

# Forces and Relaxation

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- Literature:
  - S.O. Kasap “Principles of Electronic Materials and Devices”
  - D. Marx, J. Hutter “Ab Initio Molecular Dynamics”
  - R. Martin “Electronic Structure”



**DMR-2326558**

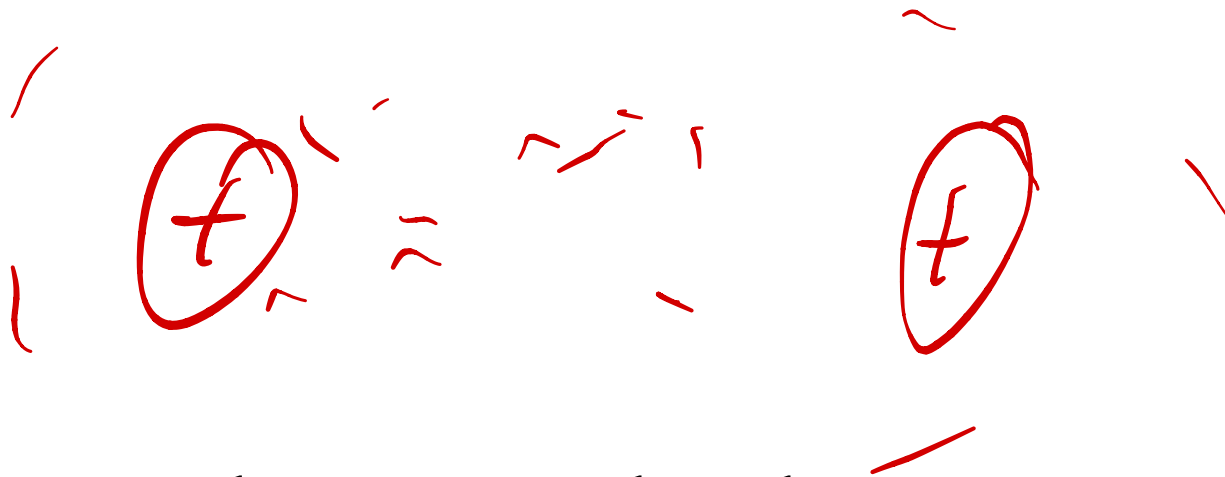


**I-MRSEC**

**DMR-1720633**

# Forces and Relaxation

- For this lecture: Classical nuclei, quantum-mechanical electrons



- Simple example:  $\text{H}_2^+$  molecule
- More complicated: Potential Energy surface in solids
- In practice: DFT to solve the underlying QM problem
- In practice: Forces within DFT
- Context: Problems and Applications

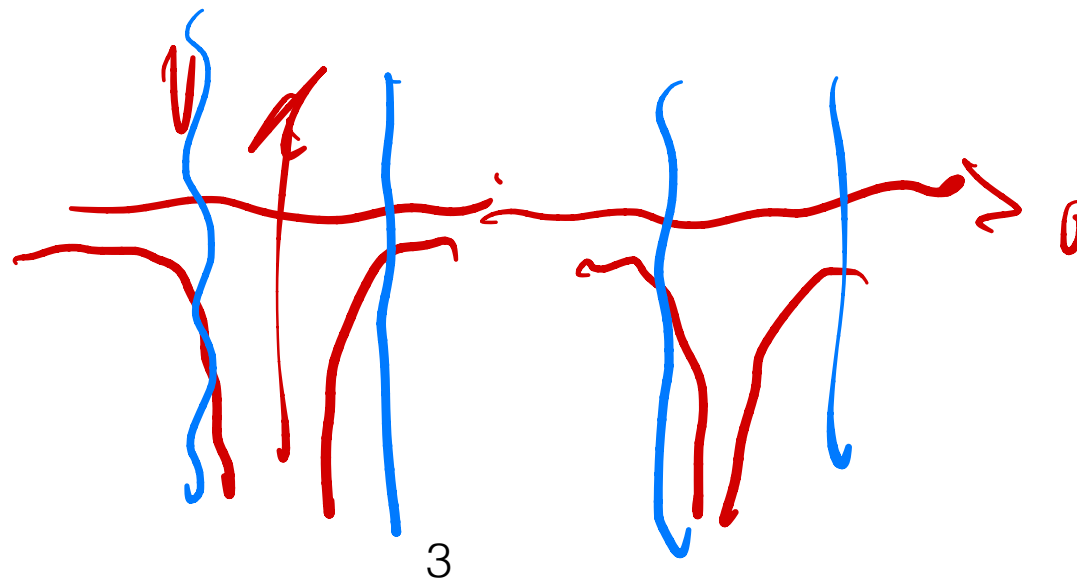
# Multiple Nuclei: What causes Forces?

- Simplest system with multiple nuclei is the  $\text{H}_2^+$  ion
- Two nuclei (protons), one electron
- Exact solution: from Schrödinger Equation in 3D

$$\hat{H} = \left( \hat{T}_{\text{el}} + \hat{V}_{ab} + \hat{V}_a + \hat{V}_b \right)$$

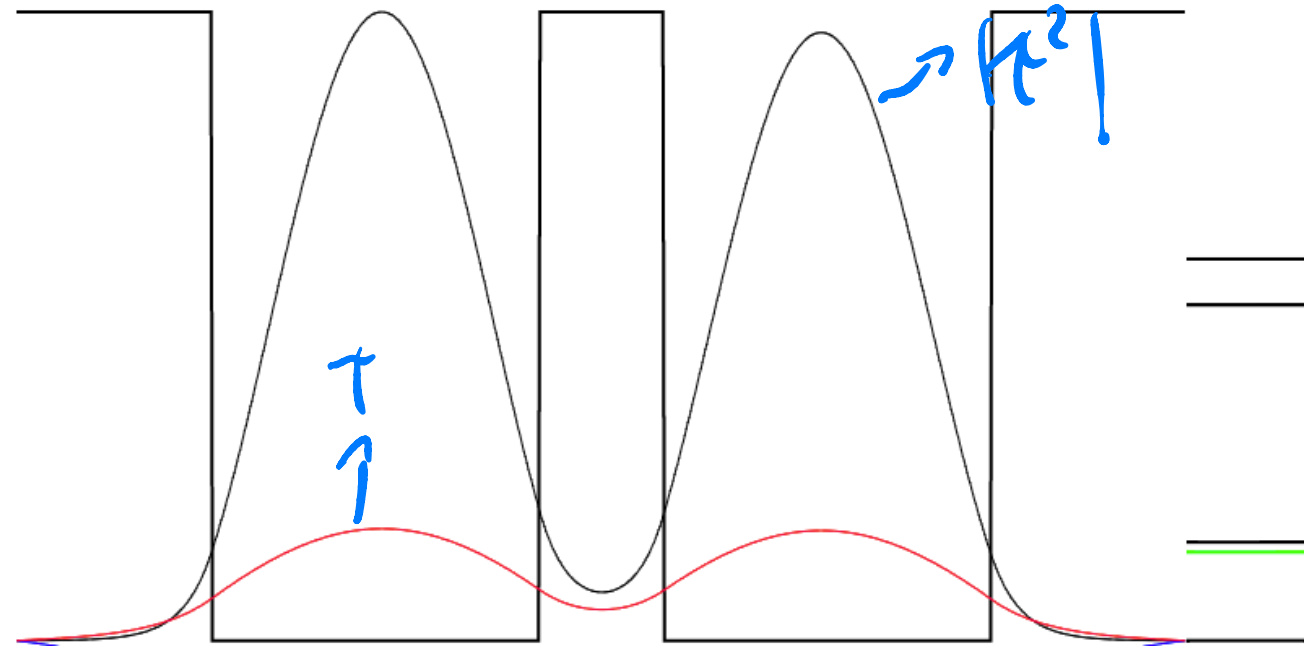
- Here: approach the problem in several steps
- First step: 1D and well potentials

$$\left( -\frac{\hbar^2}{2m} \Delta - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) \psi = E\psi$$

