



TECHNISCHE  
UNIVERSITÄT  
WIEN

## **165.144 Simulation of condensed matter**

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## Summary chapter 6

- Interatomic potentials are usually derived from expanding the interaction energy as a sum of  $n$ -body potentials and subsequently finding the optimal parameters for the chosen potential
- Gases can usually be modeled with two-body potentials
- Solids can usually be modeled with modified two-body potentials, some of which have a term to weaken a bond based on the neighbors of an atom (bond-order potentials)
- Molecules can usually be modeled with a sum of bonded (up to 4-body terms for bonds, angles, dihedrals) and non-bonded (2-body terms for van-der-Waals and electrostatic interactions) terms
- Especially for molecules, we need a lot of parameters that we need to fit either to quantum-mechanical or experimental data



## Chapter 7: Interatomic potentials II + Quantum mechanics

## Transferability of force fields

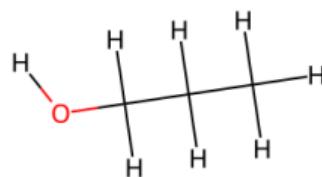
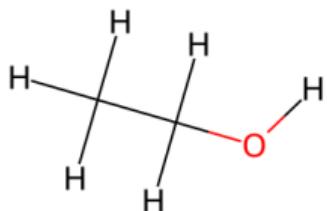
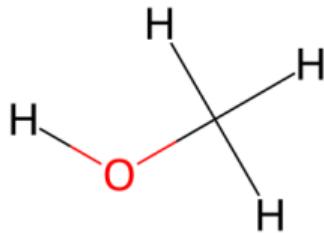
Very wide range of applications and systems:

- Force fields for a single atomic or molecular species under a wider range of conditions
- Force fields for specific class of molecules, e.g. the AMBER force field for proteins and nucleic acids
- Very general force fields model the entire periodic table

**Rule of thumb:** A good general force field can often outperform a poor specific force field

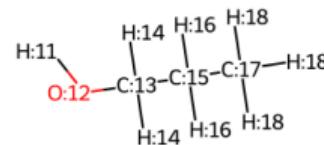
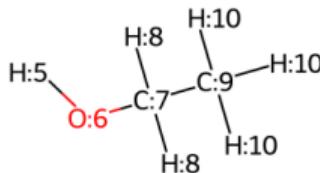
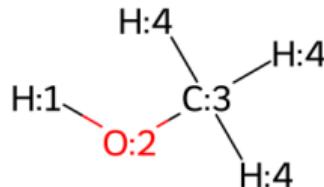
**Question:** How can we transfer parameters from one molecule to another?

## Transferability of force fields



How to best parametrize?

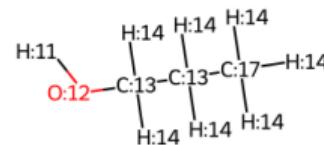
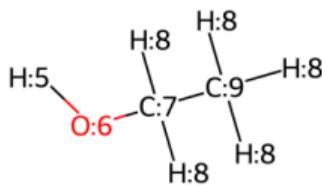
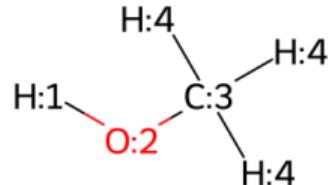
## Transferability of force fields: Specialized



- 4 atom types
  - 3 bond terms
  - 3 angle terms
  - 1 dihedral term
- 6 atom types
  - 5 bond terms
  - 7 angle terms
  - 4 dihedral term
- 8 atom types
  - 7 bond terms
  - 11 angle terms
  - 8 dihedral term

Total: 18 atom types, 15 bond terms, 21 angle terms, 13 dihedral terms

## Transferability of force fields: Specialized + atom types



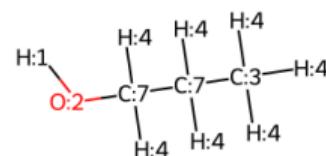
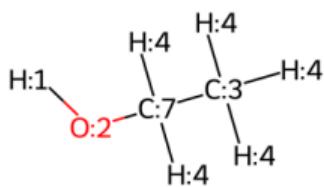
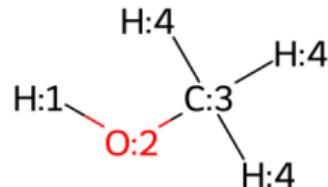
- 4 atom types
- 3 bond terms
- 3 angle terms
- 1 dihedral term

