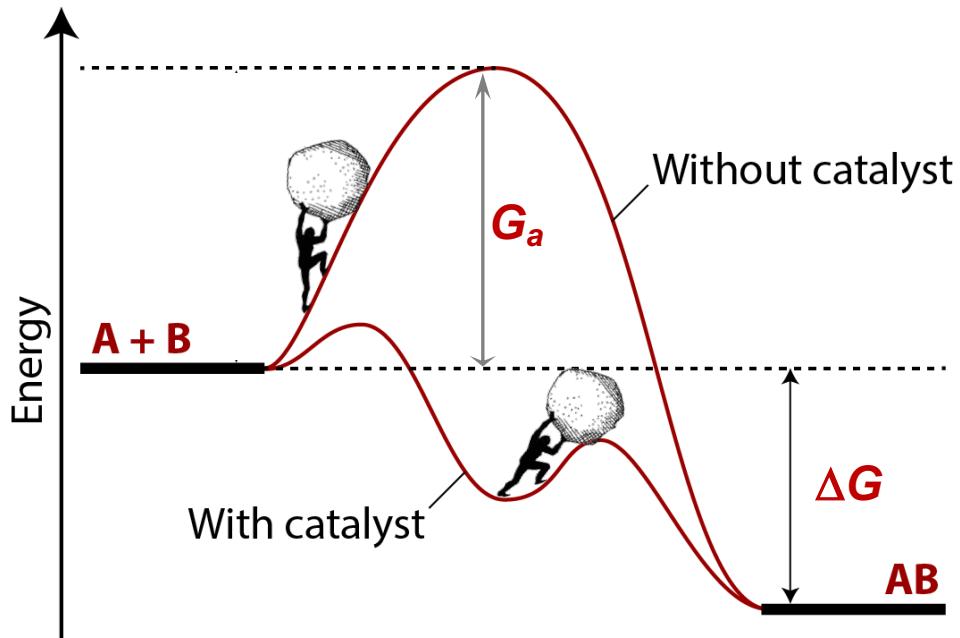


Reaction energetics of catalytic processes

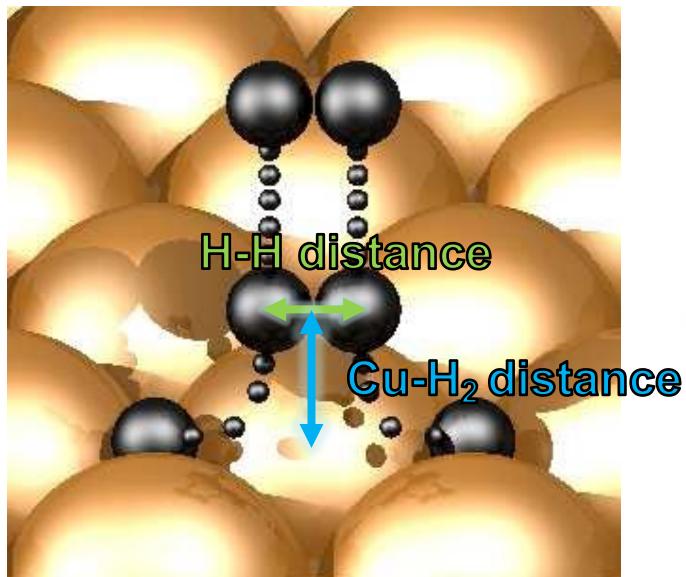
What is a catalyst?



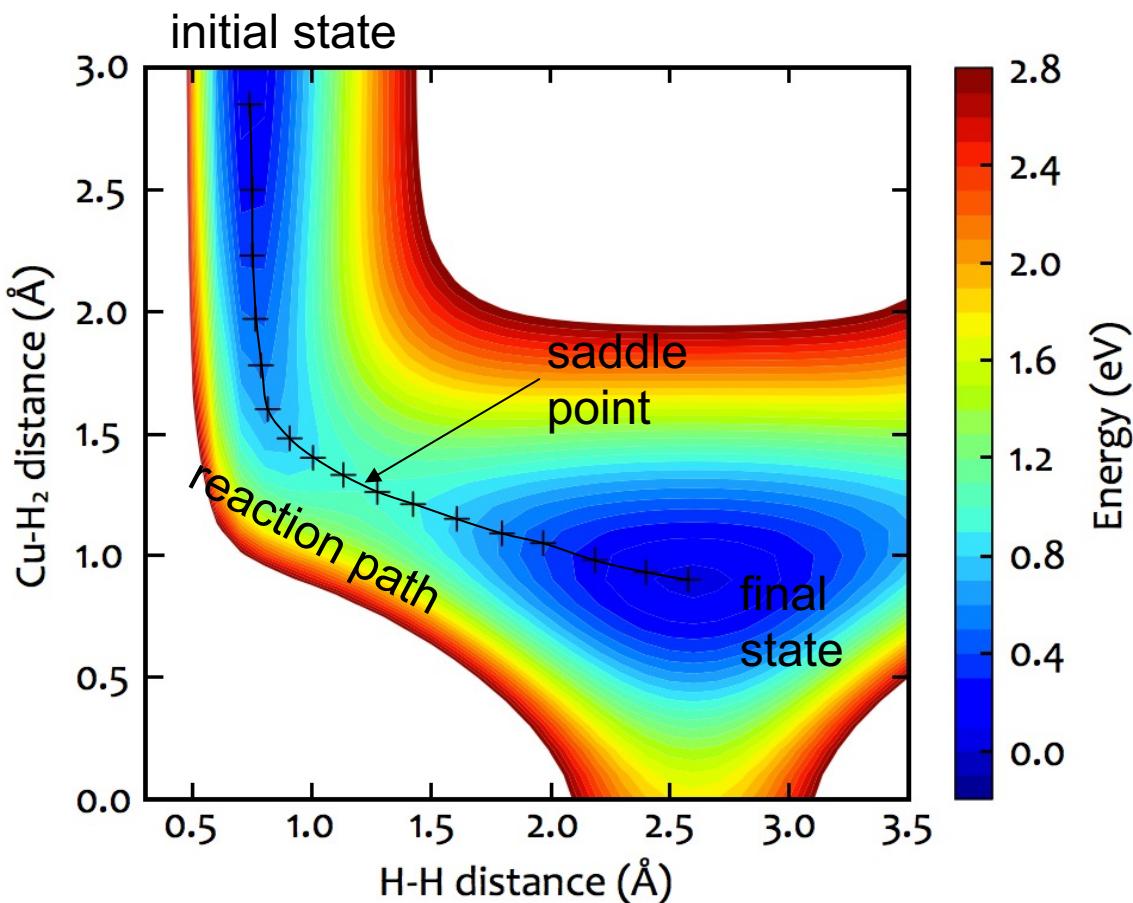
What governs the energetics?