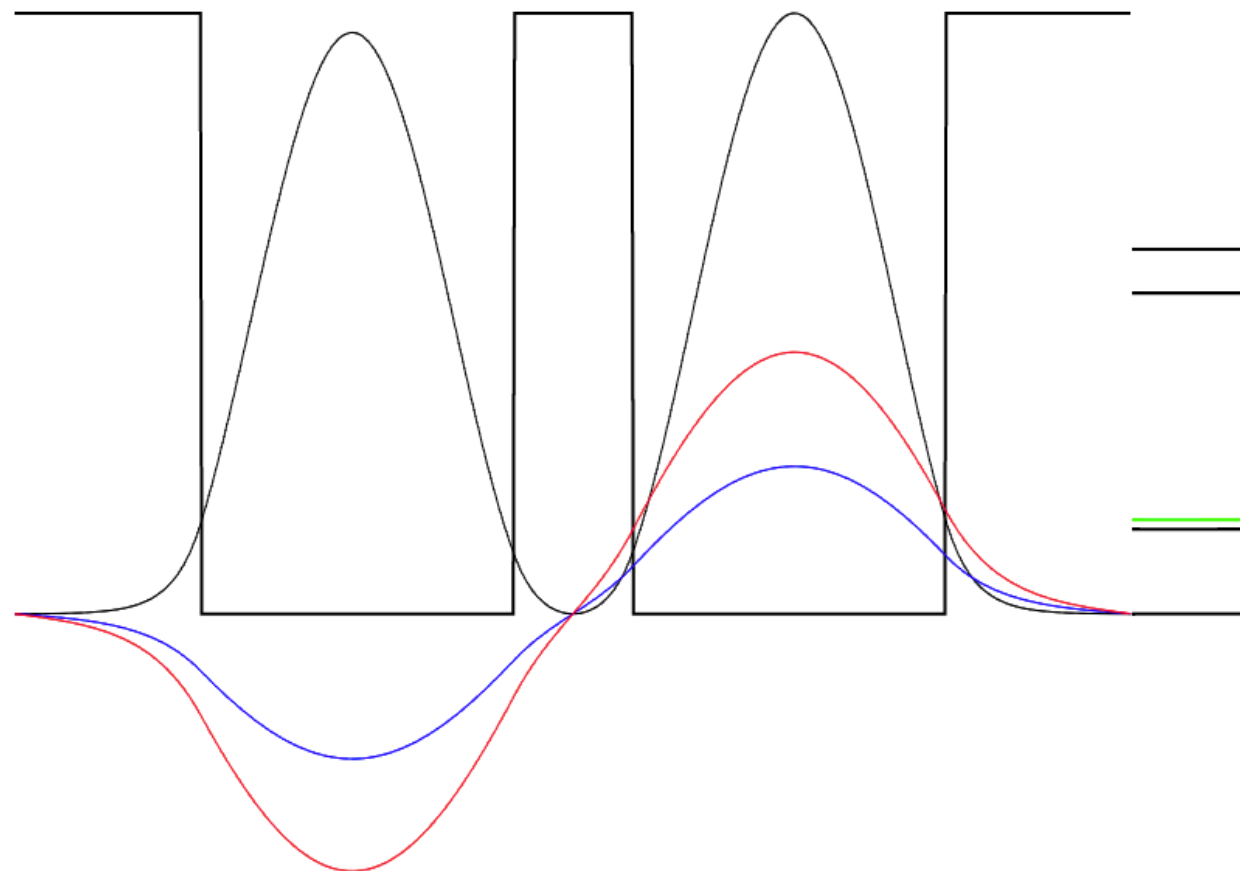


# Multiple Nuclei: Introduction

1D Arbitrary Potential Well

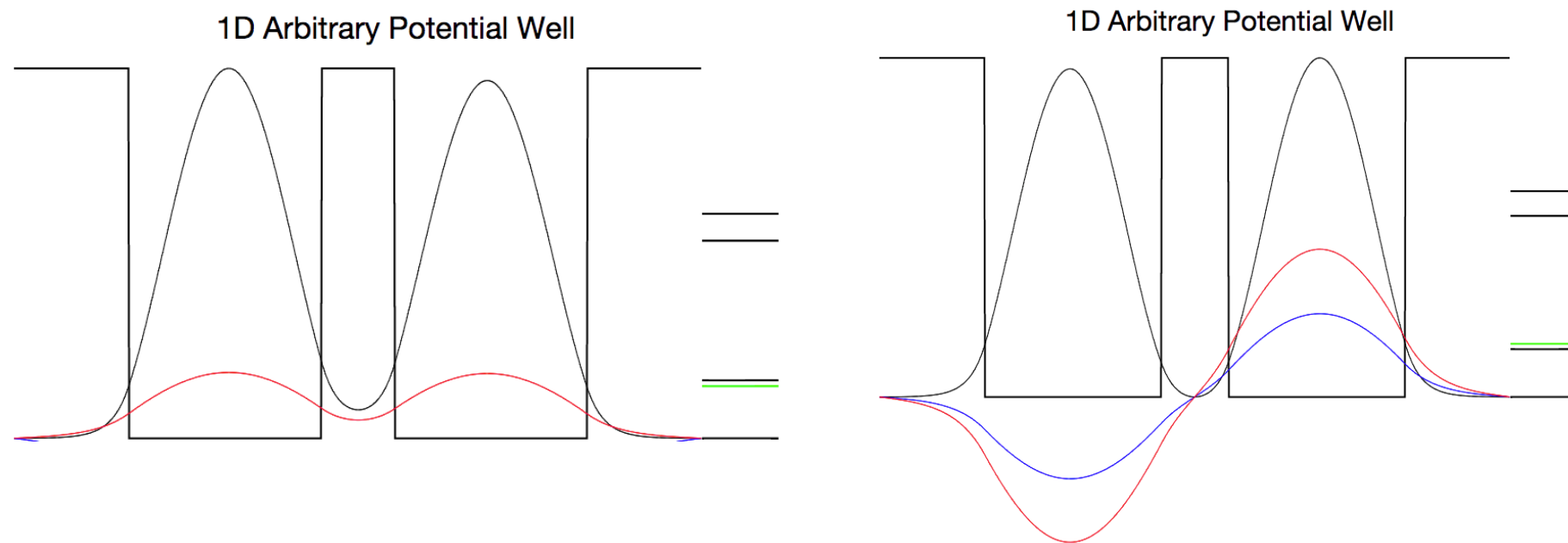


1D Arbitrary Potential Well



# Multiple Nuclei: Introduction

- Here: approach the problem in several steps
- First step: 1D and well potentials



- Second step: 1D and Coulomb potentials

[http://quells.github.io/QuantumWells/arbitrary\\_well.html](http://quells.github.io/QuantumWells/arbitrary_well.html)

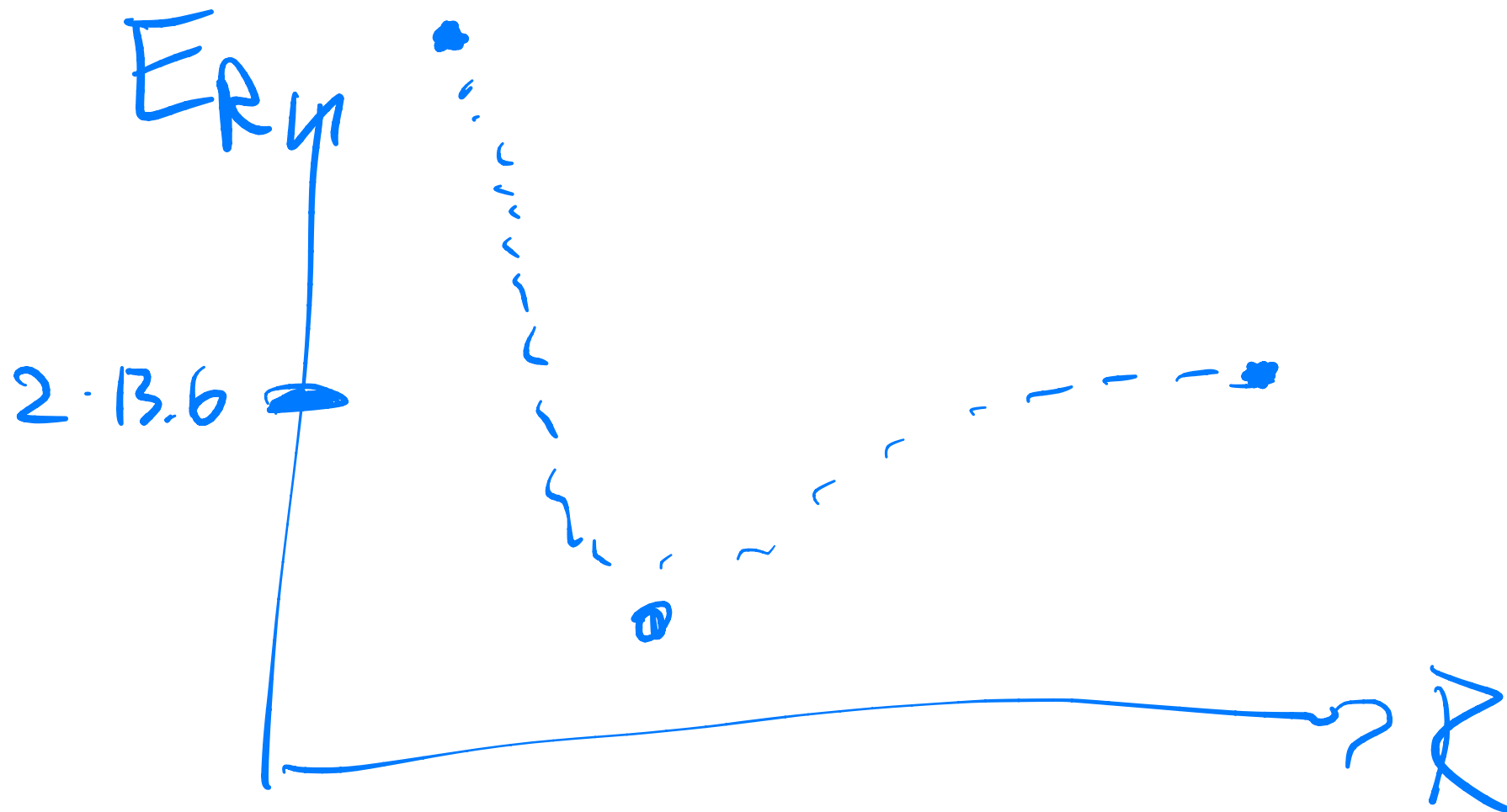
# Multiple Nuclei: What causes Forces?