- 5 atom types
- 5 bond terms
- 7 angle terms
- 4 dihedral term

- 5 atom types
- 6 bond terms
- 9 angle terms
- 8 dihedral term

Total: 14 atom types, 14 bond terms, 19 angle terms, 13 dihedral terms

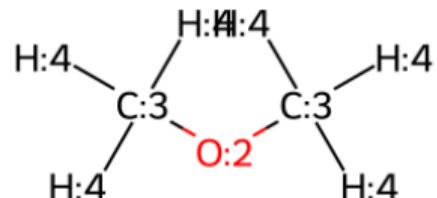
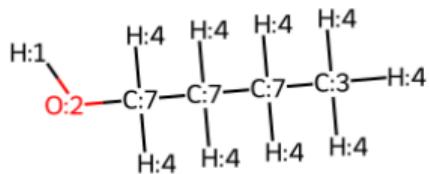
## Transferability of force fields: General + atom types



- 4 atom types
  - 3 bond terms
  - 3 angle terms
  - 1 dihedral term
- 5 atom types
  - 5 bond terms
  - 7 angle terms
  - 4 dihedral term
- 6 atom types
  - 6 bond terms
  - 9 angle terms
  - 8 dihedral term

Total: 5 atom types, 7 bond terms, 12 angle terms, 11 dihedral terms

## Transferability of force fields: New molecules



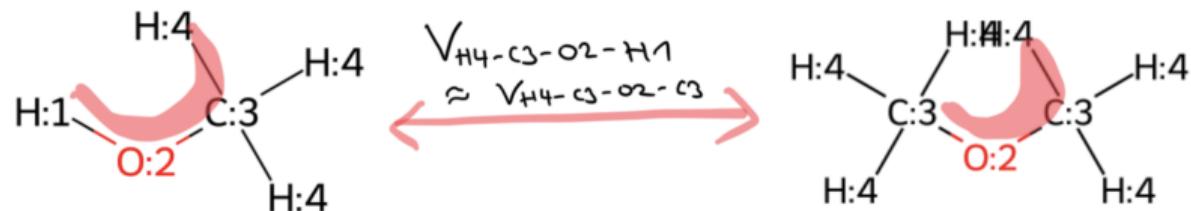
- 0 new atom types
- 0 new bond terms
- 0 new angle terms
- 0 new dihedral term

- 0 new atom types
- 0 new bond terms
- 1 new angle terms
- 1 new dihedral term

# Transferability of force fields: New molecules

## How to guess the missing parameters?

- Guess parameters



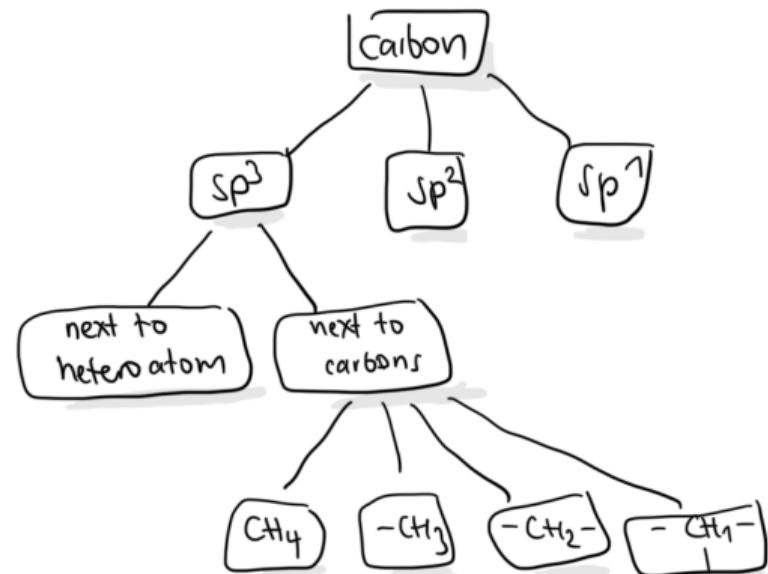
- Derive parameters from atomic properties
  - Reference bond lengths: Sum of the van-der-Waals radii + correction for bond order and electronegativity
  - Bond force constants: Proportional to product of effective atomic charges and inversely proportional to the cube of the equilibrium distance (Badger's rule)
  - Effective atomic charges are usually fit on diatomic molecules

