PHYSICS 140A--SOLID STATE PHYSICS
WINTER QUARTER, 2015-16
SYLLABUS

Instructor: Professor Charles S. Fadley, Physics 241
Office hours: 1:30-2:30 Tuesdays and Thursdays, or by appointment
E-mail: fadley@physics.ucdavis.edu (best way to get through)
Telephone: 510-334-8567
TA: Tanat Kissikov, Physics 231; E-mail: tkissikov@ucdavis.edu

• *Course website:* http://140a.physics.ucdavis.edu . **Regularly updated throughout the quarter.**
• *Class meetings:* **Tuesdays and Thursdays, 10:30 AM - 11:50 AM, 140 Physics**

• *Textbooks*
-- M. Ali Omar, "Elementary Solid-State Physics", Revised Printing, Addison-Wesley-Longman, 1993. Primary text for lecture, reading, and homework problems. Clearly written, although older. Out of print, but can be purchased in international edition for $18.50 from:
http://www.valorebooks.com/textbooks/elementary-solid-state-physics-principles-and-applications/9780201607338
--H. Ibach and H. Luth, "Solid-State Physics: An Introduction to Principles of Materials Science", 4th edition, Springer, 2009. Much more up-to-date and advanced. Will be used for some reading assignments as well. Available as a free download from the Library or at the course website for UCD students, or in paperback for about $50 or less.

• *A couple good websites for viewing crystal structures, with others as we go along:*
http://www.dawgsdk.org/crystal/
http://www.fhi-berlin.mpg.de/KHsoftware/Balsac/pictures.html **(A downloadable program for creating your own structures)**

• *Course grading:* **Based on the following breakdown--**

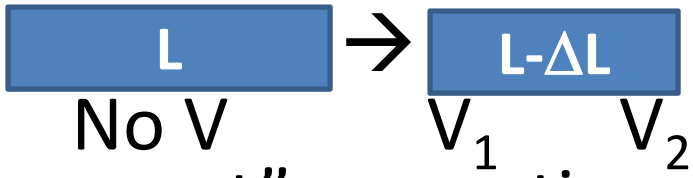
Graded problem sets:	25%
Midterm examination	25%
Final examination	50%
	100%

Exam crib sheet: You may bring in one 8.5" x 11" sheet with important equations and results written on it to both the midterm and the final.

• *Tentative syllabus:* **Readings below are mostly from Omar, but complementary reading from Ibach and Luth will also be assigned throughout the quarter. Copies of viewgraphs and other supplementary material will be posted at the class website and will be an important component of study for the course and exams.**

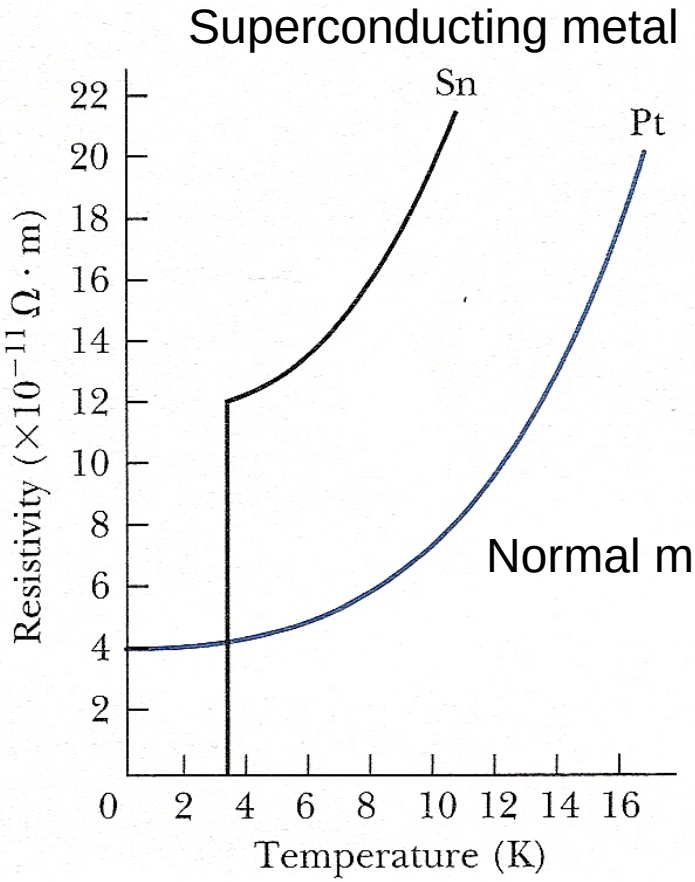
Week	*Dates*	*Topic [Reading: O = Omar, IL = Ibach and Luth]*
1	1/5-1/7	Course intro., Crystal bonding and structure [O-Ch.1, App A1-A8; IL-Ch. 1]
2	1/12-1/14	Crystal bonding and structure (continued)
3	1/19-1/21	Diffraction in Crystals [O-Ch. 2]
4	1/26-1/28	Diffraction (continued)
5	2/2-2/4	Lattice vibrations [O-Ch. 3]
6	2/9	Midterm Examination
	2/11	Lattice vibrations (continued)
7	2/16	Lattice vibrations (continued)
	2/18	The free-electron model [O-Ch. 4]
--Approximately here, optional tour of Lawrence Berkeley National Laboratory solid state research facilities--		
8	2/23-2/25	The free-electron model (continued)
9	3/1-3/3	Energy bands in solids [O-Ch. 5]
10	3/8-3/10	Energy bands in solid (continued)
Final	3/19, Saturday	Final Examination: 10:30 AM-12:30 PM, Physics/Geology 140

