

Lecture 13

Basis Sets

Atom-centered basis functions; plane-wave basis functions

Prof. David A. Kofke

CE 500 – Modeling Potential-Energy Surfaces


Department of Chemical & Biological Engineering

University at Buffalo

1-electron wavefunctions form the foundation for all electronic-structure calculations

- 1-electron wavefunction → “molecular orbital”
- Molecular orbitals are written as a linear combination of basis functions, the “basis set”
 - Molecular orbitals combined anti-symmetrically to form wavefunction
- Basis sets are developed and optimized for individual atoms, and combined across atoms to form the orbitals for a molecule
 - Basis functions are atomic orbitals
 - Separate into radial and spherical-harmonic parts

$$\phi_{nlm_A}(r_A, \theta_A, \phi_A) = f_n(r_A)Y_\ell^m(\theta_A, \phi_A)$$

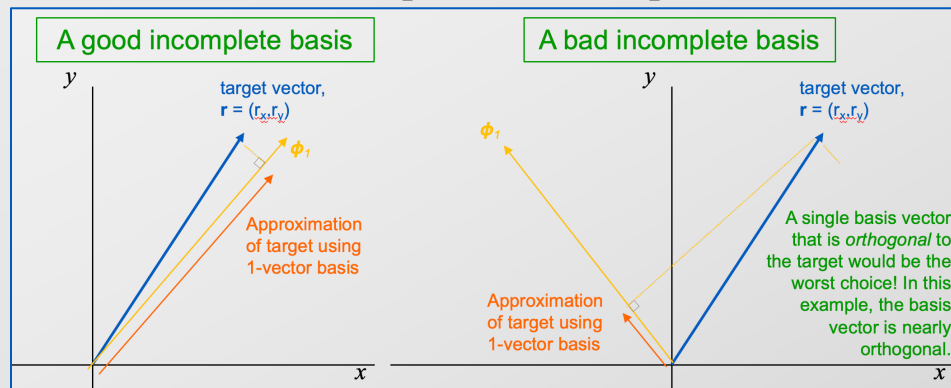
atom A 

In principle, the use of a basis set to represent a wavefunction is not an approximation

- If the basis set is *complete*, it can represent the wavefunction without adding any error (beyond that in the theory, e.g., HF)
- A complete basis set requires an infinite number of functions
 - So in practice, the use of a basis introduces approximation
 - Selection of basis set is important
 - Basis set specifies where electrons can and cannot be

Example for a 2-D space

Lecture 7



Several desirable features of a basis set can be identified. Different sets prioritize these differently

- Reflect the nature of the problem
 - Good accuracy with a minimal set
- Able to generate a complete basis set,
 - Well-defined basis set limit can be obtained
- Available in several hierarchical levels
 - each level provides a well-defined accuracy
 - hierarchy systematically converges the result towards the basis set limit.
 - Ideally the basis set convergence should be monotonic and fast
- As computationally efficient as possible
- Universal
 - Suitable for different methods (HF, DFT,...) and properties (energy, geometry, electrostatics,...)
- Available for all atoms, or at least a large fraction of the periodic table

A natural choice for basis functions starts from the 1-electron atomic orbitals

Lecture 7

- Slater-type orbitals (STO)

$$\chi_{\mu}(\mathbf{r}) = R_{\mu}^{\text{STO}}(r)Y_l^m(\theta, \phi)$$

$$R_{\mu}^{\text{STO}}(r) \propto r^{n-1} e^{-\zeta_{\mu}|\mathbf{r}-\mathbf{R}_{\mu}|}$$