# General force fields

## Examples:

- OPLS-All-Atom (OPLS-AA)
- CHARMM General Force Field (CGenFF)
- General AMBER Force Field (GAFF)
- Merck Molecular Force Field (MMFF)
- GROMOS

Decision tree:



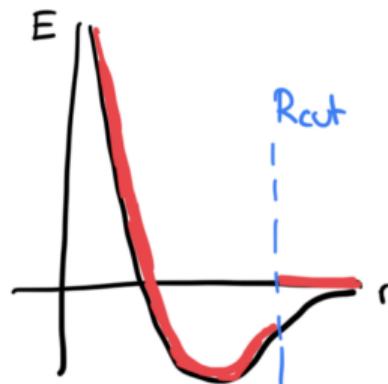
# Potential cutoffs

Most pair potentials

- Decay quickly with  $R$  (short sighted)
- But have a non-zero value for any finite  $R$  (non-bounded support)

We have already seen how computing all  $R_{IJ}$  in a simulation is computationally expensive. Further, for periodic boundary conditions, we will count atoms multiple times if we do not limit  $R_{IJ}$  to a maximum value (smaller than half of the shortest box length)

**Naive approach: Direct cutoff**

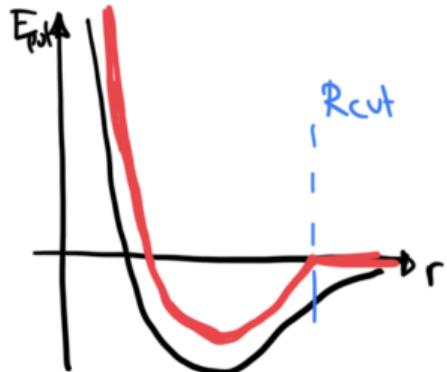


set  $E_{\text{pot}} = 0$  after  $R_{\text{cut}}$

X Discontinuity in  $E_{\text{pot}}$   
X Forces undefined

# Potential cutoffs

## Shifting

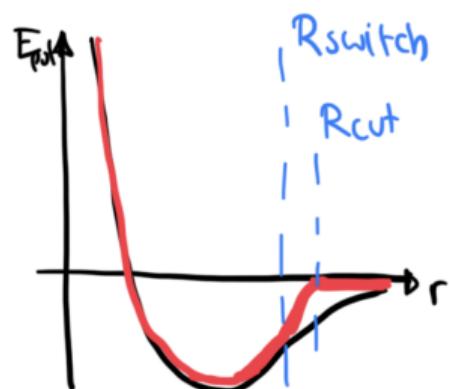


Rigid displacement: add  $E_{\text{pot}}(R_{\text{cut}})$  to whole function

✓  $E_{\text{pot}}$  continuous

✗ Forces undefined

## Switching



Multiplication with smooth function  
(1 at  $R_{\text{switch}}$ , 0 at  $R_{\text{cut}}$ ) e.g.  $\frac{e^{-1/t}}{e^{-1/t} + e^{-1/t}}$

✓  $E_{\text{pot}}$  continuous

✓ Forces defined

## Ewald summation

Assigning partial charges to atoms gives rise to a big problem: Coulombic interactions are long-range by nature, and a simple cutoff (like for the LJ potential) will introduce large errors.

How can we compute electrostatic interactions with periodic boundary conditions without using a cutoff?