Potential Energy Surface and Activation Energy

Example: dissociative adsorption
of H₂ on a copper (Cu) surface

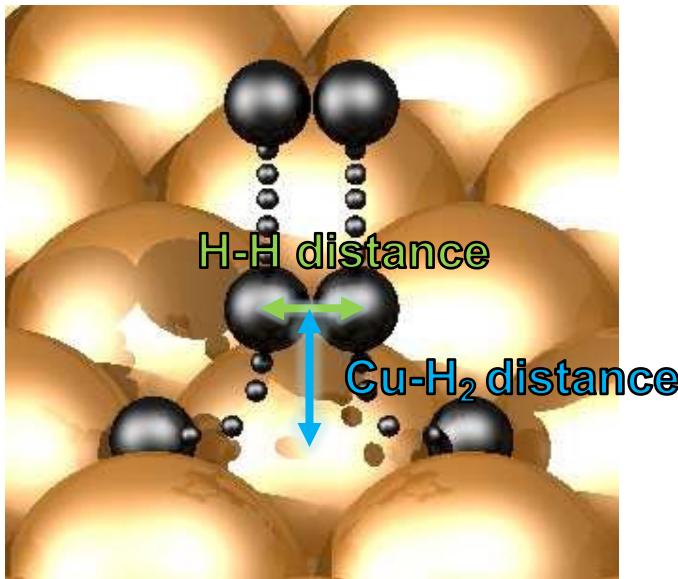


Potential energy surface



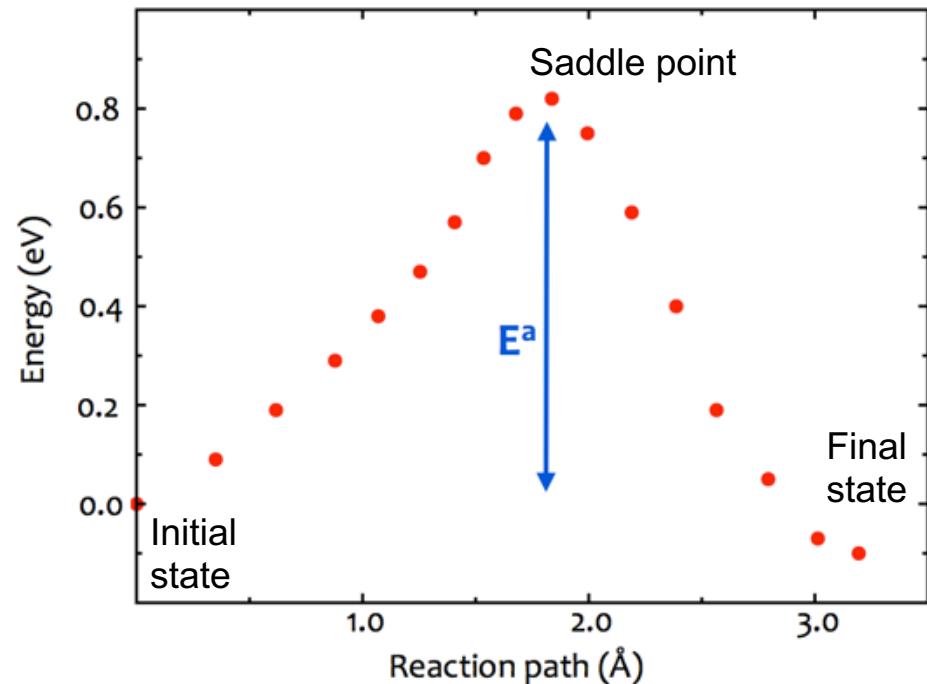
Potential Energy Surface and Activation Energy

Example: dissociative adsorption of H₂ on a copper (Cu) surface



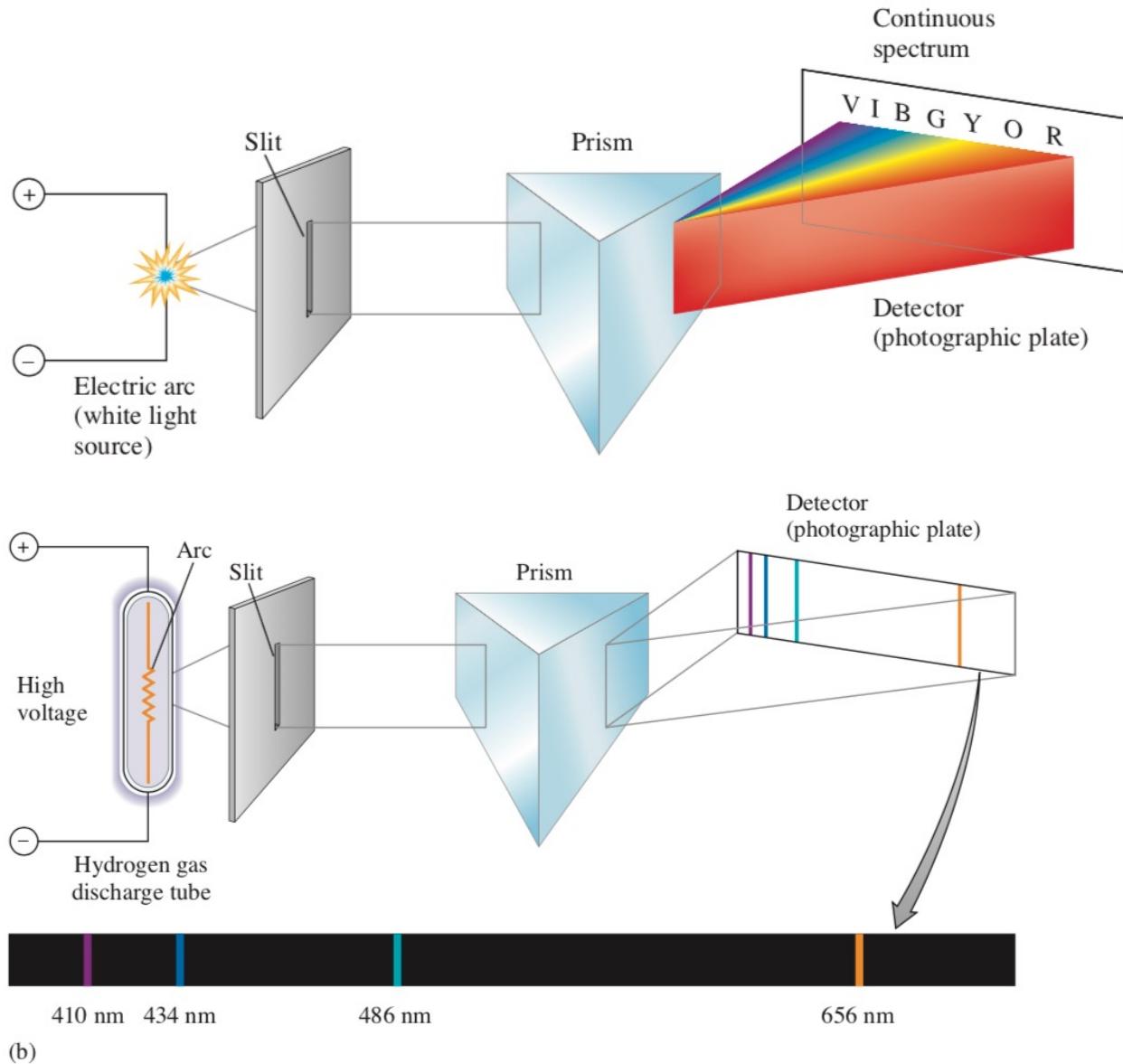
This class: you will see the dissociative adsorption of H₂O₂