- QM: Solution from Schrödinger equation:

$$\hat{H}\psi = E\psi$$

$$\hat{H}_{\mathbf{R}}(\mathbf{r})\psi_{\mathbf{R}}(\mathbf{r}) = E_{\mathbf{R}}\psi_{\mathbf{R}}(\mathbf{r})$$

- Thought experiment for H<sub>2</sub> molecule:

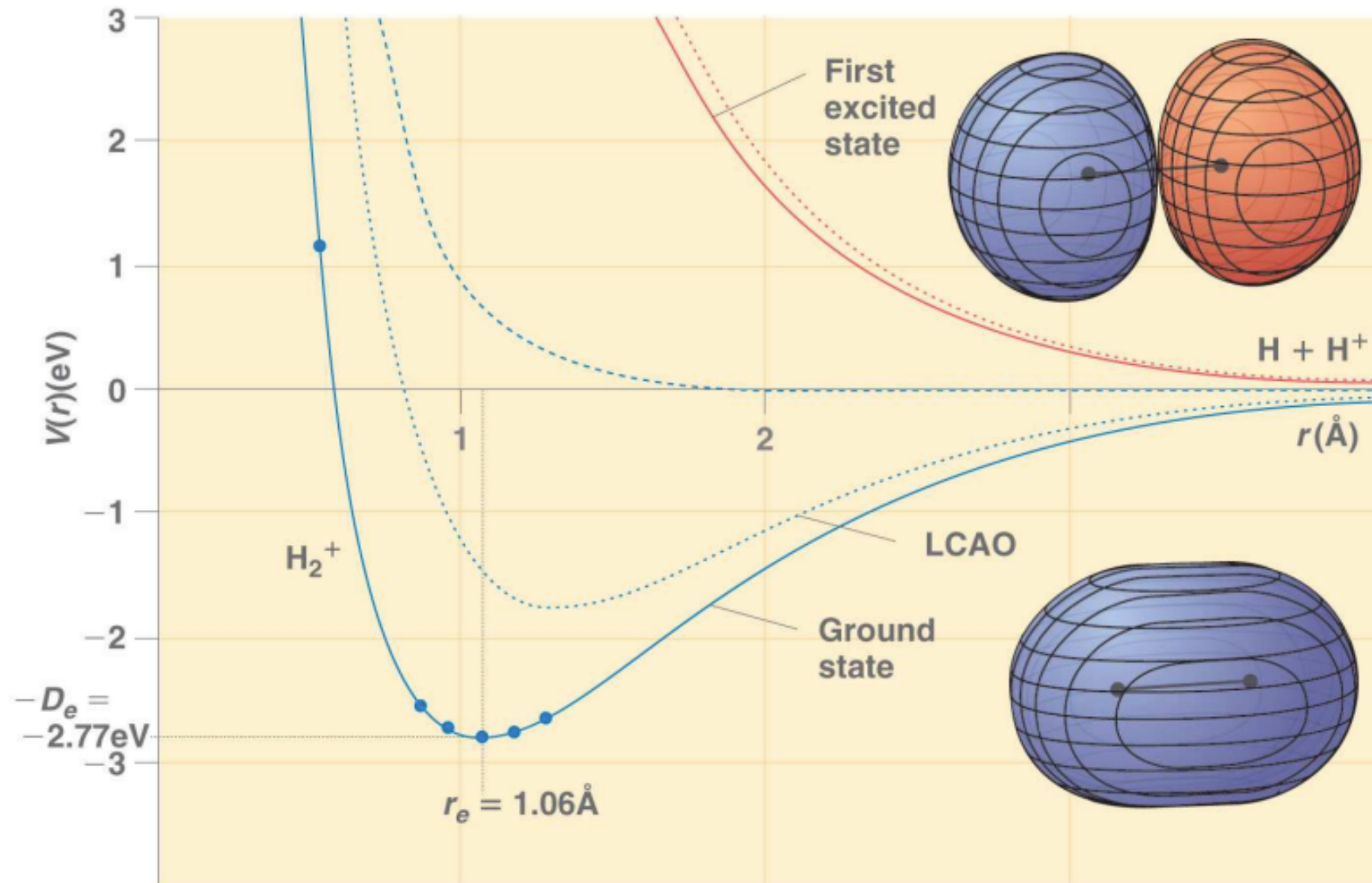


# Multiple Nuclei: $\text{H}_2^+$ ion

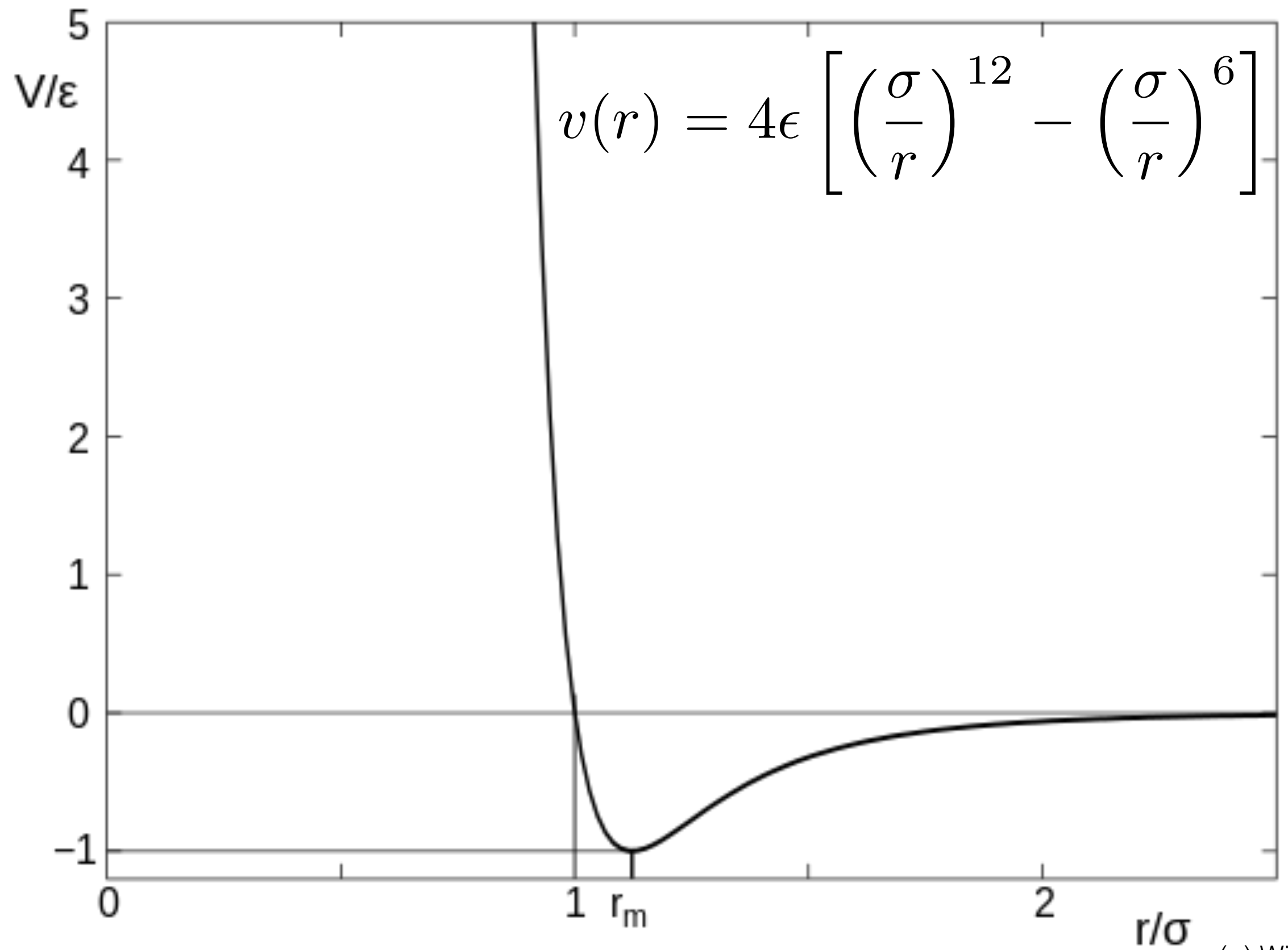
- what we plot here:

$$\hat{H}\psi = E\psi$$

$$\hat{H}_{\mathbf{R}}(\mathbf{r})\psi_{\mathbf{R}}(\mathbf{r}) = E_{\mathbf{R}}\psi_{\mathbf{R}}(\mathbf{r})$$



# Analytical example: Lennard Jones Potential

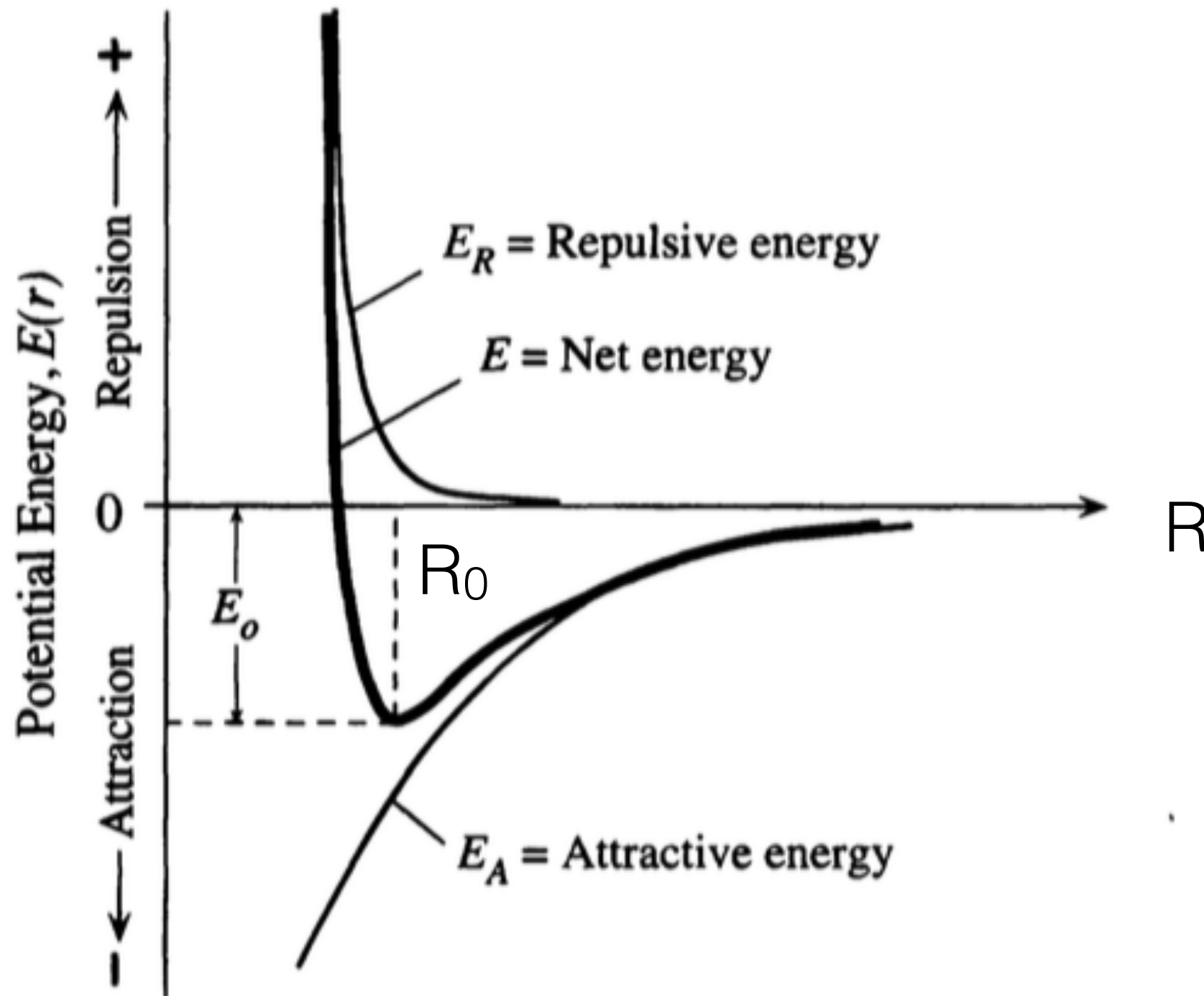


(c) Wikipedia



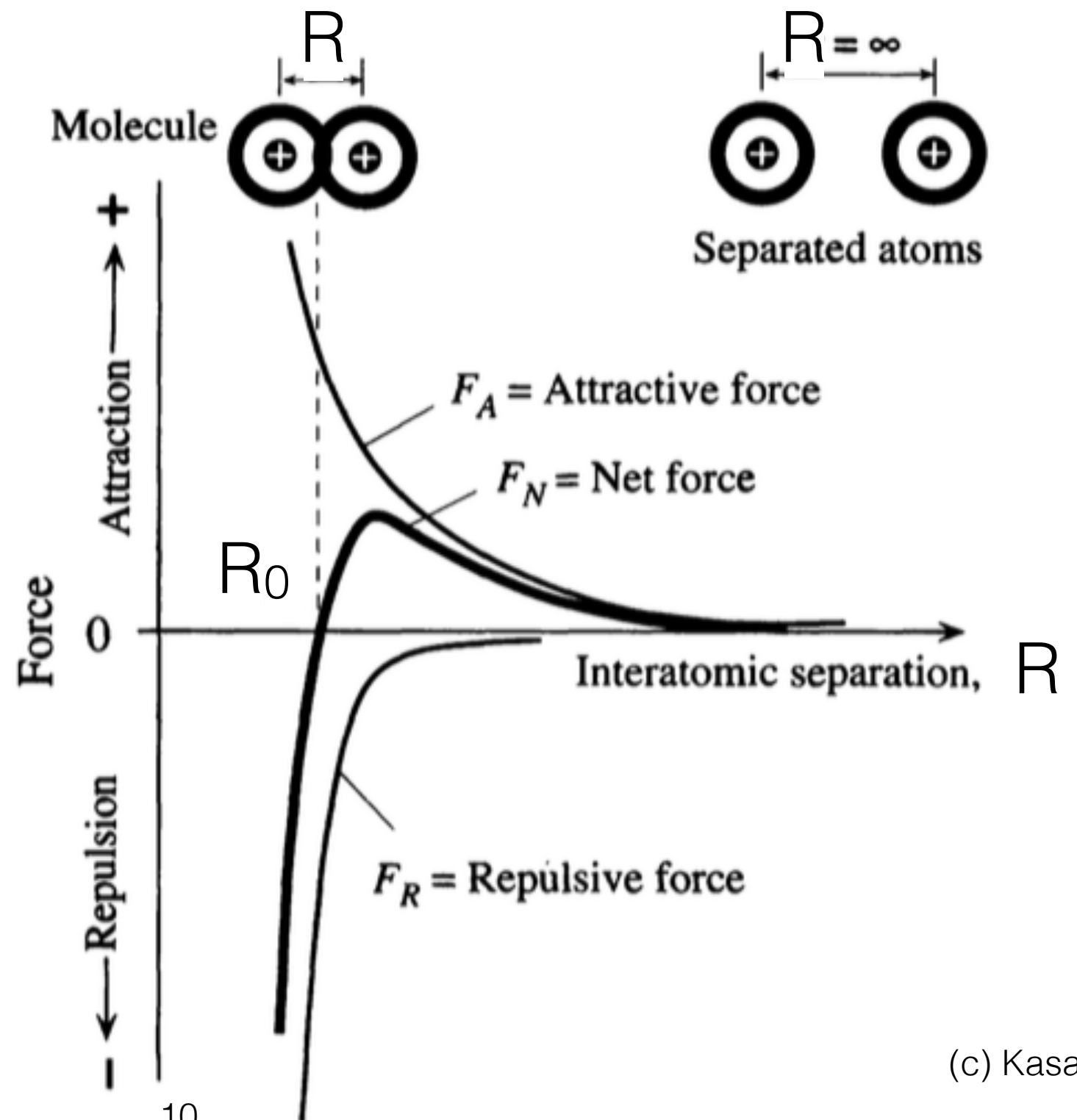
# Multiple Nuclei: What causes Forces?