### Approach (Ewald summation):

Originally developed in 1921 to compute the Madelung constant of ionic crystals. Works for periodic systems where the unit cell is charge-neutral.

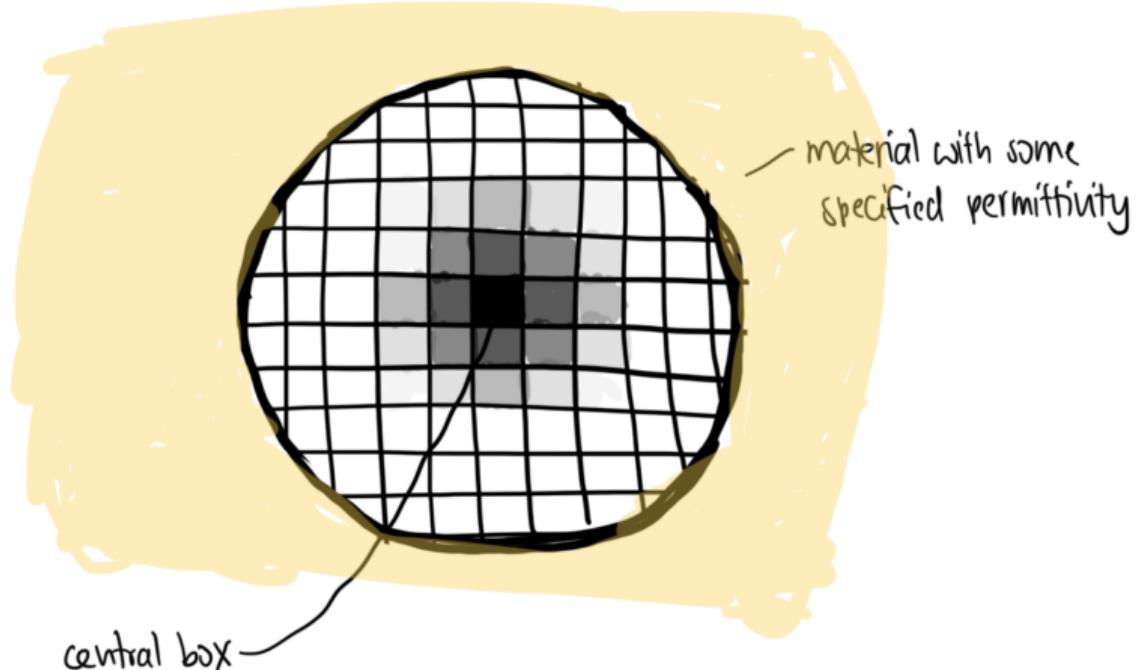
$$V_{\text{Coulomb}} = V_{\text{short-range}}(\vec{R}) + V_{\text{long-range}}(\vec{R})$$

↑  
easy to converge in  
real space

↑  
easy to convert in  
reciprocal space

## Ewald summation

Example: Cubic unit cell



## Ewald summation

$$V_{\text{Coulomb}} = \frac{1}{2} \sum_{\vec{n}} \sum_i \sum_j \frac{q_i q_j}{4\pi\epsilon_0 |\vec{r}_{ij} + \vec{n}|} \quad \text{with } i \neq j \text{ if } |\vec{n}| = 0$$