The corresponding energy profile (barrier) along reaction path



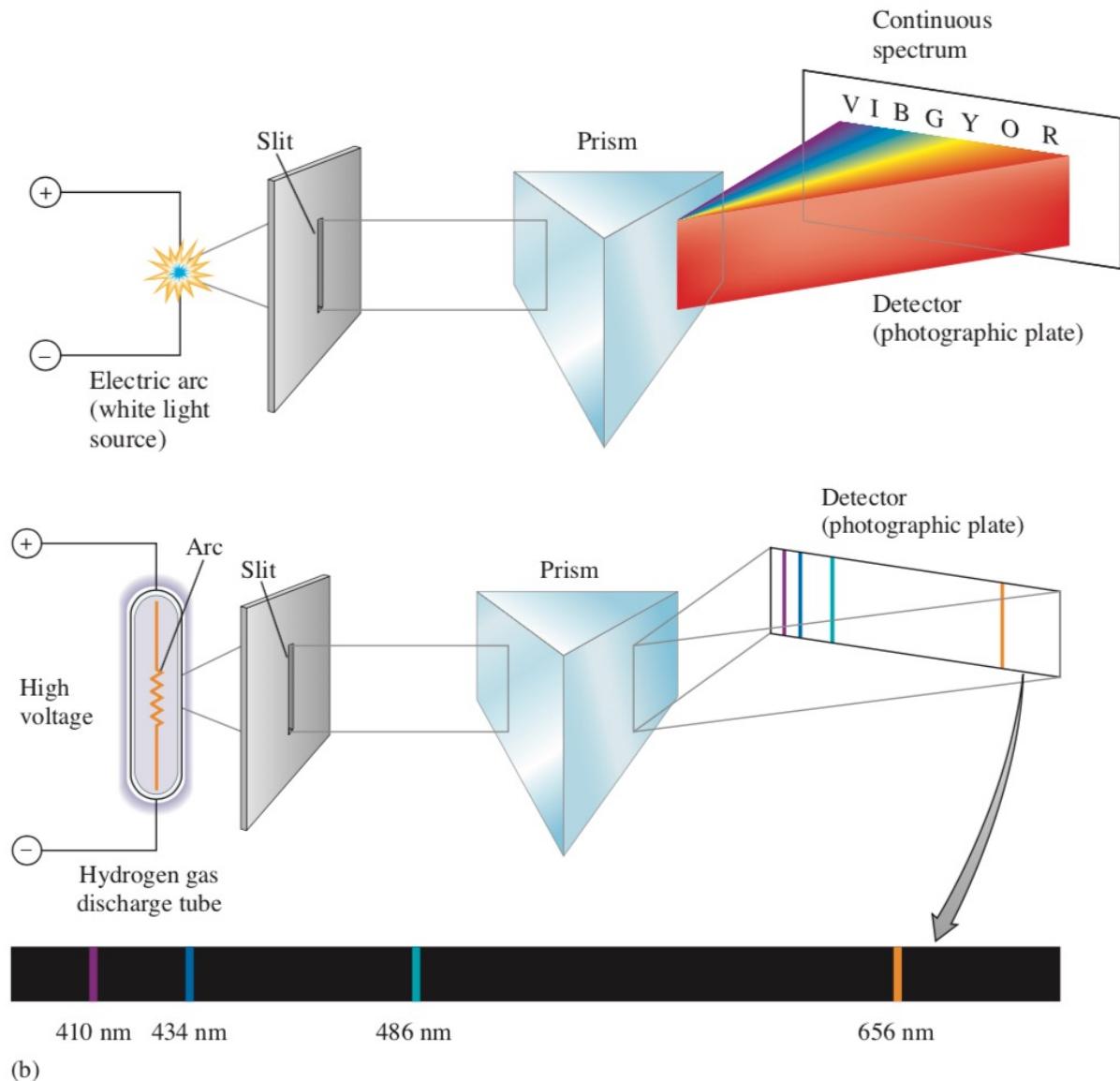
The energetics are determined by the *electronic structure* of the catalysts, which is described by quantum mechanics

Atomic spectra of the hydrogen atom



What does this spectrum have to do with the electronic energy levels in hydrogen?

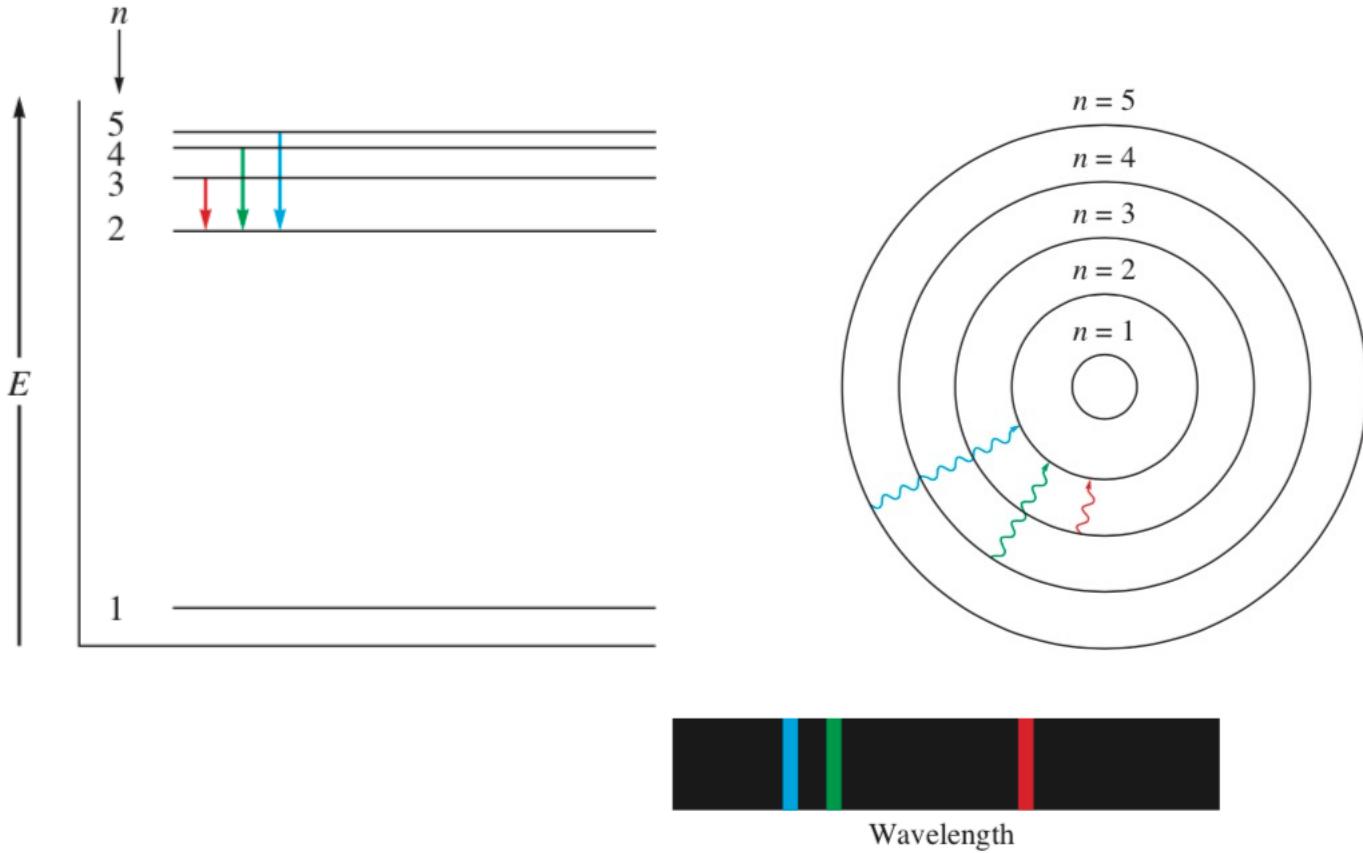
Atomic spectra of the hydrogen atom



What does this spectrum have to do with the electronic energy levels in hydrogen?

They are "quantized" in the H atom (only discrete energy levels allowed)

Bohr model of H atom



Transitions amongst various states lead to light emitted of discrete wavelengths

"Fails" for multi-electron atoms

The Schrödinger equation

“wave function”: is related to a probability density of electrons $|\Psi(\mathbf{r})|^2$

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Hamiltonian operator

Total energy

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$$

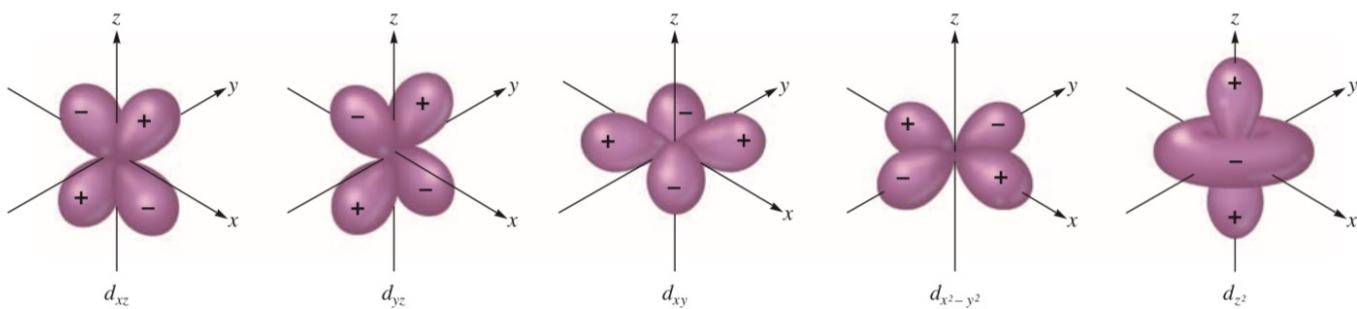
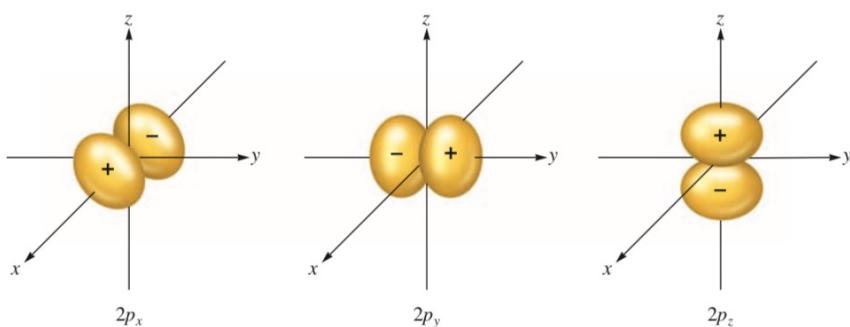
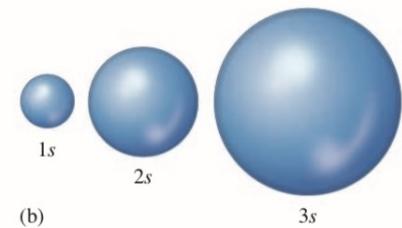
Kinetic energy