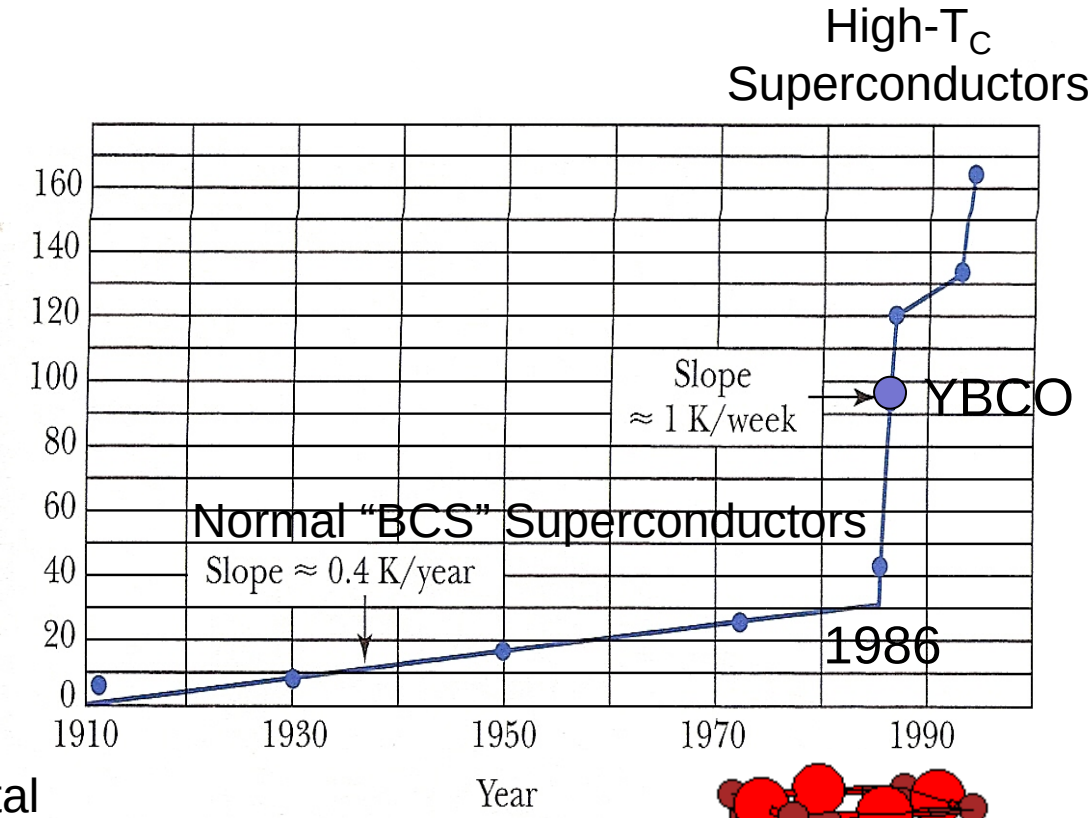
Some properties of solids/condensed matter