$$\vec{n} = (n_x L, n_y L, n_z L)$$

e.g.  $(0, 0, 0) \cdot L$  ... central box

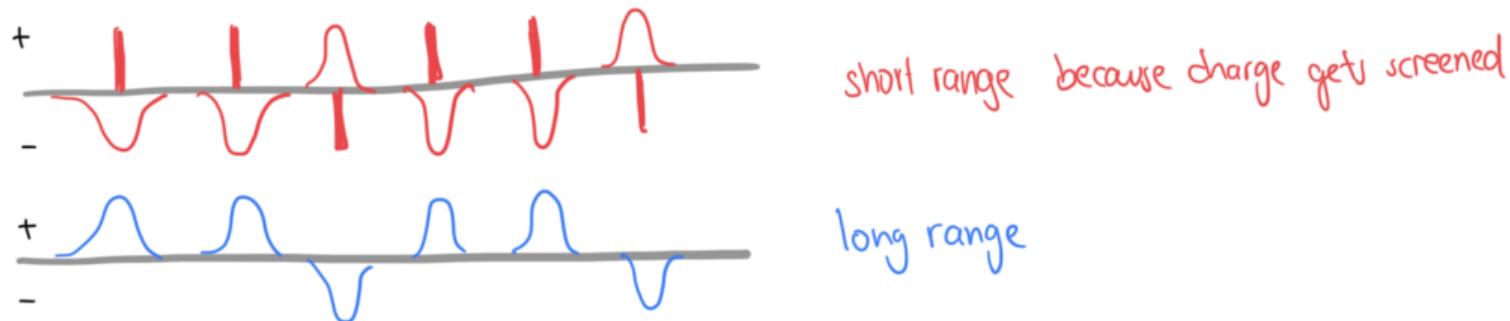
e.g.  $(1, 0, 0) \cdot L$  ... first image to the right

$$|\vec{n}| = 0, 1, \sqrt{2}, \sqrt{3}, 2, \dots \cdot L$$

... very slow convergence, and conditionally convergent (meaning that there is a mixture of positive and negative terms, which both diverge on their own)

... Reformulate using the following idea:  $\frac{1}{r} = \frac{f(r)}{r} + \frac{1-f(r)}{r}$  where we choose an appropriate function  $f(r)$  to get rapid conversion for both

## Ewald summation



We assume that the neutralising charge distribution is Gaussian:

$$\rho_i(\vec{r}) = \frac{q_i \alpha^3}{\pi^{3/2}} e^{-\alpha^2 r^2}$$

The interaction with point charges + neutralising charges then becomes:

$$V_{\text{short-range}} = \frac{1}{2} \sum_{\vec{n}} \sum_i \sum_j \frac{q_i q_j \operatorname{erfc}(\alpha |\vec{r}_{ij} + \vec{n}|)}{4\pi\epsilon_0 |\vec{r}_{ij} + \vec{n}|}$$

with  $\operatorname{erfc}(x) = \frac{2}{\pi} \int_x^\infty e^{-t^2} dt \dots$  which is our  $f(r)$  from the previous slide

## Ewald summation

This summation (which is the **short term, real space** summation) converges very rapidly and can be considered negligible after some cutoff:

- Narrow Gaussian (large  $\alpha$ ): Faster convergence
- Wide Gaussian (small  $\alpha$ ): Slower convergence
- $\alpha$  should always be chosen such that the only term in the series are those for  $|\vec{n}| = 0$

Contribution from second charge distribution (which is the **long-term, reciprocal space summation**) converges very rapidly in Fourier space:

$$V_{\text{long-range}} = \frac{1}{2} \sum_{k \neq 0} \sum_i \sum_j \frac{1}{\pi L^3} \frac{q_i q_j}{4\pi\epsilon_0} \frac{4\pi^2}{k^2} e^{-\frac{k^2}{4\alpha^2}} \cos(\vec{k} \cdot \vec{r}_{ij})$$

with the reciprocal vectors  $\vec{k} = \frac{2\pi \vec{n}}{L}$

- Narrow Gaussian (large  $\alpha$ ): Slower convergence
- Wide Gaussian (small  $\alpha$ ): Faster convergence
- Default:  $\alpha \simeq 5/L$  with 100-200 reciprocal vectors  $\vec{k}$

## Ewald summation

Correction term for the interaction of each Gaussian with itself in real-space:

$$V_{\text{corr}} = -\frac{\alpha}{\sqrt{\pi}} \sum_{k \neq 0} \frac{q_k^2}{4\pi\epsilon_0}$$

If surrounding medium is vacuum, then even another correction term is needed (for a conducting medium with infinite relative permittivity, no further correction is needed).