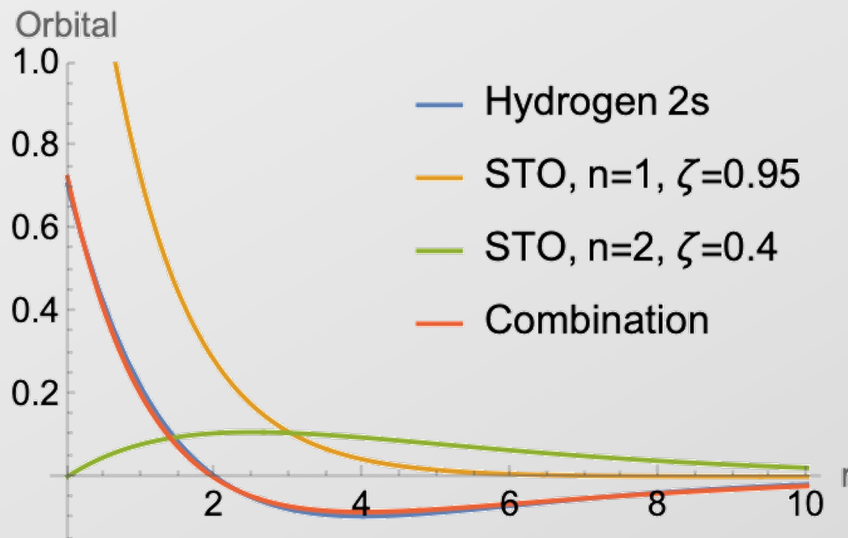
atom center

- Radial component is nodeless
 - Nodes complicate HF calculation
 - STO orbitals are not orthogonal
- Combinations of STO orbitals can mimic true atomic orbitals

Compare to H atomic orbital

$$R_{n,\ell}(r) = r^{\ell} P_{n,\ell}(r) e^{-(Z/na)r}$$

polynomial of degree $n-\ell-1$



Evaluation of 3- and 4-center cannot be done analytically with STO orbitals

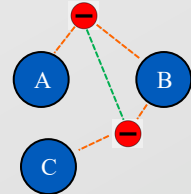
- Here is the 2-electron Coulomb integral

$$[11|22] = \int \varphi_1^*(\tau_1) \varphi_1(\tau_1) \frac{1}{r_{1,2}} \varphi_2^*(\tau_2) \varphi_2(\tau_2) d\tau_1 d\tau_2$$

- If the molecule has at least 3 atoms, we'll have an integral like this (for example)

$$\begin{aligned} & \int e^{-\zeta_1((x_1-x_A)^2+(y_1-y_A)^2)^{1/2}} e^{-\zeta_2((x_1-x_B)^2+(y_1-y_B)^2)^{1/2}} \\ & \times e^{-\zeta_2((x_2-x_B)^2+(y_2-y_B)^2)^{1/2}} e^{-\zeta_3((x_2-x_C)^2+(y_2-y_C)^2)^{1/2}} \\ & \times ((x_1-x_2)^2+(y_1-y_2)^2)^{-1/2} dx_1 dy_1 dx_2 dy_2 \end{aligned}$$

sqrt



z coordinate omitted for simplicity of example

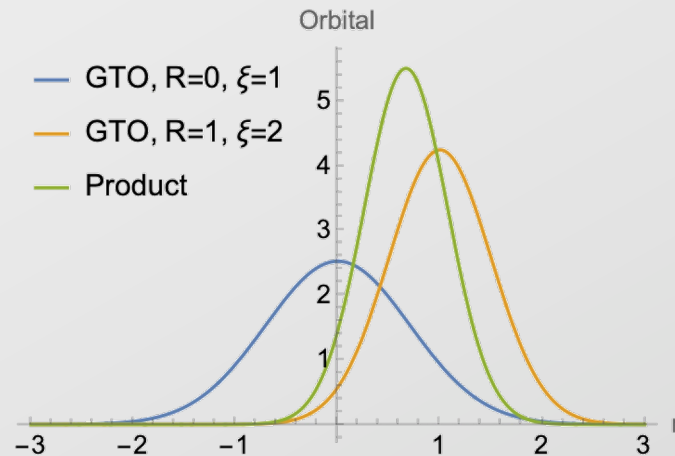
Gaussian-type orbitals (GTO) have advantages and are most-often used now

Lecture 7

$$\chi_{\zeta, l_x, l_y, l_z}(x, y, z) \propto x^{l_x} y^{l_y} z^{l_z} e^{-\zeta(x^2 + y^2 + z^2)}$$

$l_x = l_y = l_z = 0$ *s*-type orbital
 $l_x + l_y + l_z = 1$ *p*
 $l_x + l_y + l_z = 2$ *d*
etc.

