Introduction to Computational Materials Science and Materials Data Science (590400)
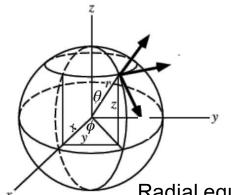
Hui-Chia Yu 游輝嘉

Department of Computational Mathematics, Science and Engineering

Department of Chemical Engineering and Materials Science

Michigan State University

Solving Schrödinger equation for hydrogen atom

In spherical coordinate system

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi(r,\theta,\phi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\psi(r,\theta,\phi) +$$

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

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

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

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

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

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

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

Radial equation:

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

Solution of radial equation:

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

Associated Laguerre polynomials

Table 3.2   The quantum number n, ℓ, and m_ℓ

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 $|m_\ell| \leq \ell$

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
4	0	0	4s	1	2
	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.
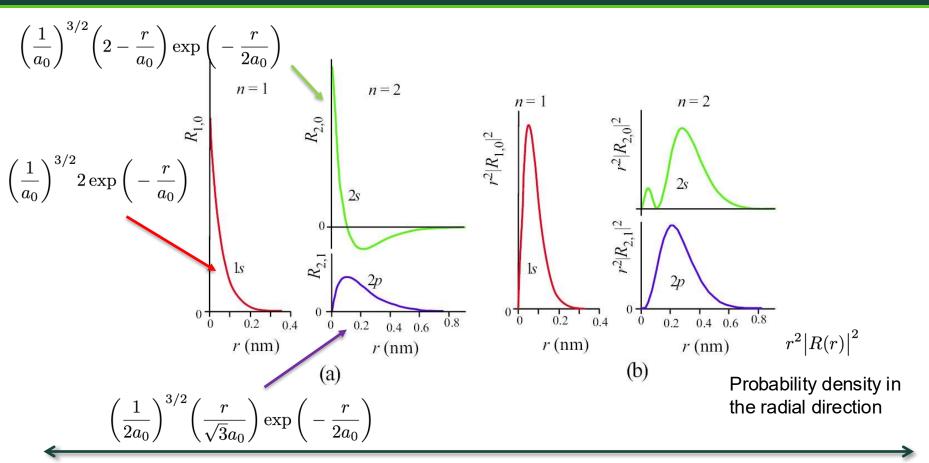
Table 3.4 The radial and spherical harmonic parts of the wavefunction in the hydrogen atom ($a_o = 0.0529$ nm)

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

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

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

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

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

(a)

(b)

$$r^2\left|R(r)\right|^2$$

Probability density in the radial direction

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

$l = 0, m = 0$

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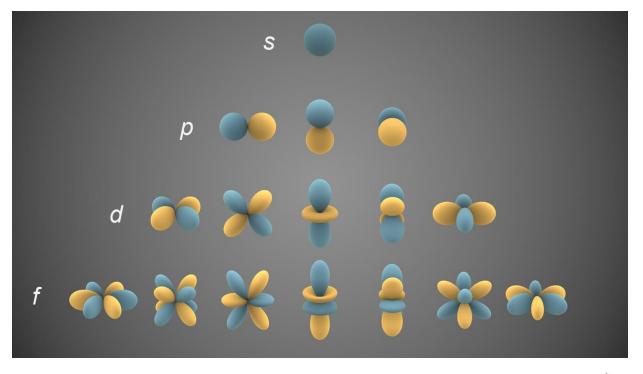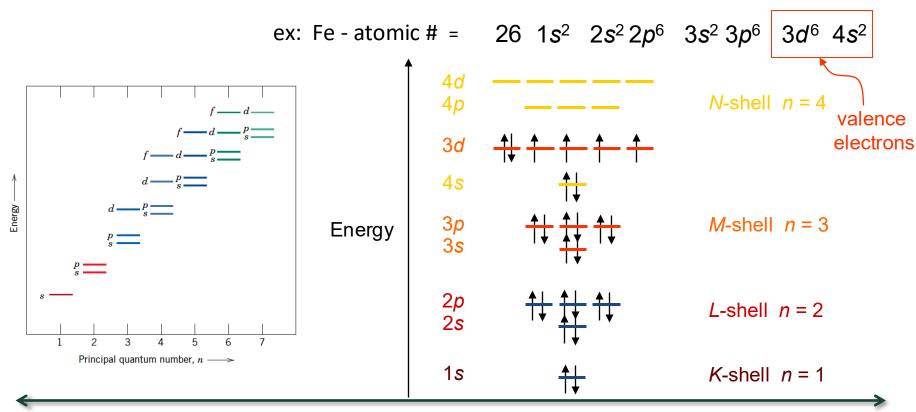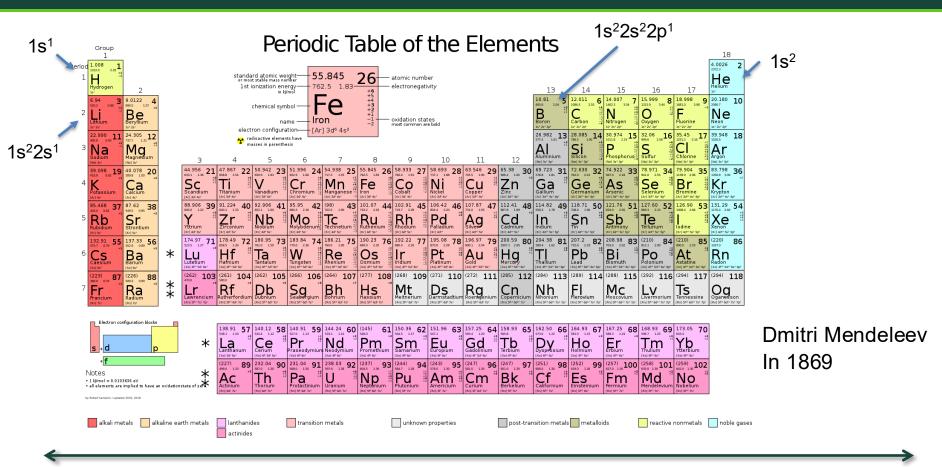
$l = 2$
$m = -2, -1, 0, +1, +2$