- total energy can be viewed as sum of an attractive term and a repulsive term



# Bonding in Solids: Forces

- Force follows from energy:  $F(\mathbf{R}) = -\nabla E(\mathbf{R})$
- Equilibrium separation:  
Bond length  $R_0$
- Energy at that length:  
Bonding energy
- this overall picture works also for solids
- we can even use it to derive thermal expansion and bulk modulus
- (strong) directional dependence possible:  
Potential energy surface

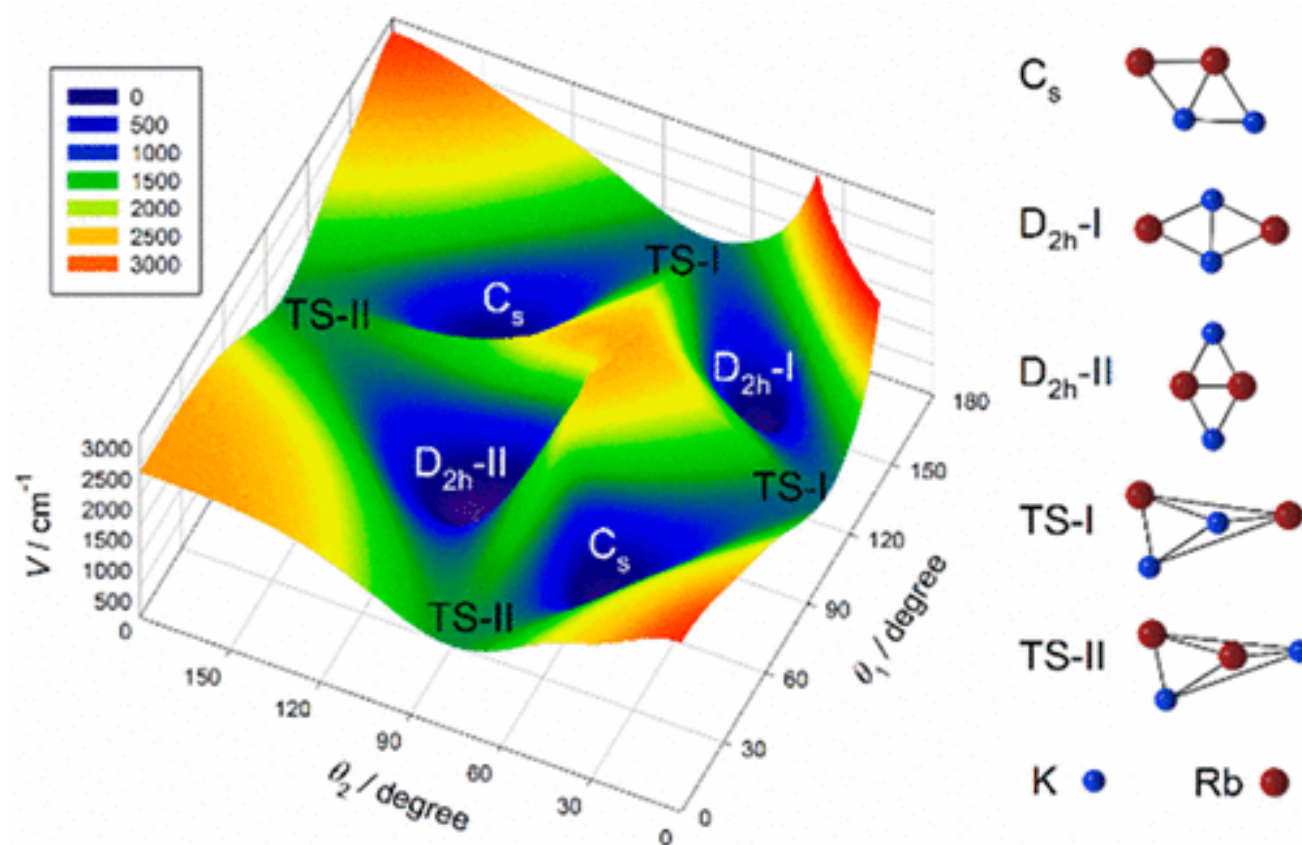


# Bonding in Solids: Quantum Mechanics

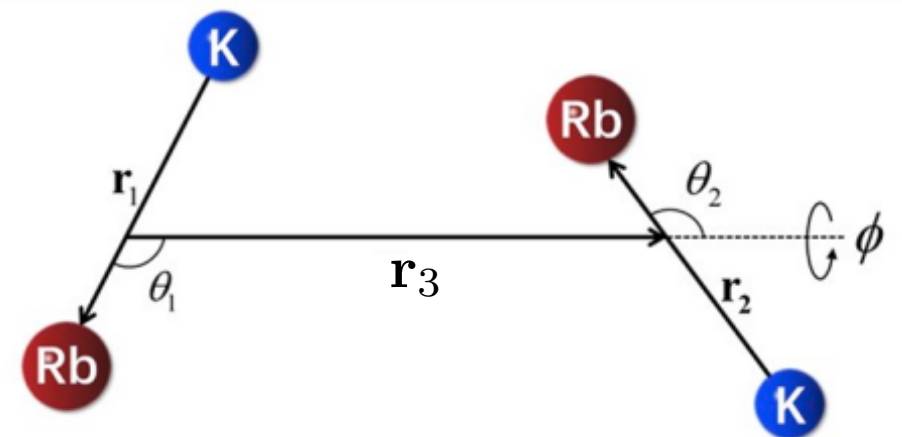
- More complicated for solids, but the concept of a “potential energy surface” holds; solve:

$$\hat{H}_{\mathbf{R}}(\mathbf{r})\psi_{\mathbf{R}}(\mathbf{r}) = E_{\mathbf{R}}\psi_{\mathbf{R}}(\mathbf{r})$$

- Example of a potential energy surface:



(c) J. Phys. Chem. Lett. 2020, 11, 7, 2605–2610

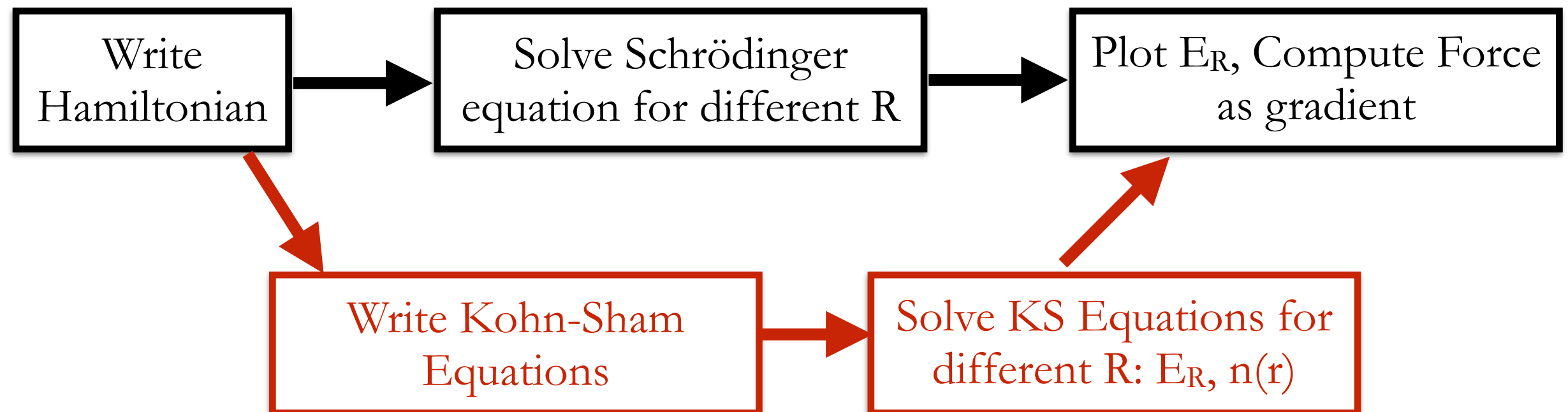


- Forces from gradient!