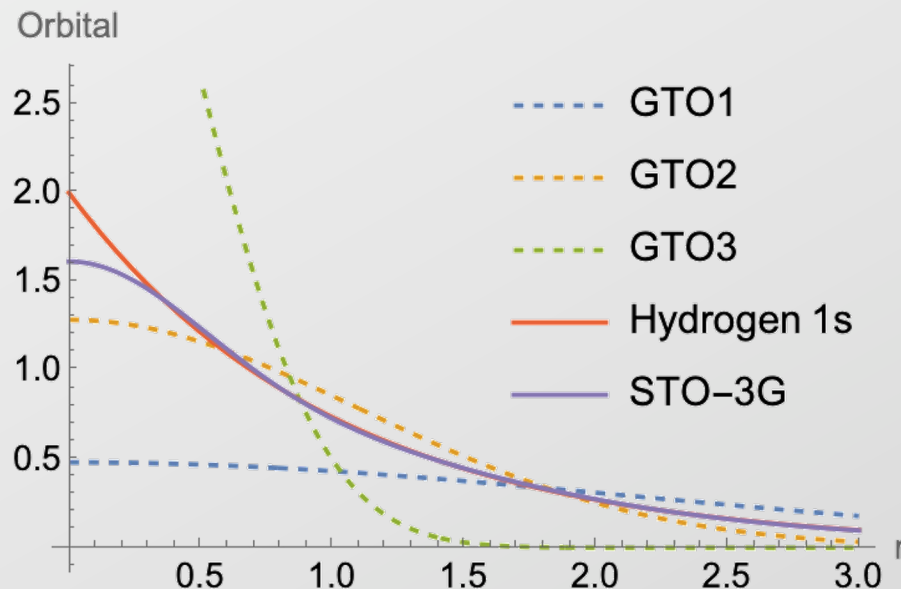
- Products of Gaussians with different centers are still Gaussians, at a new center
 - 4- or 3-center integrals become 2-center integrals
- Almost always centered at nucleus, but sometimes put elsewhere
 - Center of a bond, or between nonbonded atoms to improve vdW interactions



Gaussians have the wrong shape at the origin. *Contracted sets* are used to mimic STO

Lecture 7

- They also decay too fast for $r \rightarrow \infty$
- Several Gaussians added in a fixed way define a new basis function
- These are called contracted basis functions



Contracted orbitals add to the computation, but not as much as adding a basis function

- More integrals to evaluate, but size of Fock matrix unaffected

$$\begin{aligned}
 [11|22] &= \int \overbrace{(\varphi_{1a}(1) + \varphi_{1b}(1))^* (\varphi_{1a}(1) + \varphi_{1b}(1))}^{\text{Contracted basis functions}} \varphi_2^*(2) \varphi_2(2) \frac{1}{r_{12}} d1 d2 \\
 &= \int \underbrace{\varphi_{1a}^*(1) \varphi_{1a}(1)}_{\text{Primitive basis functions}} \varphi_2^*(2) \varphi_2(2) \frac{1}{r_{12}} d1 d2 \\
 &\quad + \int \varphi_{1a}^*(1) \varphi_{1b}(1) \varphi_2^*(2) \varphi_2(2) \frac{1}{r_{12}} d1 d2 \\
 &\quad + \int \varphi_{1b}^*(1) \varphi_{1a}(1) \varphi_2^*(2) \varphi_2(2) \frac{1}{r_{12}} d1 d2 \\
 &\quad + \int \varphi_{1b}^*(1) \varphi_{1b}(1) \varphi_2^*(2) \varphi_2(2) \frac{1}{r_{12}} d1 d2
 \end{aligned}$$

equal, for real basis

$$\Phi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_N(N) \end{vmatrix}$$

$\varphi_{1a} + \varphi_{1b}$

- Segmented sets* vary number of primitives: $(10s4p1d/4s1p) \rightarrow [3s2p1d/2s1p]$
 Non-H / H atoms \rightarrow e.g., 6,3,1
- The added cost is more than offset by the ease of evaluation of multi-center Gaussian integrals

Nevertheless, STO basis functions are still used in some circumstances

- Atomic and diatomic systems
- Semi-empirical methods, which introduce approximations that eliminate four-center integrals
 - E.g., “neglect of diatomic differential overlap”, NDDO
- DFT, when classical Coulomb energy is evaluated using fit of density function

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad \frac{1}{2} \sum_i^N \left\langle \varphi_i \left| \int \frac{\rho(\mathbf{r})}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \right| \varphi_i \right\rangle$$