- Hard→soft, ductile
- Conducting→Semiconducting→Insulating
- Superconducting: current with no voltage!
- Magnetic: Ferromagnetic (…↑↑↑↑…), Anti-ferromagnetic (…↑↓↑↓…),…
- Piezoelectric: 

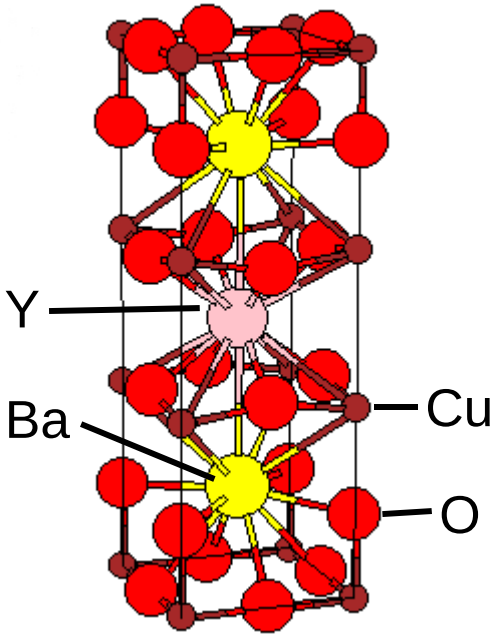
- Surprising/"Emergent" properties: Complex mixtures or multilayer nanostructures or nanoparticles
- And much more…