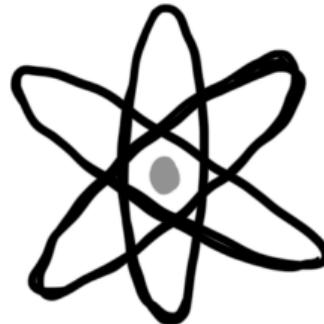
The Ewald sum is really accurate, but scales with  $N^2$

Faster: **Particle-mesh Ewald (PME)** which scales with  $N \log N$ :

- Real space ("particle" part of PME) as above, but Fourier space ("mesh" part of PME) uses the fast Fourier transform instead.
- Since FFT only works with discrete data, we have to fit our atomic point charges on continuous coordinates to a grid-based charge distribution.

## A brief overview of quantum mechanics

Previously, we have used quantum mechanics (QM) to obtain reference values for parametrizing a force-field. We will also use it in the exercises, so it is important to understand at least the very basics. If you are familiar with QM, feel free to skip the following slides.



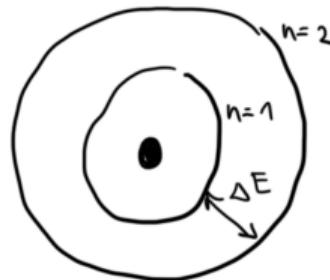
# Basic concepts

1900 Plank: Quantization of light

$$E = h\nu = \hbar\omega$$

↑ energy      ↑ constant      ↑ frequency

1913 Bohr: Quantized electron orbits



1926 Schrödinger: Wave equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x) \Psi$$

or  $E\Psi = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x) \Psi$

1905 Einstein: Quantization due to photons

$$E = pc$$

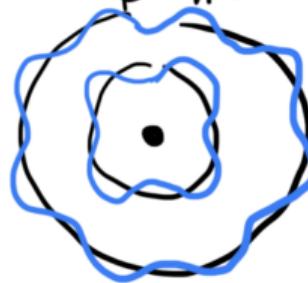
↑ momentum      ↑ for photons      ↑ speed of light

$$\omega = ck$$

↑ wave number =  $\frac{2\pi c}{\lambda}$

1924 De-Broglie: Standing wave model

$E = \hbar\omega$  and  $p = \hbar k$  also valid for particles



1926 Born: Wave = probability amplitude

$|\Psi|^2$  ≈ probability of finding a particle at a given location

# Basic concepts

The Schrödinger equation can actually be derived starting with the classical energy of a particle, and the de-Broglie relation:

In 1D

$$E = \frac{p^2}{2m} + V(x)$$

$$\text{(with } E_k = \frac{1}{2}mv^2 = \frac{p^2}{2m})$$

$$\text{with } E = \hbar\omega \\ p = \hbar k$$

multiply by wavefunction

$$\text{with } \Psi = e^{-i\omega t} \cdot \underbrace{Ae^{ikx}}_{\Psi'}$$

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V(x)$$

$$\hbar\omega \Psi = \frac{\hbar^2 k^2 \Psi}{2m} + V(x) \Psi$$

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi}$$

$$\hbar\omega e^{-i\omega t} \Psi' = -\frac{\hbar^2}{2m} e^{-i\omega t} \frac{\partial^2 \Psi'}{\partial x^2} + V(x) e^{-i\omega t} \Psi'$$

$$\boxed{E\Psi' = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi'}{\partial x^2} + V(x) \Psi'}$$

$$\text{Assume general wave } \Psi = A e^{i(kx - \omega t)}$$

$$\Rightarrow \frac{\partial \Psi}{\partial t} = -i\omega \Psi$$

$$\rightarrow \omega \Psi = i \frac{\partial \Psi}{\partial t}$$

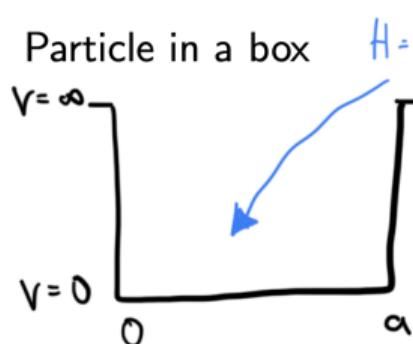
$$\Rightarrow \frac{\partial^2 \Psi}{\partial x^2} = -k^2 \Psi$$