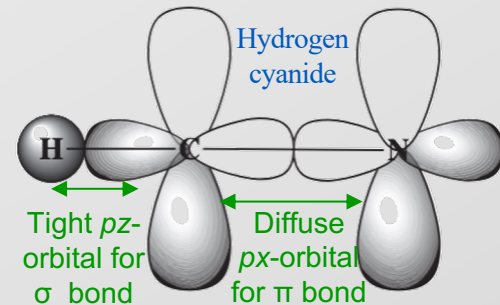
- and exchange functional replaces exchange integral

The zeta classification specifies the size of the basis set

- Minimal basis set is single-zeta (SZ)
 - Number of basis functions enough to provide only the necessary number of occupied orbitals
 - Typically $N/2$ functions for N electrons
 - E.g., one 1s function for H_2 or He
- Double zeta (DZ) uses 2 basis functions for each orbital
 - E.g., 1s and 1s' for H_2 or He, differing in value of ζ
 - Allows differential bonding with different atoms
- Valence and core orbitals may be different zeta
 - Split valence* basis set

$$\chi^{\text{STO}} \propto r^{-\zeta r} \quad \text{zeta}$$

Triple zeta (TZ), Quadruple zeta (QZ), 5Z, 6Z also seen

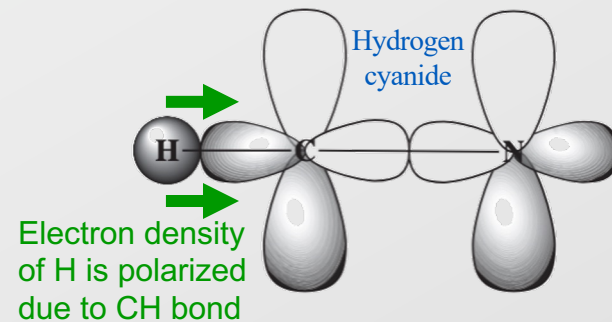


F. Jensen

Polarization functions are added to enable asymmetry that results from bonds

- A (spherical) s valence orbital does not describe well the polarization that accompanies a bond
 - Adding a p orbital can help
 - Likewise, adding d orbital to p , or f to d
- Polarization functions are particularly important in allowing correlation (post-HF)
 - Give electrons a way to avoid each other
 - Adding p , d , f gives angular freedom (e.g., opposite sides of nucleus)
 - Giving same angular momentum with different ζ gives radial freedom
 - Angular momentum convergence is slower than radial

“DZP” – double-zeta
plus polarization




Basis-set *balance* means to not overdo it. Excessive large- ℓ basis fns can cause artifacts

***Augmented* basis sets introduce basis functions that focus on a specific property**

- Usually basis sets are constructed for energy minimization
- Some properties depend on parts of wavefunction that do not contribute as much to the energy
 - E.g., more diffuse (low ζ) functions added for properties that are sensitive to the tail of the wavefunction (away from nucleus)
 - Polarizability is an example of such a property

Standard basis sets serve the purpose for most applications

- Don't try to design your own basis set
- Standard sets from websites or included in software

 **Basis Set Exchange** Download GitHub Feedback About Help Request a Basis set

All roles All

2ZaPa-NR
2ZaPa-NR-CV
3-21G
3ZaPa-NR
3ZaPa-NR-CV
4-31G
4ZaPa-NR
4ZaPa-NR-CV
5-21G
5ZaPa-NR
5ZaPa-NR-CV
6-21G
6-31++G
6-31++G*
6-31++G**
6-31++G**~J
6-31+G
6-31+G*
6-31+G*~J
6-31+G**
6-311++G
6-311++G(2d,2p)
6-311++G(3df,3pd)
6-311++G*

Need to interpret all this

search basis sets...

References for selected basis

Plain Text Get References

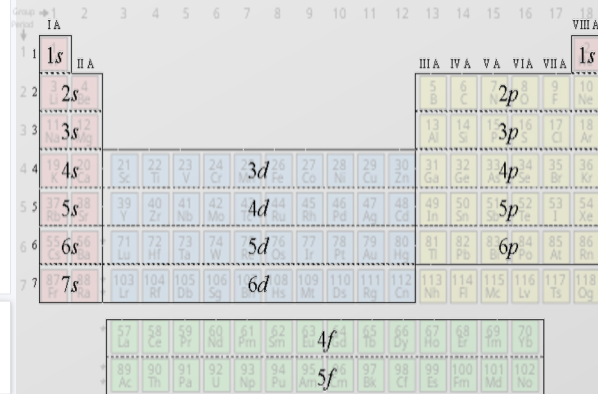
Total found: 689 basis sets

Select All Reset Selection

Download basis set

Format NWChem Get Basis Set Advanced

<https://www.basissetexchange.org/>



Periodic table showing orbital shells (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, 6s, 6p, 6d, 7s, 7p, 7d, 7f) and their corresponding principal quantum numbers and subshells.