- 6 variables: Bond lengths and angles, hence a 6D potential energy surface
- Only 2 variables shown
- Pronounced directional dependence visible

# Forces and Relaxation

- Simple example:  $\text{H}_2^+$  molecule
- More complicated: Potential Energy surface in solids
- In practice: DFT to solve the underlying QM problem
- In practice: Forces within DFT
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# Forces in DFT: Hellmann-Feynman Theorem

- Still need to actually compute the forces, here within DFT

$$\mathbf{F}_I = -\nabla_I \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle = -\nabla E(\mathbf{R})$$

- Finite-difference method costly and inaccurate
- Instead: Analytical evaluation:

$$\nabla_I \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle =$$

$$\langle \Psi_0 | \nabla_I \mathcal{H}_e | \Psi_0 \rangle + \langle \nabla_I \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \langle \Psi_0 | \mathcal{H}_e | \nabla_I \Psi_0 \rangle$$

- Hellmann-Feynman theorem says:

$$\mathbf{F}_I^{\text{HFT}} = -\langle \Psi_0 | \nabla_I \mathcal{H}_e | \Psi_0 \rangle$$

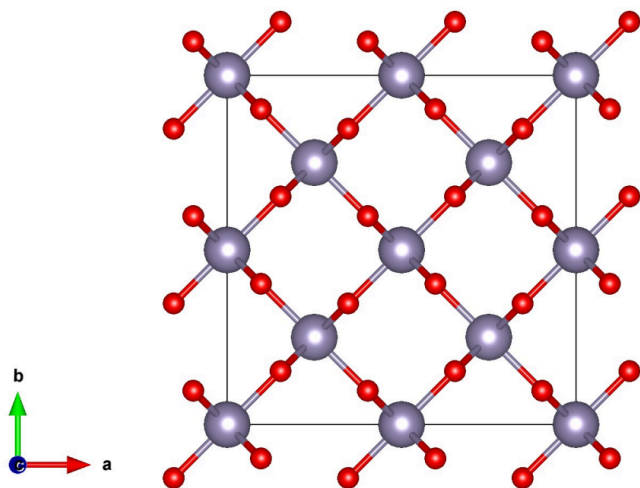
... if wave function is an exact eigenfunction

# Forces in DFT: Forces on atoms

- DFT total energy:  $E_{\text{tot}} = E_{\text{kin}} + E_{\text{loc}}^{\text{PP}} + E_{\text{nloc}}^{\text{PP}} + E_{\text{xc}} + E_{\text{ES}}$

$$\frac{\partial E_{\text{tot}}}{\partial R_{I,s}} = \frac{\partial E_{\text{loc}}^{\text{PP}}}{\partial R_{I,s}} + \frac{\partial E_{\text{nloc}}^{\text{PP}}}{\partial R_{I,s}} + \frac{\partial E_{\text{ES}}}{\partial R_{I,s}}$$

- Evaluate derivatives analytically; leads to expressions in terms of electron density+plane-wave coefficients (see Marx, Hutter)
- These are implemented in DFT codes
- Use this to “relax” atomic positions, i.e. move until  $F=0$



- Unit cell unchanged here (no change in shape and size)
- Update positions of the atoms in the cell using, e.g., gradient descent

- Tip: Relaxation can be slow (Plot forces, change stepsize)

# Forces in DFT: Forces on cells, Stress tensor

- If simulation cell is changed (in shape or size), electronic internal stress tensor is required:

$$\Pi_{uv} = -\frac{1}{\Omega} \sum_s \frac{\partial E_{\text{tot}}}{\partial h_{us}} h_{sv}^T \quad \mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$$

- Using total energy from previous slide:

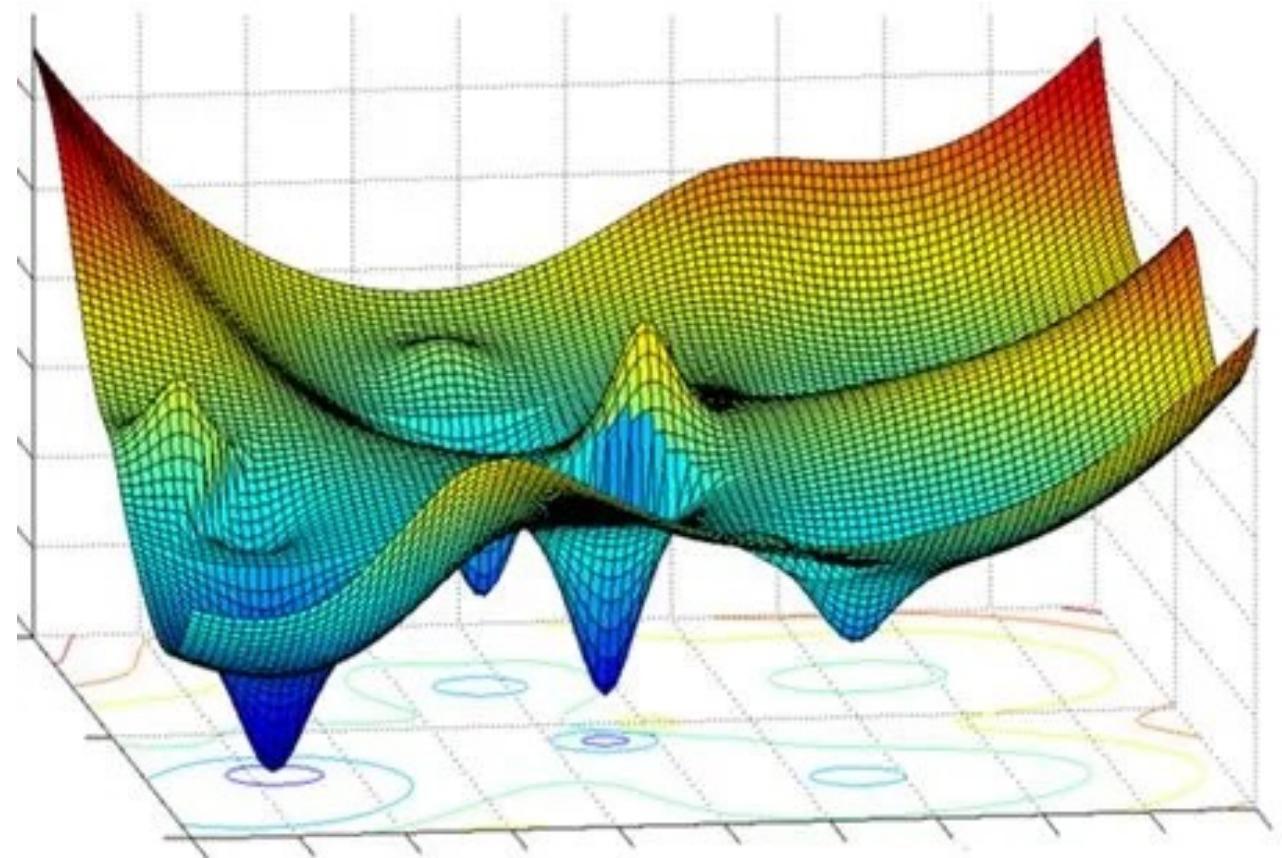
$$\frac{\partial E_{\text{tot}}}{\partial h_{uv}} = \frac{\partial E_{\text{kin}}}{\partial h_{uv}} + \frac{\partial E_{\text{loc}}^{\text{PP}}}{\partial h_{uv}} + \frac{\partial E_{\text{nloc}}^{\text{PP}}}{\partial h_{uv}} + \frac{\partial E_{\text{xc}}}{\partial h_{uv}} + \frac{\partial E_{\text{ES}}}{\partial h_{uv}}$$

- Also do these analytically; again expressions in density and plane-wave basis set (see Marx+Hutter for explicit equations)
- Implemented in DFT codes; with these, cell shape and cell volume can be relaxed (until external stress=0)
- Tip: Larger plane-wave cutoff required to achieve convergence (larger than your previous test of total-energy convergence)