$$\rightarrow k^2 \Psi = -\frac{\partial^2 \Psi}{\partial t^2}$$

Hamilton operator

$$\triangleq H\Psi = E\Psi$$

## Simple cases

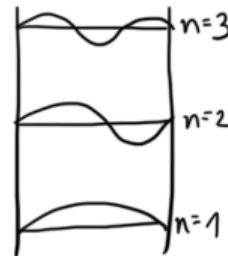


$$H = -\frac{\hbar^2}{2m} \nabla^2 \rightarrow -\frac{\hbar^2}{2m} \nabla^2 \psi_n = E_n \psi_n$$

$$\psi_n(0) = \psi_n(a) = 0$$

$$\rightarrow \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$



Hydrogen atom

$$H = -\frac{\hbar^2}{2me} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2 e}{r}$$

or  $-\frac{\nabla^2}{2} - \frac{Z}{r}$  in atomic units

$$\psi(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

radial solution  $U = rR$

$$U = N_{nl} e^{-2l/n} \sum_{j=0}^{n-l-1} c_j r^{l+j+1}$$

angular solution  
Spherical harmonics

$\hookrightarrow$  orbitals



# Slater determinants and the variational principle

For systems with more than one electron, we need to satisfy some boundary conditions:

- we can use one-electron orbitals (= wavefunctions) to build many-electron wavefunctions

→ but only describes noninteracting particles!

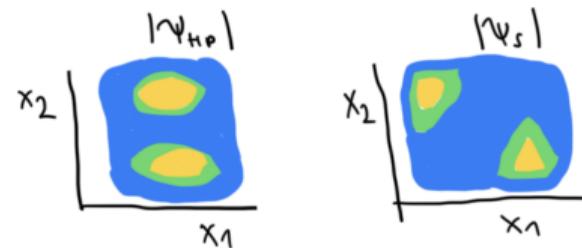
→ Hartree-Product  $\Psi_{\text{HP}}(x_1, x_2) = \Psi(x_1) \cdot \Psi(x_2)$  (for 1 dimension)

→ not correct for indistinguishable particles!

→ Slater determinant  $\Psi_s(x_1, x_2) = \frac{1}{\sqrt{2}} [\Psi(x_1)\Psi(x_2) - \Psi(x_2)\Psi(x_1)]$  antisymmetric

Example: 2 electrons in 1D box occupying

the first two states of  $\Psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$



Variational principle: Ground state = state with lowest energy of all possible anti-symmetric  $\Psi$  with energy  $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$

## Basis sets

Instead of the actual solutions for e.g. the hydrogen atom, we can use a superposition of simpler functions, such as Gaussians

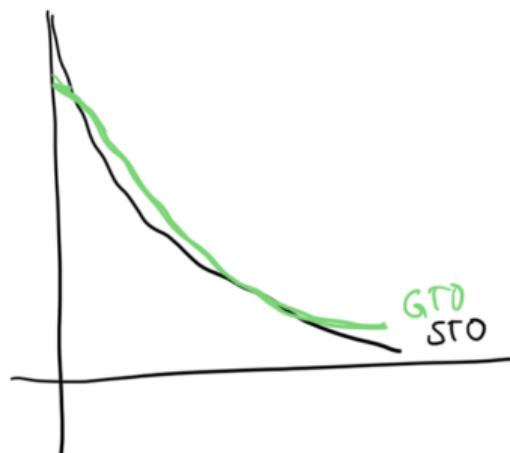
Atomic orbitals:  $\phi(\vec{r}) = R_{nl}(\vec{r}-\vec{R}_n) Y_{lm}(\theta, \varphi)$

Instead of computing  $R_{nl}$ , we could fit them

using

$$R_{nl}^S(r) = N_{nl} P_{nl}(r) e^{-\xi_j r} \dots \text{Slater-type orbital STO}$$

where we have to find  $\xi_j$  ( $= \frac{2}{n}$  for hydrogen)



Even simpler: Fit each STO with a sum of Gaussians,  
e.g. 3 (= STO-3G basis set)

This is beneficial since we have to evaluate integrals

like  $\sum_j \sum_{M_1 M_2} c_{M_1}^{j*} c_{M_2}^j \langle \phi_{M_1} \phi_{M_2} | \frac{1}{r_{12}} | \phi_{M_2} \phi_{M_1} \rangle$

which is very easy with Gaussians!