Pople-style basis sets

- STO- n G: Slater-type orbitals, formed from n primitive GTOs
 - Single zeta, with GTO exponents part of fit to the STO
 - $n > 3$ is not considered worthwhile
 - E.g., carbon STO-3G: (6s3p) \rightarrow [2s1p]
- k - n lmG: split valence
 - k : PGTOs in core orbitals
 - n lm: number and split of PGTOs in valence
 - 3-21G: core contracts 3 PGTOs, inner valence 2 PGTOs, outer, 1 PGTO
 - 6-31G has same number of contracted basis functions, but more PGTOs
 - 6-311G: core 6 PGTOs, 3 valence functions from 3,1,1 PGTOs, resp.
- Observed method/basis error cancellation, e.g. B3LYP/6-31G*

Addition of diffuse functions, e.g., 6-31++G
+ \rightarrow diffuse s,p functions added on non-H
++ \rightarrow also diffuse s function added on H

Addition of polarization, e.g., 6-31+G(2df,2pd)
2 d -type and 1 f -type polarization on non-H atoms
2 p and 1 f on H atoms
6-311++G(3df,3pd) is largest Pople-style basis set
6-31G* \rightarrow 6-31G(d), and 6-31G** \rightarrow 6-31G(d,p)

A variety of named basis sets have been developed

- Dunning-Huzinaga
- Karlsruhe
- Atomic Natural Orbital (ANO)
- Correlation consistent (cc)
 - Add functions consistent with how they lower the energy (by accounting for correlation)
 - E.g., cc-pVDZ → correlation consistent polarized Valence Double Zeta

F. Jensen

Augmentation by diffuse functions indicated by *aug* prefix
→ 1 extra function for each angular momentum (spdf) present

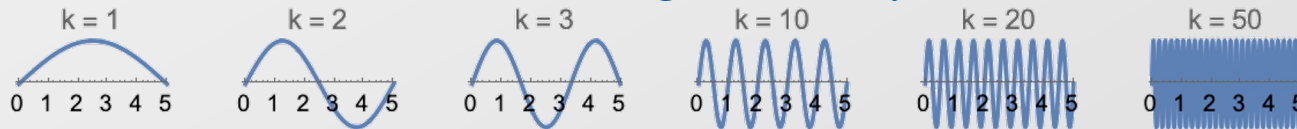
C indicates an added tight core function, e.g. cc-pCVDZ

Table 5.3 Composition in terms of contracted and primitive basis functions for the correlation consistent basis sets.

Basis	Hydrogen		Second row elements		Third row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
cc-pVDZ	2s1p	4s	3s2p1d	9s4p	4s3p2d	12s8p
cc-pVTZ	3s2p1d	5s	4s3p2d1f	10s5p	5s4p3d1f	15s9p
cc-pVQZ	4s3p2d1f	6s	5s4p3d2f1g	12s6p	6s5p4d2f1g	16s11p
cc-pV5Z	5s4p3d2f1g	8s	6s5p4d3f2g1h	14s8p	7s6p5d3f2g1h	20s12p
cc-pV6Z	6s5p4d3f2g1h	10s	7s6p5d4f3g2h1i	16s10p	8s7p6d4f3g2h1i	21s14p