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

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

valence electrons

4d

4p — N-shell $n = 4$

3d

4s

3p — M-shell $n = 3$

3s

Energy

2p — L-shell $n = 2$

2s

1s — K-shell $n = 1$

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

Schrödinger equation

Discrete electrons

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

Density functional theory (DFT)

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

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

Kohn-Sham equation

Schrödinger equation

Discrete electrons

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

Density functional theory (DFT)

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

Continuous electron density function

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

Solution of is ϕ_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. See the JB file. We will learn more when learning phase field methods.

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

Electron-electron interaction other than coulombic

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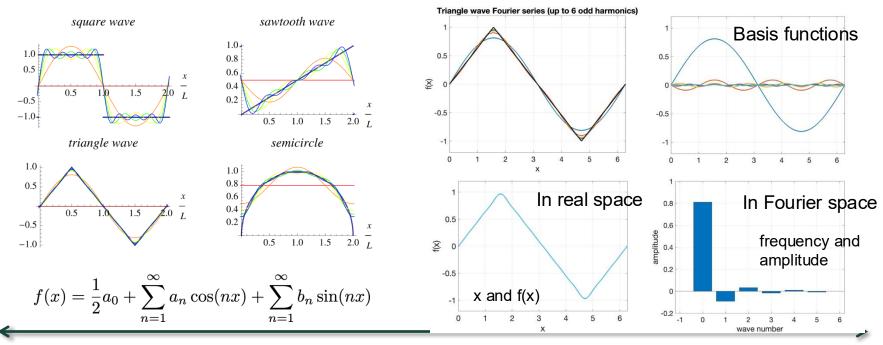
Generalized gradient approximation (GGA): E_{xc} is a function of $n(\mathbf{r})$ and the gradient of $n(\mathbf{r})$, i.e., $E_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$

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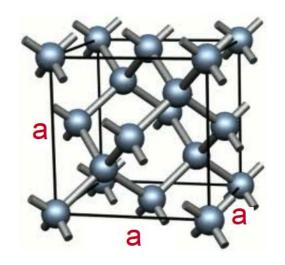
- Fourier transformation: any function can be represented by a series of sin and cos .
- Solving differential equation in Fourier space is much faster.
- For periodic lattice structure in solids, wave-functions are solved using Fourier spectrum method, which is much faster than classical solving methods.

square wave

sawtooth wave

triangle wave

semicircle

Triangle wave Fourier series (up to 6 odd harmonics)

Basis functions

In real space

In Fourier space

frequency and amplitude

x and f(x)

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

Example: Si of diamond structure

Primitive fcc cell vectors
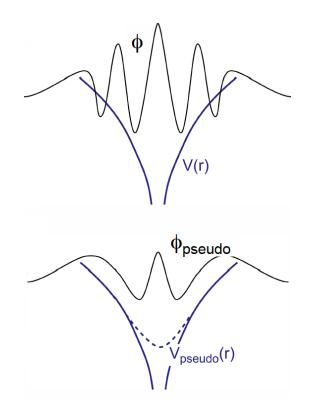
(0, ½, ½)   (½, 0, ½)   (½, ½, 0)

Basis atomic positions

(0, 0, 0)   (1/4 ,1/4, 1/4)
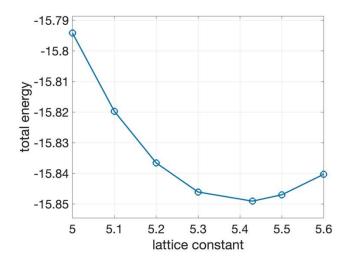
All atoms can be found at the multiple of

(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)

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

- 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 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

Plane-wave basis: solved in Fourier space; PAW is another solving method.

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

[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