# Beyond hydrogen atoms

Many-electron atoms and many-nuclei systems: electronic Schrödinger equation

$$H = T_e + V_{eN} + V_{ee} + T_N + V_{NN}$$

↑ kinetic energy electrons      ↑ attraction between electron and nuclei      ↑ repulsion between electrons      ↑ kinetic energy nuclei      ↑ repulsion between nuclei

$$T_e = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2$$

$$V_{eN} = \sum_{i,A} \frac{1}{4\pi\epsilon_0} \frac{-2ze^2}{|\vec{r}_i - \vec{R}_A|}$$

$$V_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$T_N = -\sum_A \frac{\hbar^2}{2mA} \nabla_A^2$$

$$V_{NN} = \frac{1}{2} \sum_{A \neq B} \frac{1}{4\pi\epsilon_0} \frac{2z^2 e^2}{|\vec{R}_A - \vec{R}_B|}$$

Molecules (chemical bonding)

Molecular orbitals = Linear combination of atomic orbitals  $\Psi = \sum c_i \phi_i$

$$\text{eg. for } H_2 : \quad \Psi_{H_2}^{(n)} = c_A^{(n)} \phi_A(\vec{r} - \vec{R}_A) + c_B^{(n)} \phi_B(\vec{r} - \vec{R}_B)$$

$\textcircled{A}-\textcircled{B}$  → if we already know  $\phi_A$  and  $\phi_B$  (here the 1s orbitals from A and B), we only need to compute  $c_A^{(n)}$  and  $c_B^{(n)}$  !

$$\rightarrow H(c_A^{(n)} \phi_A + c_B^{(n)} \phi_B) = E_n(c_A^{(n)} \phi_A + c_B^{(n)} \phi_B) \Rightarrow \begin{bmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = E \begin{bmatrix} 1 & S_{AB} \\ S_{BA} & 1 \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix}$$

$$\begin{aligned}
 H_{VM} &= \int \phi_V^* H \phi_M d\vec{r} \\
 &= \langle \phi_V | H | \phi_M \rangle \\
 S_{VM} &= \langle \phi_V | \phi_M \rangle
 \end{aligned}$$

# Hartree Fock

Instead of computing all pairs of interactions, we compute interactions with the "mean field" of the other particles

Iterative procedure:

- Guess a wavefunction, compute the mean field
  - Solve the HF-version of the Schrödinger equation to get the wavefunction
  - Recompute the mean field
  - Recompute the wave function
- $\xrightarrow{\text{repeat until } \nabla \text{ does not change anymore}}$   
= self-consistent field procedure

HF equation:  $\hat{F} \phi_n = E_n \phi_n$  with  $\hat{F} = -\frac{\nabla^2}{2} - \sum_A \frac{Z_A}{|\vec{r} - \vec{R}_A|} + \sum_{\gamma} (\langle \phi_{\gamma} | \hat{w} | \phi_{\gamma} \rangle - |\phi_{\gamma}\rangle \langle \phi_{\gamma}| \hat{G})$

Change to basis  $\varphi_i$ :  $\phi_n = \sum_i c_i \sin \varphi_i$

one-electron Hamiltonian

$\hat{w}$  ≈ contribution from interactions  
 $\gamma$ ... occupied states

$\rightarrow \boxed{\hat{F} \vec{c}_n = E_n S \vec{c}_n}$  with  $F_{ij} = \langle \varphi_i | \hat{F} | \varphi_j \rangle$  and  $S_{ij} = \langle \varphi_i | \varphi_j \rangle$   
Roothaan-Hall-equation