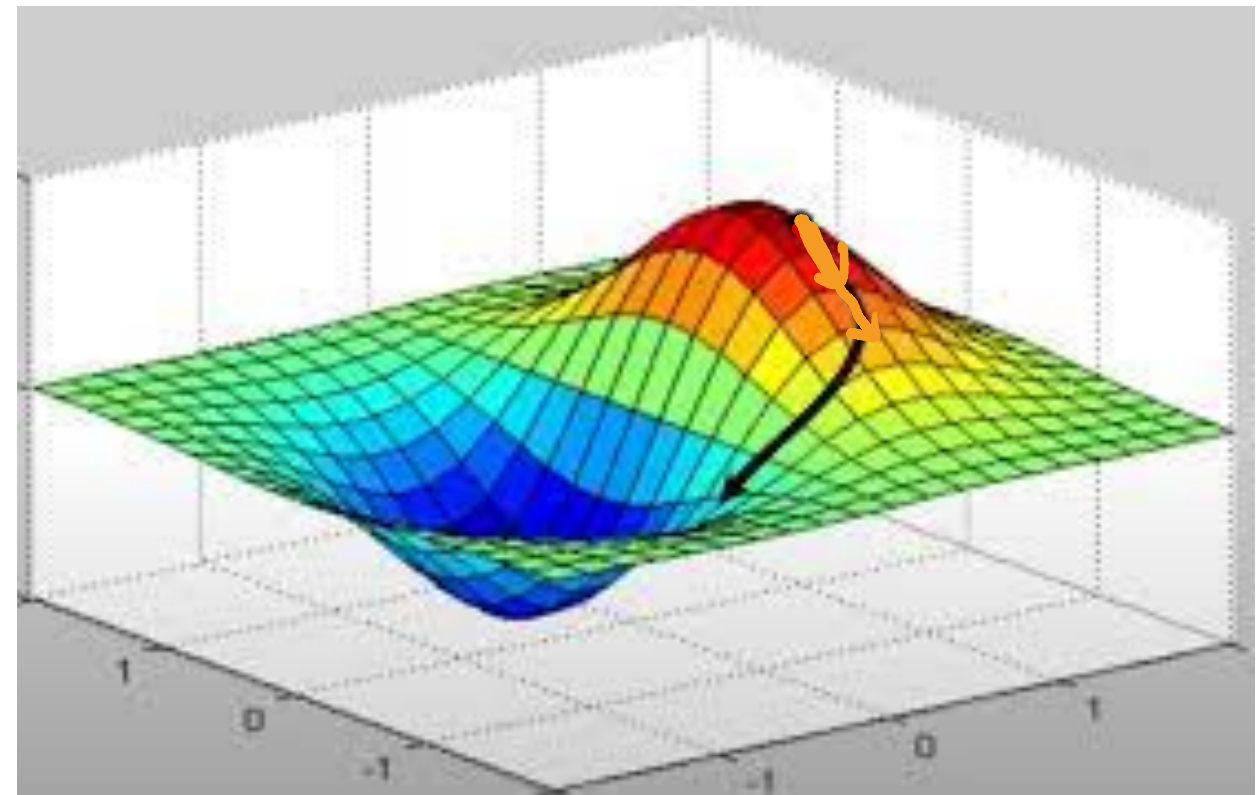


# Problems: Local Minima

- Potential-energy surface can be complicated
- Many local minima, only one global minimum
- “Relaxation” to find the global minimum
- Gradient descent approach can get stuck in local minimum
- Tips: (i) Change step size, (ii) Smart schemes to determine descent direction (BFGS), (iii) Break symmetry



(c) <https://medium.com/@ellie.arbab/maths-of-word-to-vec-8af5d9c263f2>

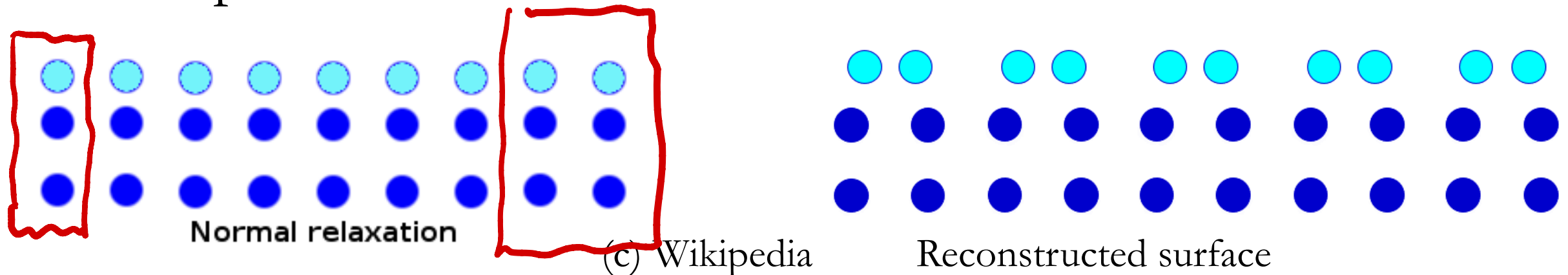


(c) <https://mriquestions.com/back-propagation.html>

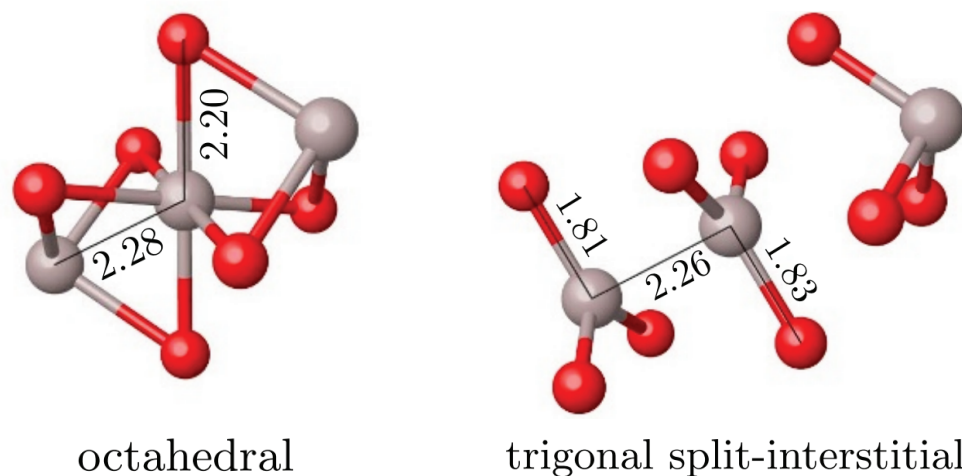


# Problems: Symmetry Breaking

- Problem: Ground-state geometry is not necessarily “obvious”
- Caution: It does not have to fit a primitive (or simple) unit cell
- Example: Surface reconstruction:



- Example: Defect atomic geometries:



Neutral aluminum interstitial geometry in  $\text{Al}_2\text{O}_3$ ; Energies differ by more than 1 eV;  
(c) J. Phys.: Cond. Mat. **35**, 334002 (2023)

- Tip: Try different unit cell sizes (even for bulk!) and distort/  
break the ideal symmetry (e.g. Voronoi method)

# Problems: Pulay Forces

- Started with:  $\nabla_I \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle =$

$$\langle \Psi_0 | \nabla_I \mathcal{H}_e | \Psi_0 \rangle + \langle \nabla_I \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \langle \Psi_0 | \mathcal{H}_e | \nabla_I \Psi_0 \rangle$$

- Hellmann-Feynman theorem:

$$\mathbf{F}_I^{\text{HFT}} = - \langle \Psi_0 | \nabla_I \mathcal{H}_e | \Psi_0 \rangle$$

... true if wave function is an exact eigenfunction

- Also true for variational wave functions, if complete basis is used, which is rarely the case
- Expand Slater determinant into basis functions

$$\phi_i = \sum_{\nu} c_{i\nu} f_{\nu}(\mathbf{r}; \{\mathbf{R}_I\})$$

- For the variation of the wave function, the gradient yields:

$$\nabla_I \phi_i = \sum_{\nu} (\nabla_I c_{i\nu}) f_{\nu}(\mathbf{r}; \{\mathbf{R}_I\}) + \sum_{\nu} c_{i\nu} (\nabla_I f_{\nu}(\mathbf{r}; \{\mathbf{R}_I\}))$$

- Allows to write:  $\mathbf{F}_I = \mathbf{F}_I^{\text{HFT}} + \mathbf{F}_I^{\text{IBS}} + \mathbf{F}_I^{\text{NSC}}$

## Problems: Pulay Forces

$$\mathbf{F}_I = \mathbf{F}_I^{\text{HFT}} + \mathbf{F}_I^{\text{IBS}} + \mathbf{F}_I^{\text{NSC}}$$