Potential energy

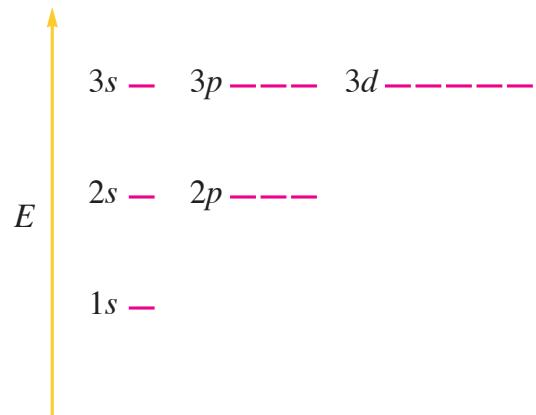
Hydrogen atom: orbitals

Solutions $\Psi(\mathbf{r})$ to the Schrodinger equation give many solutions we call “wave functions” or “orbitals”

Electron probabilities given by $|\Psi(\mathbf{r})|^2$, represented below by surfaces containing 90% of total electron probability

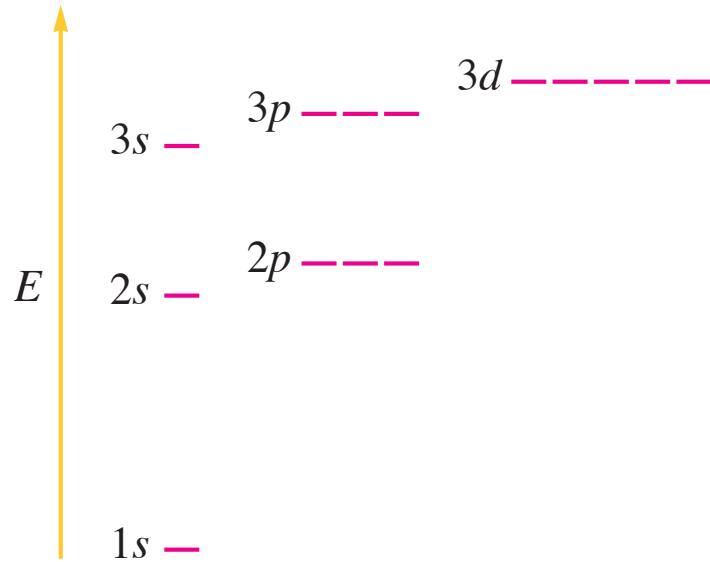


Labelling: number refers to size/energy level;
 $spd(f)$ to a shape (xyz to directionality)

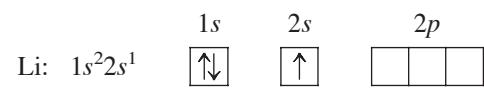
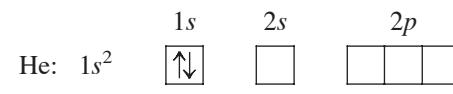
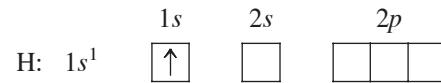


Polyelectronic atoms

Orbitals are *hydrogen-like*, with the following ordering of energies:

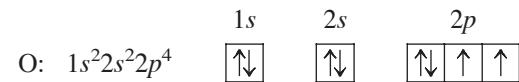
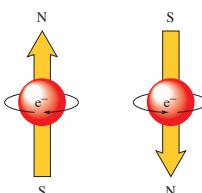


Some examples:

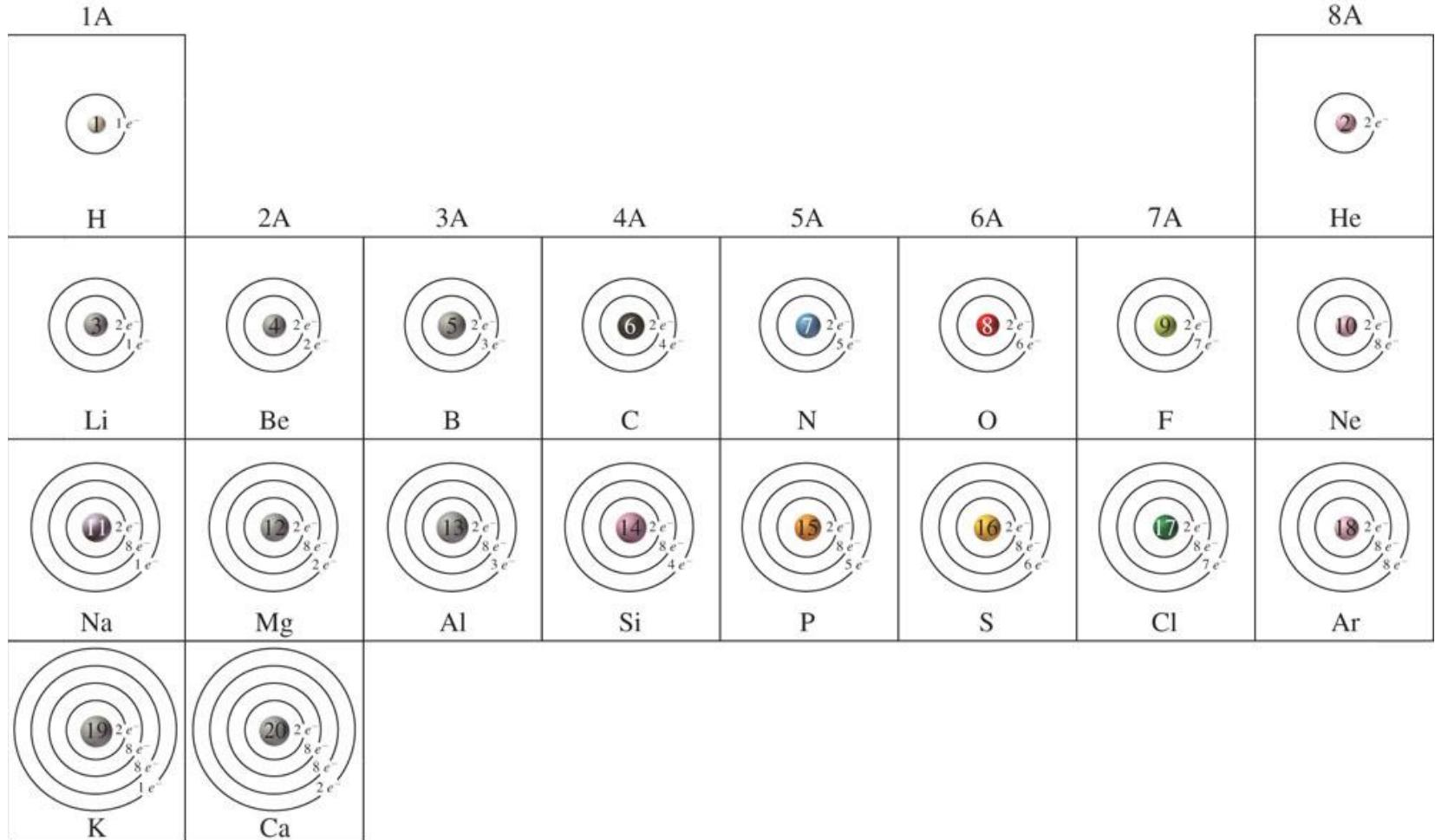


At ground state: filling of energy levels is governed by:

- 1) Pauli exclusion principle: requires that 2 electrons in the same orbital have opposite "spin" states (like a magnetic moment)
- 2) Hund's rule: lowest energy configuration has the max. unpaired electrons



Bohr model and the Periodic Table



Periodic Table

Period number, highest occupied electron level																													
Representative Elements																													
				d-Transition Elements																									
1 1A ns^1		Group numbers												Representative Elements		Noble Gases													
1 H $1s^1$	2 2A ns^2	d-Transition Elements														18 8A $ns^2 np^6$	2 He $1s^2$												
1 Li $2s^1$	2 Be $2s^2$															5 B $2s^2 2p^1$	6 C $2s^2 2p^2$												
3 Na $3s^1$	4 Mg $3s^2$	3 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^2 3d^4$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^2 3d^9$	30 Zn $4s^2 3d^{10}$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$												
11 Na $3s^1$	12 Mg $3s^2$	13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^2 3d^4$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^2 3d^9$	30 Zn $4s^2 3d^{10}$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$				
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^2 4d^3$	42 Mo $5s^2 4d^4$	43 Tc $5s^2 4d^5$	44 Ru $5s^2 4d^6$	45 Rh $5s^2 4d^7$	46 Pd $5s^2 4d^8$	47 Ag $5s^2 4d^9$	48 Cd $5s^2 4d^{10}$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$												
55 Cs $6s^1$	56 Ba $6s^2$	57 La* $6s^2 5d^1$	72 Hf $6s^2 5d^2$	73 Ta $6s^2 5d^3$	74 W $6s^2 5d^4$	75 Re $6s^2 5d^5$	76 Os $6s^2 5d^6$	77 Ir $6s^2 5d^7$	78 Pt $6s^2 5d^8$	79 Au $6s^2 5d^9$	80 Hg $6s^2 5d^{10}$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$												
87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $7s^2 6d^1$	104 Rf $7s^2 6d^2$	105 Db $7s^2 6d^3$	106 Sg $7s^2 6d^4$	107 Bh $7s^2 6d^5$	108 Hs $7s^2 6d^6$	109 Mt $7s^2 6d^7$	110 Ds $7s^2 6d^8$	111 Rg $7s^2 6d^9$	112 Uub $7s^2 6d^{10}$	113 Uut $7s^2 6d^{10} 7p^1$	114 Uuq $7s^2 6d^{10} 7p^2$	115 Uup $7s^2 6d^{10} 7p^3$	118 Uuo $7s^2 7p^6$														
f-Transition Elements																													
Lanthanides																													
Actinides																													
58 Ce $6s^2 4f^1 5d^1$	59 Pr $6s^2 4f^1 5d^0$	60 Nd $6s^2 4f^2 5d^0$	61 Pm $6s^2 4f^2 5d^1$	62 Sm $6s^2 4f^2 5d^0$	63 Eu $6s^2 4f^2 5d^1$	64 Gd $6s^2 4f^3 5d^1$	65 Tb $6s^2 4f^3 5d^0$	66 Dy $6s^2 4f^3 5d^0$	67 Ho $6s^2 4f^3 5d^0$	68 Er $6s^2 4f^3 5d^0$	69 Tm $6s^2 4f^3 5d^0$	70 Yb $6s^2 4f^4 5d^1$	71 Lu $6s^2 4f^4 5d^1$																
90 Th $7s^2 5f^0 6d^2$	91 Pa $7s^2 5f^1 6d^1$	92 U $7s^2 5f^1 6d^1$	93 Np $7s^2 5f^1 6d^0$	94 Pu $7s^2 5f^1 6d^0$	95 Am $7s^2 5f^1 6d^0$	96 Cm $7s^2 5f^2 6d^0$	97 Bk $7s^2 5f^2 6d^0$	98 Cf $7s^2 5f^2 6d^0$	99 Es $7s^2 5f^2 6d^0$	100 Fm $7s^2 5f^2 6d^0$	101 Md $7s^2 5f^2 6d^0$	102 No $7s^2 5f^2 6d^0$	103 Lr $7s^2 5f^2 6d^0$																

Similarities in electronic configurations down *columns* give rise to common properties!

Periodic Table

d-block transition elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac [†]	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub

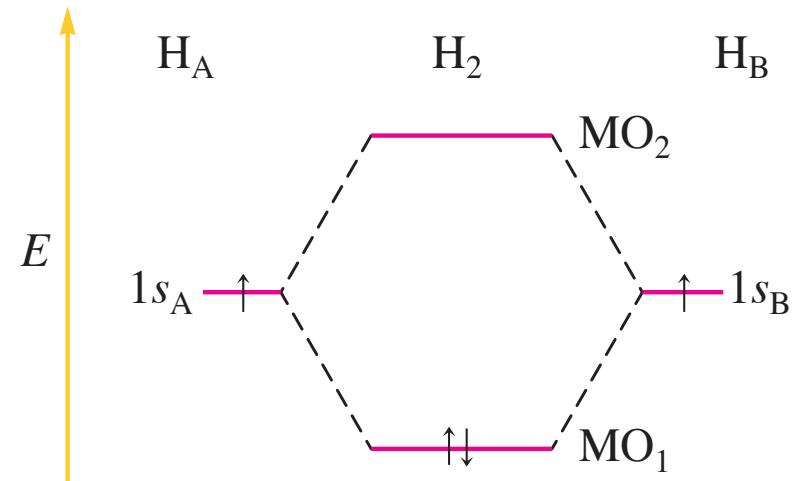
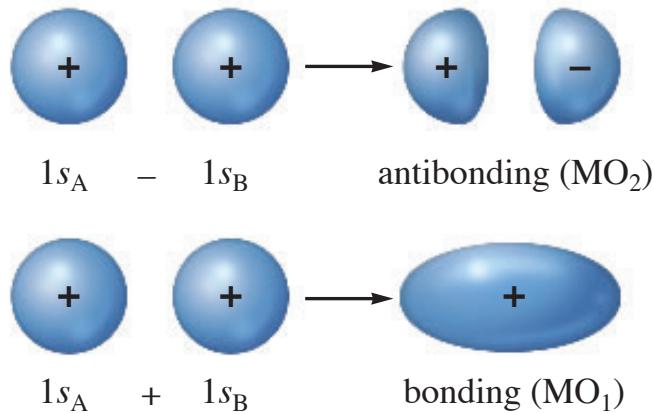


Have partly filled d-shells

Many heterogeneous catalysts
are transition elements

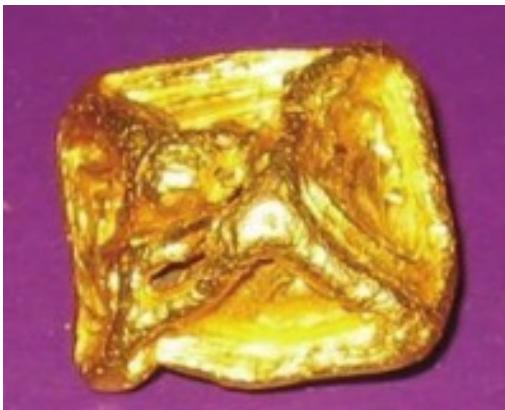
Molecular orbitals: e.g. H₂

Molecular orbitals can be approximated by "summing" orbitals of the corresponding atoms



