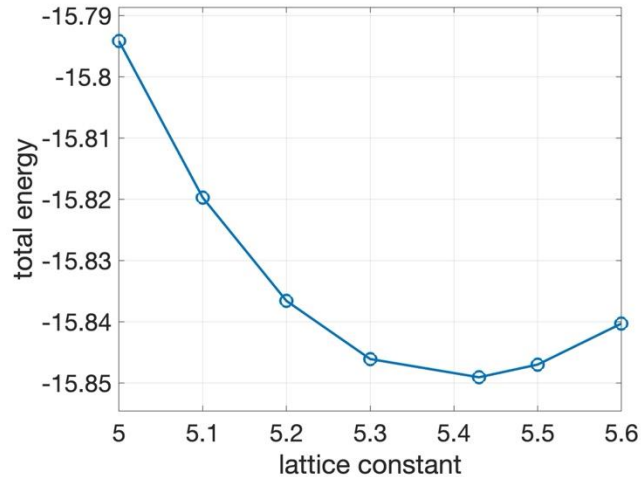
All atoms can be found at the multiple of

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



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

- 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