Plane waves form a completely different class of basis functions

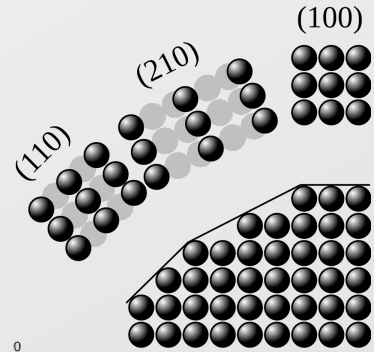
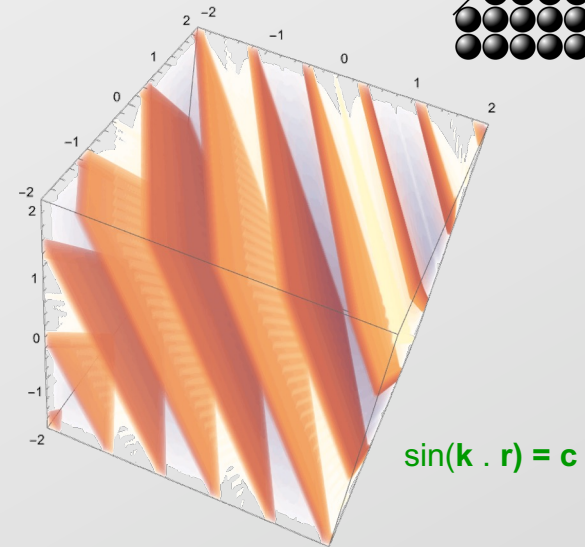
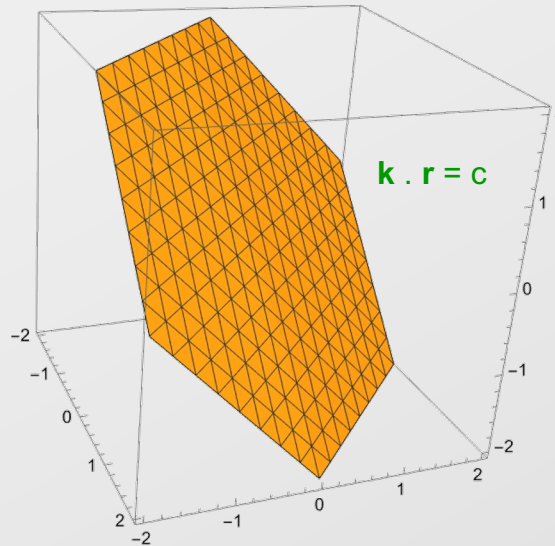
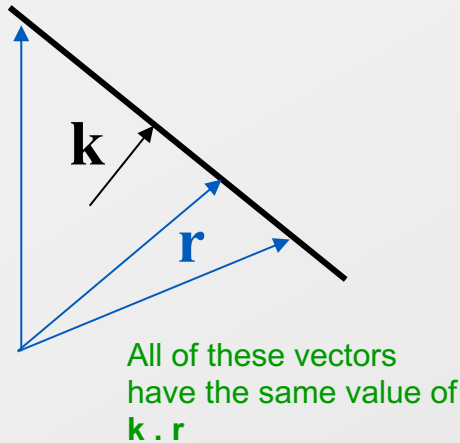
- Extended systems (e.g., crystals) suggest use of functions with “infinite” range
- Valence electrons of metals are like free electrons (PiaB), so their wavefunction provides a natural basis
 - In 1-D $\phi(x) = Ae^{ikx} + Be^{-ikx} = A' \cos kx + B' \sin kx$
 - Energy $E = k^2/2$
 - “wave number” \rightarrow large k , short wavelength, small k , long wavelength
 - k discretized according to the crystal unit cell translation vector \mathbf{t}



$$\mathbf{k} \cdot \mathbf{t} = 2\pi m$$

In 3 dimensions, a wave vector \mathbf{k} defines a set of planes

- $\mathbf{k} \cdot \mathbf{r} = \text{constant}$ defines a plane
- $\exp(i\mathbf{k} \cdot \mathbf{r})$ defines a *plane wave*



Plane wave basis sets typically use many more functions than atom-centered ones

- Number depends on
 - Largest wave vector (energy)
 - Volume of the unit cell
 - $M_{\text{PW}} = (1/2\pi^2)V E_m^{3/2}$
- Quality of basis set characterized by E_m
 - *E.g.*, $E_m = 200$ eV, 15 Å unit cell, $M_{\text{PW}} \sim 20,000$ functions
 - Integrals are easier to evaluate (not atom centered)
 - Does not depend on the actual system inside the cell
- Primarily for periodic systems, but also applied to molecules

Suggested Reading/Viewing

- Frank Jensen, Introduction to Computational Chemistry, 3rd ed., Wiley (2017).
 - Chapter 5
 - Available online via UB library
- Autschbach, chapter 11
- Cramer
 - Video 4.01: <https://www.youtube.com/watch?v=43Kd3yUG5io>