Similar arguments can be made for more complex molecules

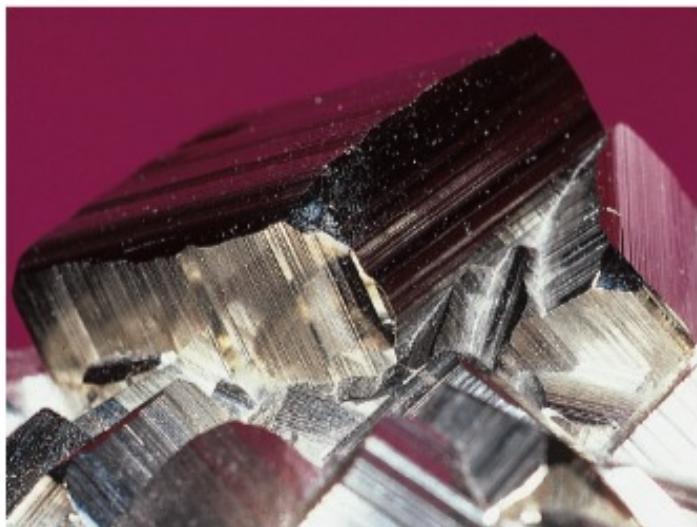
Crystalline Solids



gold



salt (NaCl with trace minerals)

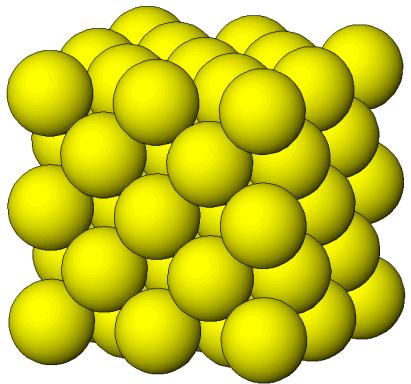


pyrite (FeS_2)

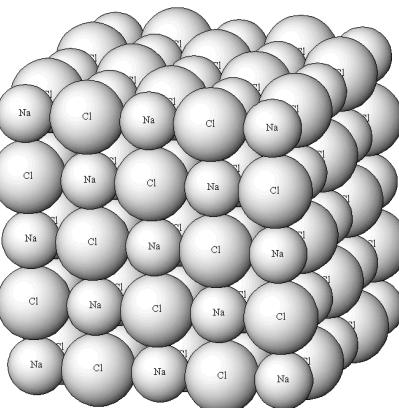


amethyst (SiO_2 with trace elements)

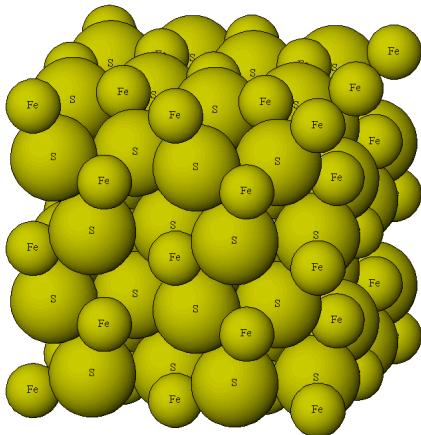
Crystalline Solids



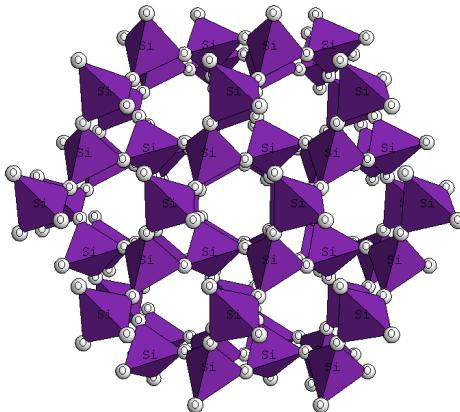
gold



salt (NaCl with trace minerals)



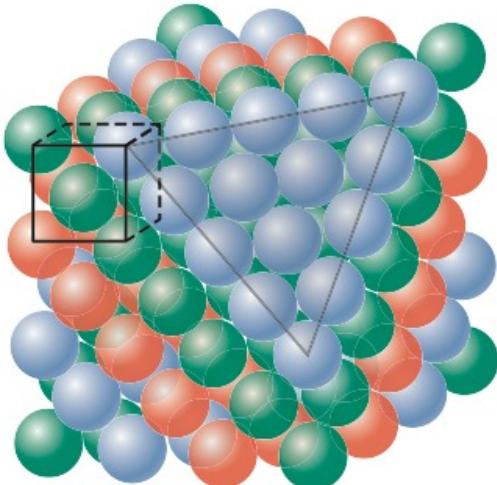
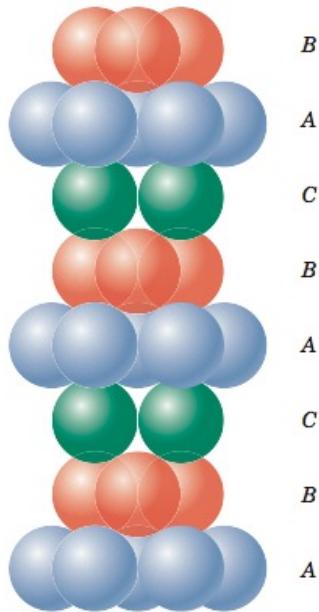
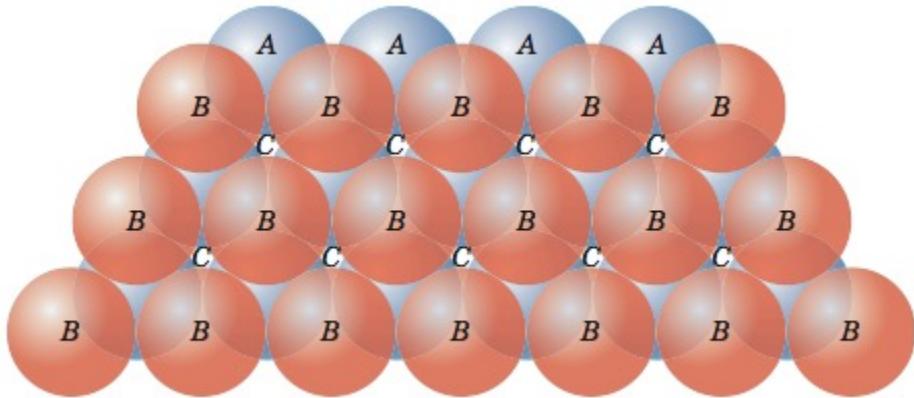
pyrite (FeS₂)



amethyst (SiO₂ with trace elements)

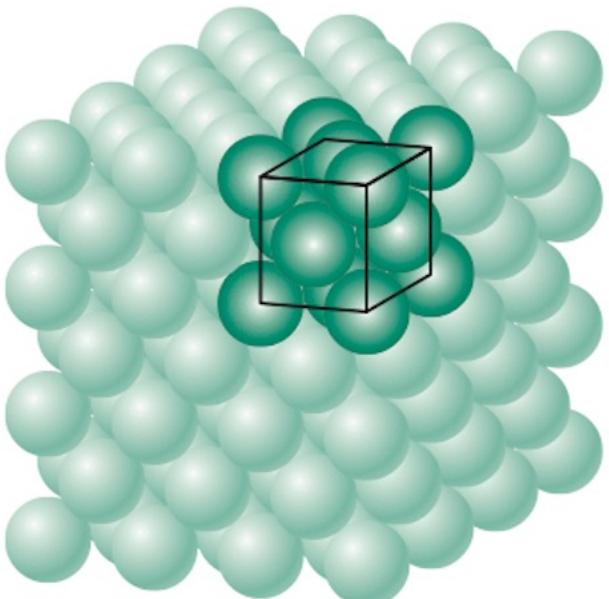
The Face-Centered Cubic (FCC) structure

Common structure for transition metals

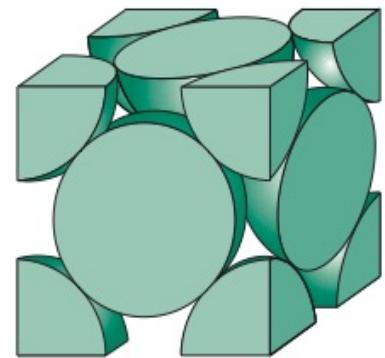
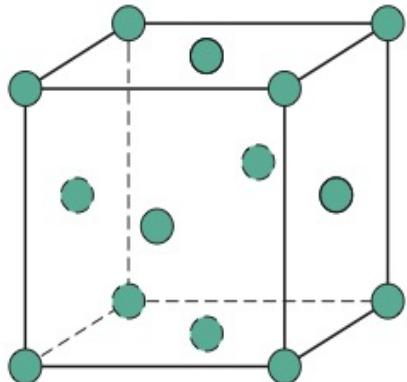