- Pulay force vanishes exactly if origin-less basis (e.g. plane waves) are used and the number of basis functions is kept fixed (careful when the volume of your cell changes!)
- For other basis sets: Pulay needs to be included explicitly

- Non-selfconsistency error can be made small by achieving high self consistency

$$|\langle \phi_0 | \phi_0 \rangle|^2 = n_0$$

$$H[n_i] |\phi_{i+1}\rangle = E |\phi_{i+1}\rangle$$

$$|\langle \phi_{i+1} | \phi_{i+1} \rangle|^2 = n_{i+1}$$

- Tip: Pulay corrections (likely already implemented or not needed (plane waves)); high accuracy criterion for self-consistency

# Applications: Ab-Initio Molecular dynamics

- Disclaimer: Details by Sara Bonella, Monday at 11 am
- Basic idea: Let's do statistical mechanics ( $T_{\text{latt}} > 0 \text{ K}$ )! (Instead of relaxing/finding minimum energy configuration)
- Come up with initial conditions and propagate  $F = ma$
- Molecular Dynamics:
  - Compute force  $F$
  - Move ions/nuclei according to  $F=ma$  (using e.g. Verlet scheme for Newton's equations of motion)
  - Repeat
- Classical MD: Use classical (analytical or ML) potentials for  $F$
- Ab-initio MD: Find DFT ground state at each step and compute  $F$  (as done on previous slides)

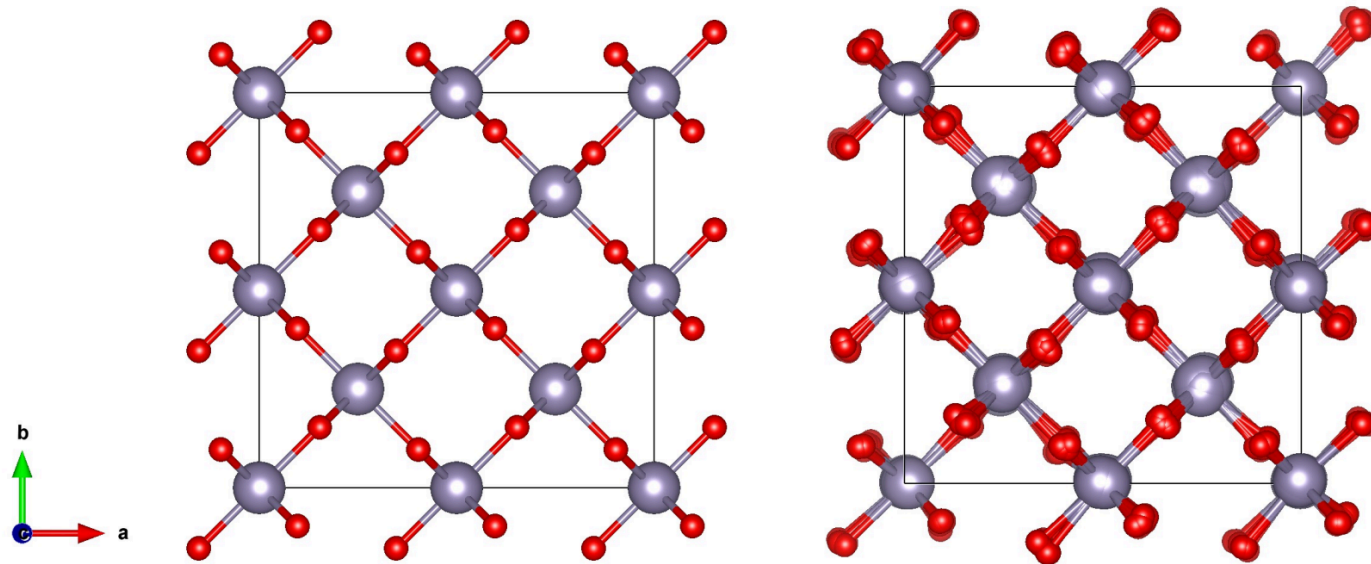
# Applications: Ehrenfest dynamics

- Ab-initio MD: Find DFT **ground state** at each step and compute F
- Ehrenfest dynamics: Force does not need to be computed from an electronic ground state!
- If you have a time-dependent electron density  $n(t)$ , e.g. from time-dependent DFT, you can use Hellmann-Feynman theorem and proceed as discussed on previous slide
- $n(t)$  is not a ground state, but an excited-state density
- Applications include, for instance, radiation damage problems

AIMD	Nuclei	Electronic structure
BO	$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\{\phi_i\}} \{ \langle \Psi_0   H_e   \Psi_0 \rangle \}$	$0 = -H_e \phi_i + \sum_j \Lambda_{ij} \phi_j$
E	$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \langle \Psi_0   H_e   \Psi_0 \rangle$	$i\hbar \dot{\Psi}_0(t) = H_e \Psi_0$

# Applications: Phonons

- Disclaimer: Details by Cyrus Dreyer, Friday at 8.30 am



$$F = -kx$$

FIG. 1. Supercell geometries used in our simulations for  $T=0$  K (left) and for  $T=300$  K (right), where 10 configurations are superimposed for visualization.

- Harmonic force constants:  $\frac{d^2 E}{dx_i dx_j}$
- Harmonic eigenfrequencies are eigenvalues of dynamic matrix:

$$D_{I\alpha, J\beta} = \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E_{KS}}{\partial R_{I\alpha} \partial R_{J\beta}}$$

- Predict phonon frequencies!



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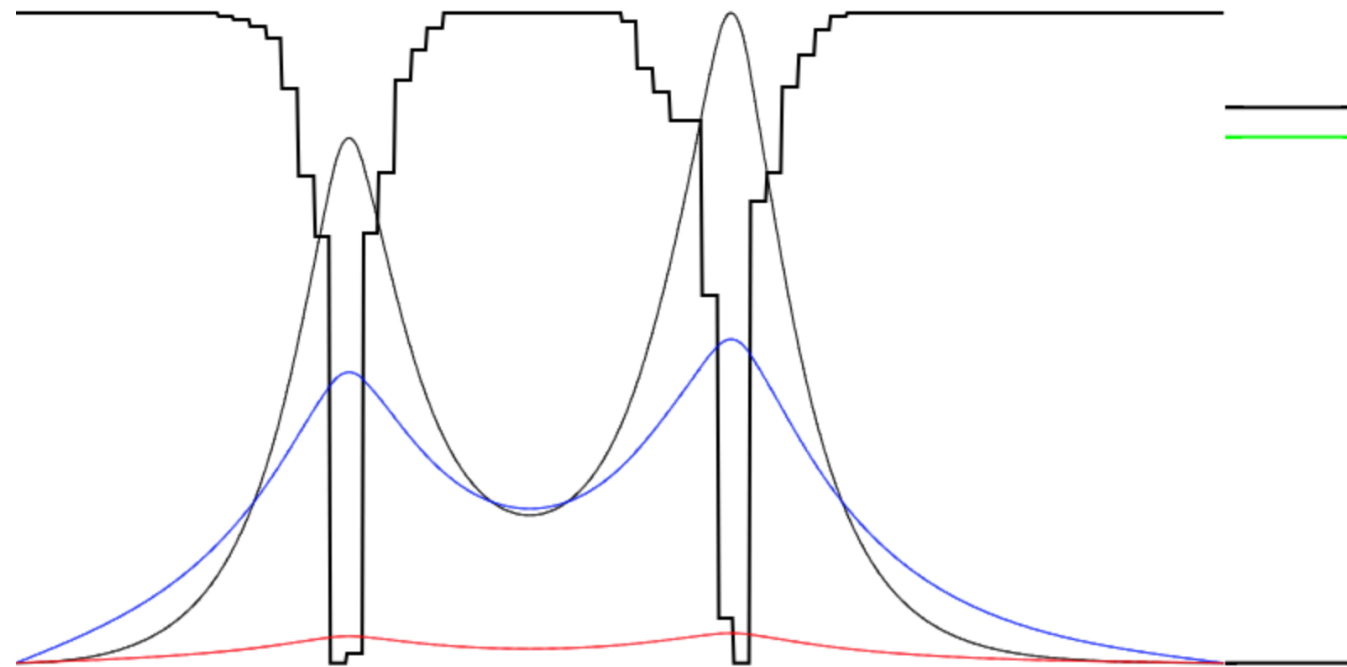


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# Multiple Nuclei: Introduction

1D Arbitrary Potential Well



1D Arbitrary Potential Well