The Face-Centered Cubic (FCC) structure

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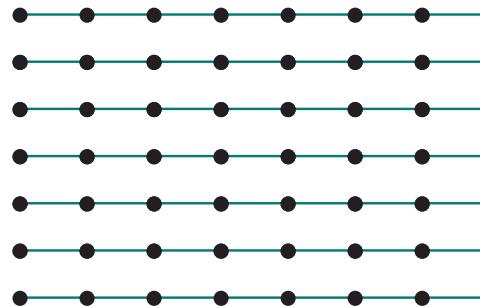
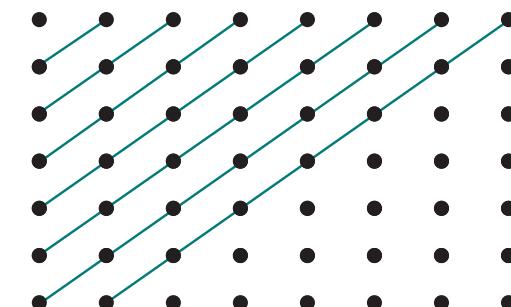
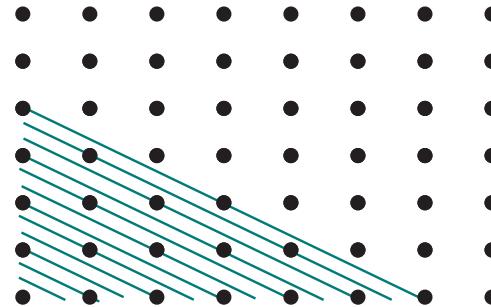
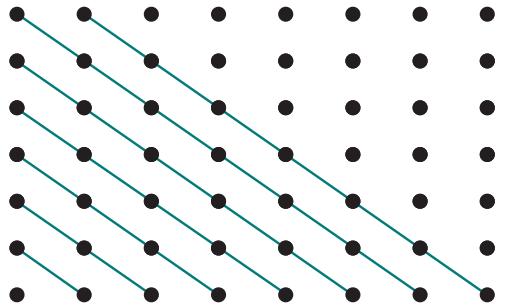


unit cell: a repeating unit
- See "face centered"-ness



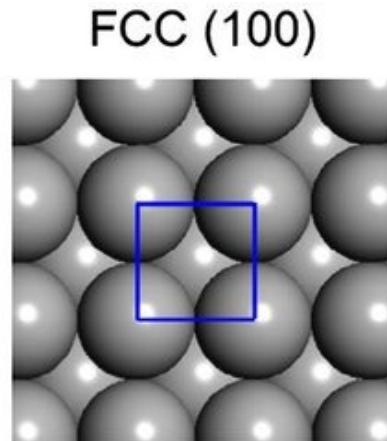
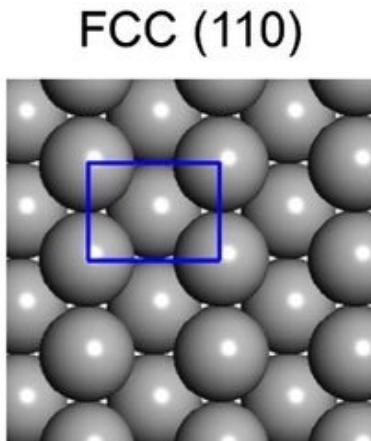
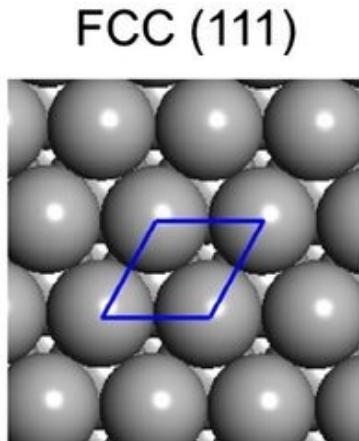
Solid Surfaces

- Cuts in different directions of crystals give surfaces with different structures
- Cuts in a hypothetical 2D structure:



Solid Surfaces

- Cuts in different directions of crystals give surfaces with different structures
- Cuts in a fcc structure



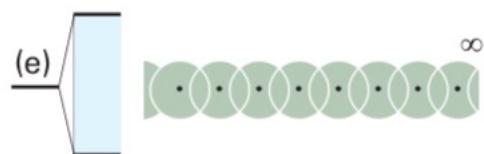
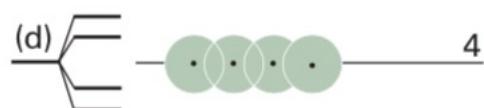
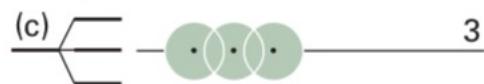
(hkl) notation

Blue lines outline a "unit cell" for the surface

This class: examine reaction energetics on the (111) surface

Bonding in solids

Consider: a 1D model



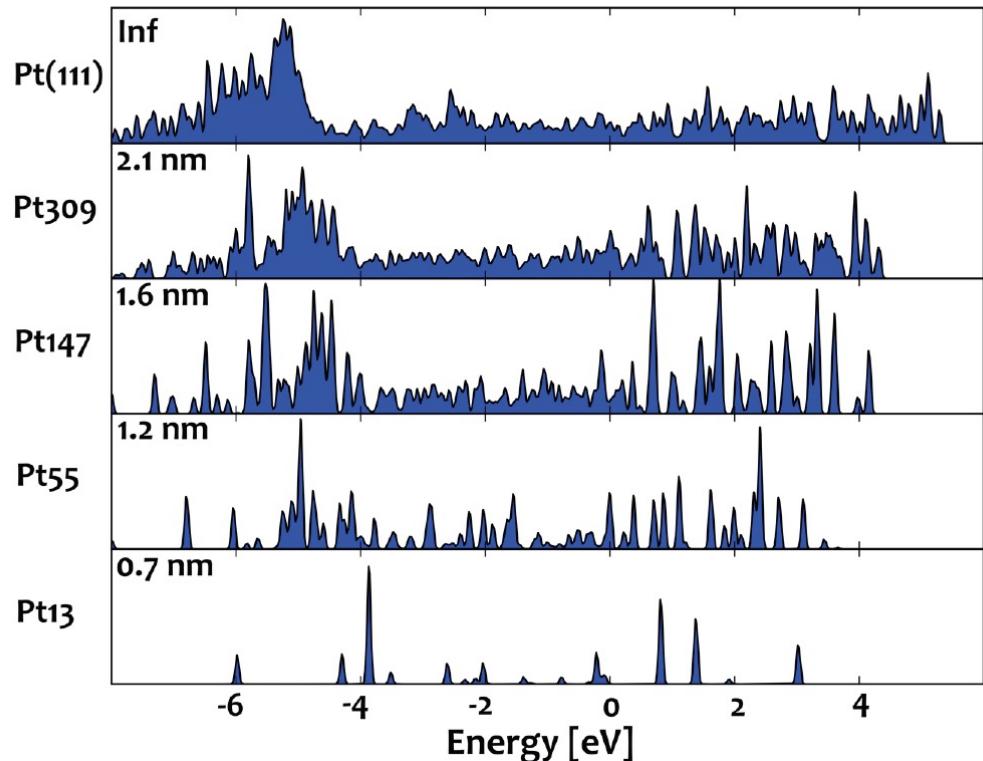
Energy
levels

Overlap of
orbitals

Analogously: the interaction of atoms arranged in a 3D periodic lattice gives rise to *bands* in energy

Bonding in solids

Pt "density" of electronic states:



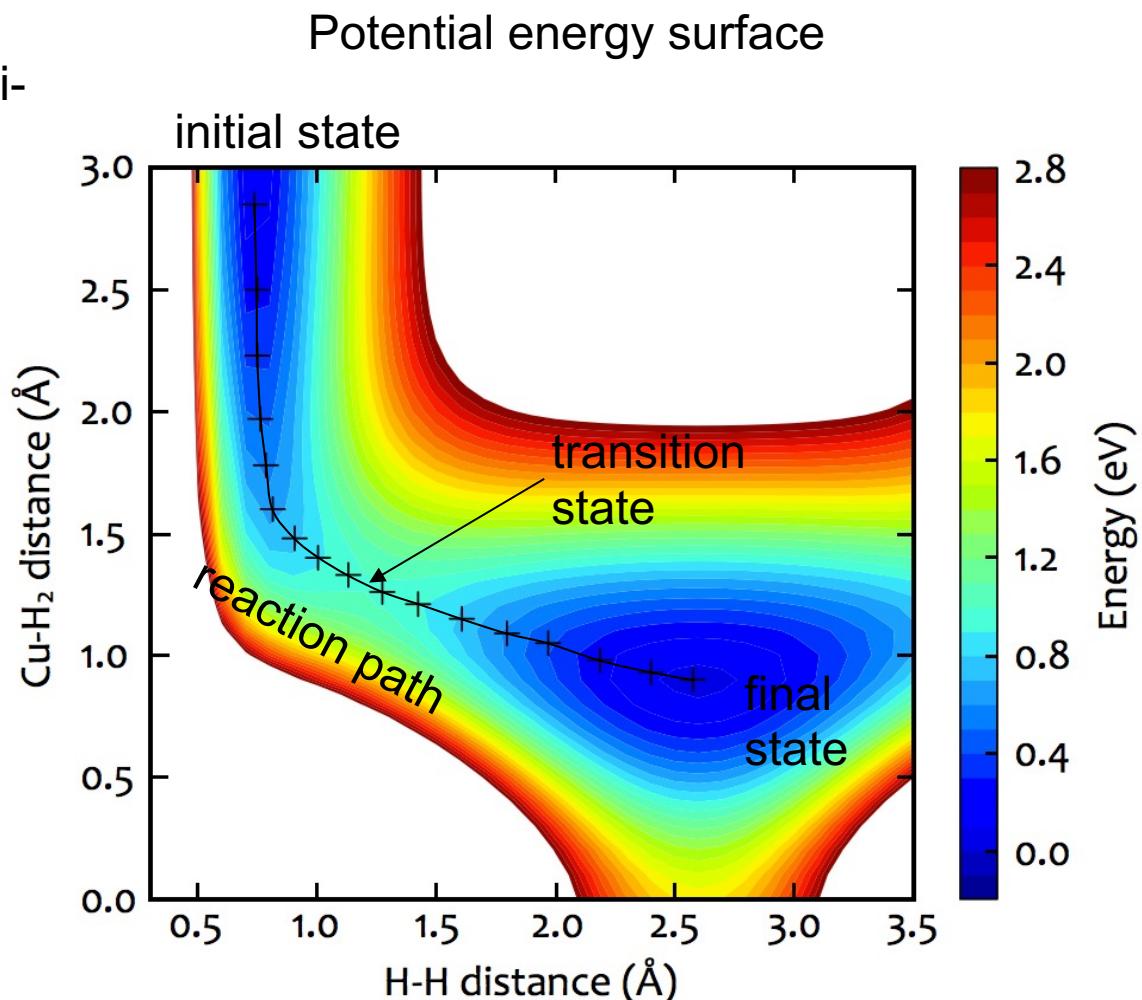
The interaction of atoms arranged in a lattice gives rise to *bands* in energy

Will see: trends in electronic structure of catalysts → trends in reaction energetics

Density Functional Theory (DFT)

An *approximate solution* to the Schrödinger equation; maps multi-electron wave function to an *electron density*

Can describe up to thousands of atoms quantitatively – e.g. in solids



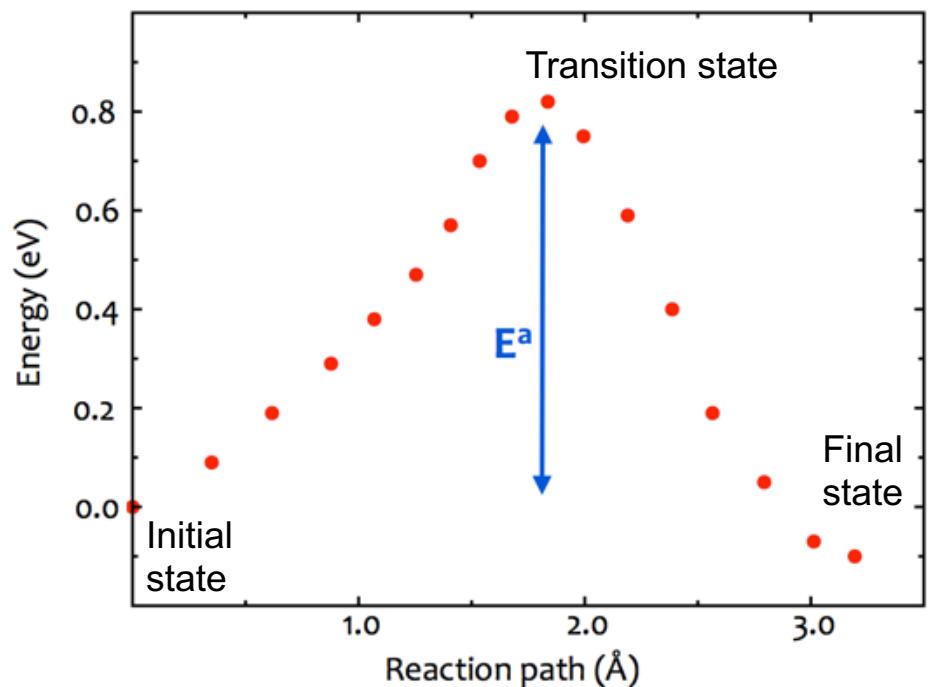
Kohn, Sham, Phys Rev. **140**, A1133 (1965)

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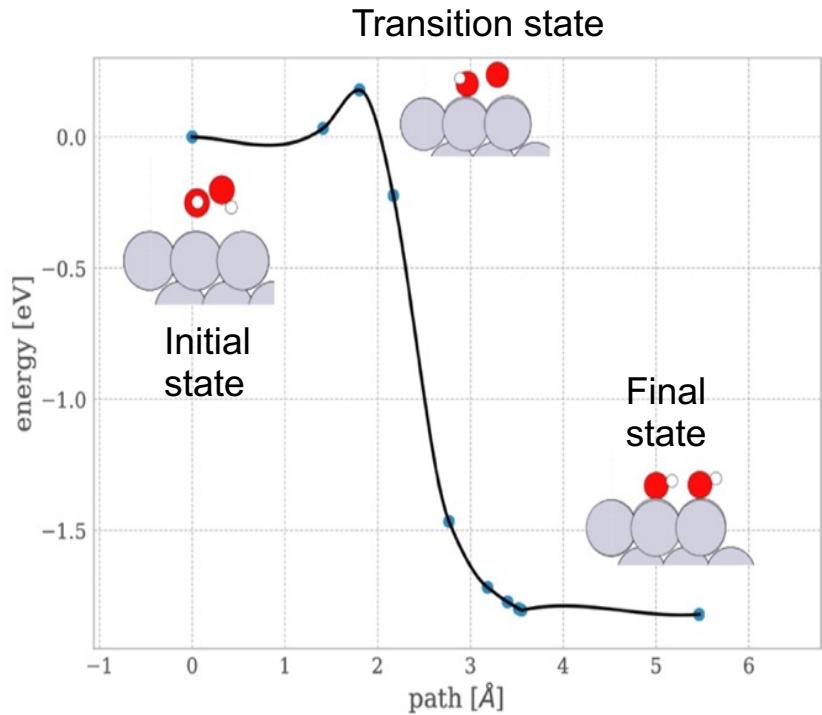


Density Functional Theory (DFT)

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In the H_2O_2 exercise: examine DFT-determined *energetics* for H_2O_2 dissociation to 2 adsorbed OH (2^*OH)



e.g. H_2O_2 dissociation on Pt