High temperature superconductivity



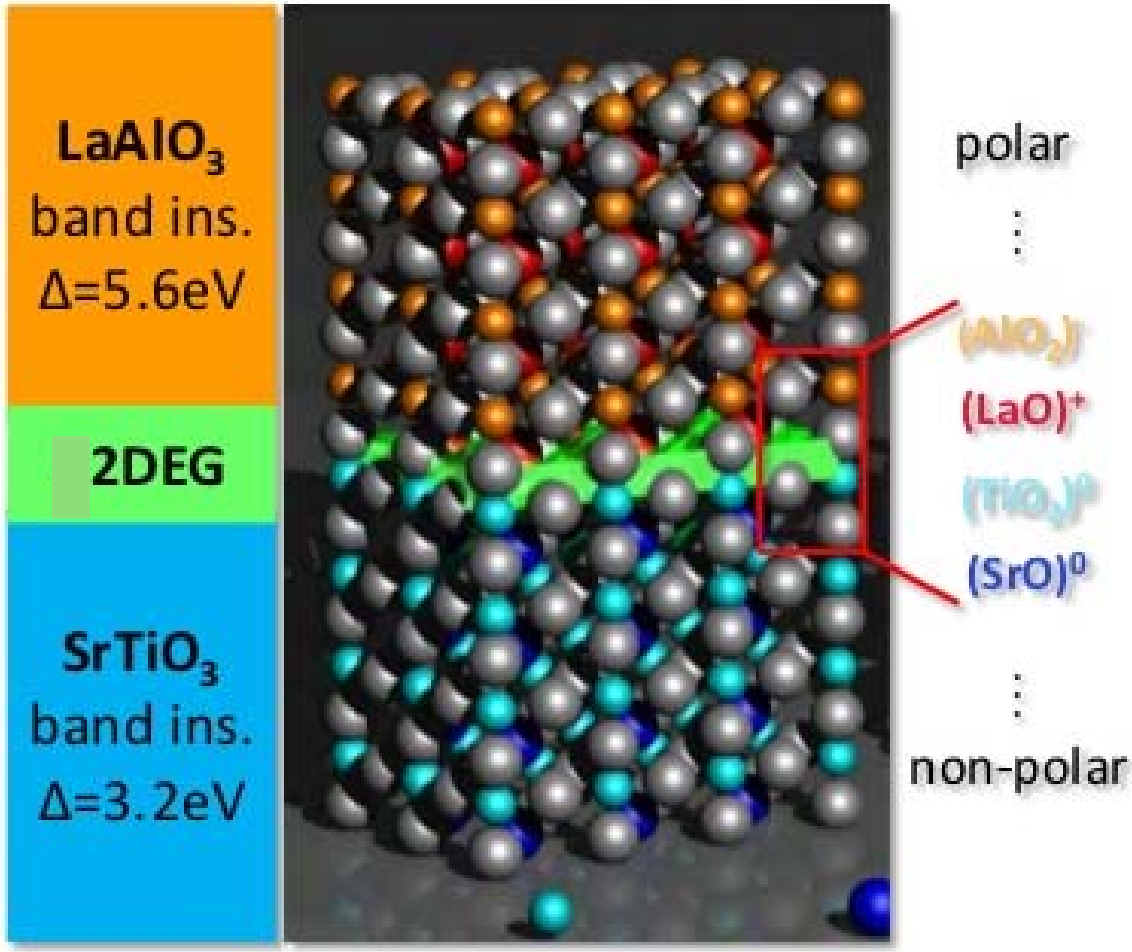


"High T_C": $YBa_2CuO_{7-\delta}$ = "YBCO"



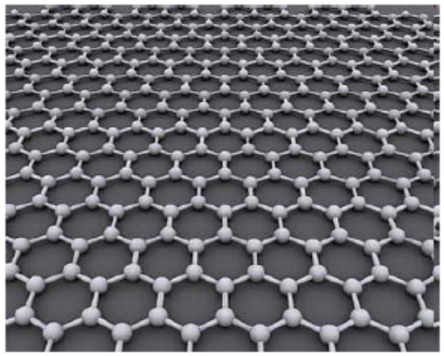
Nobel Prize in Physics 1987: Bednorz &Mueller: For their important break-through in the discovery of superconductivity in ceramic materials

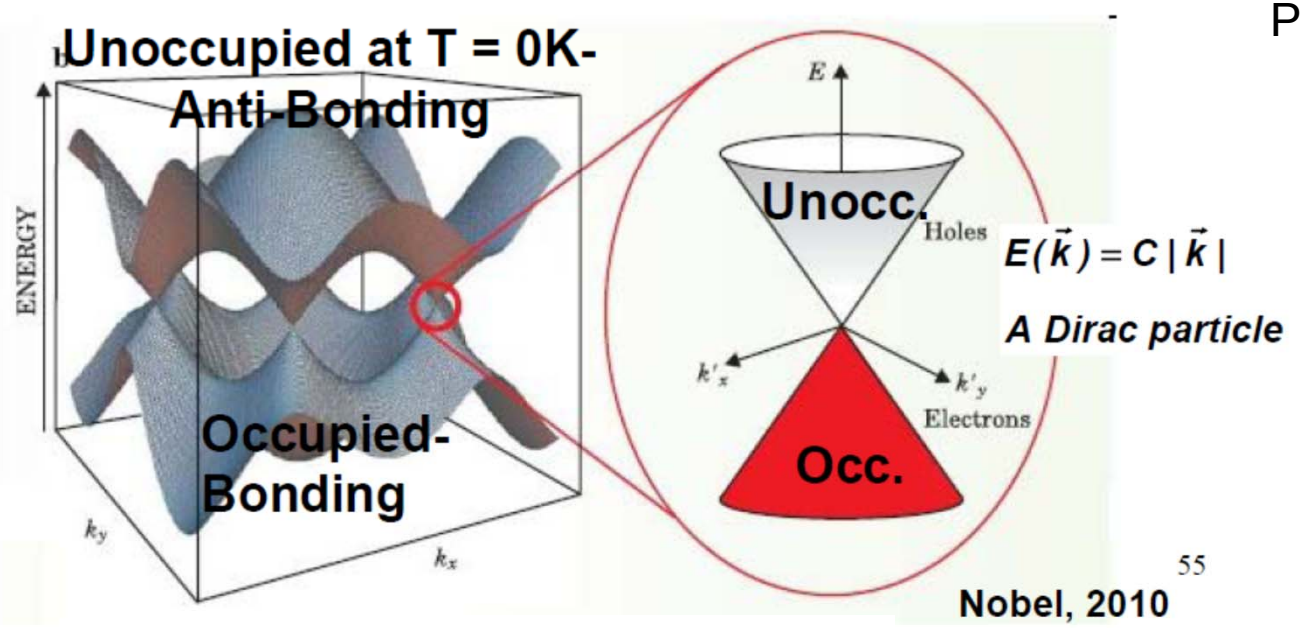
Emergent properties at interfaces



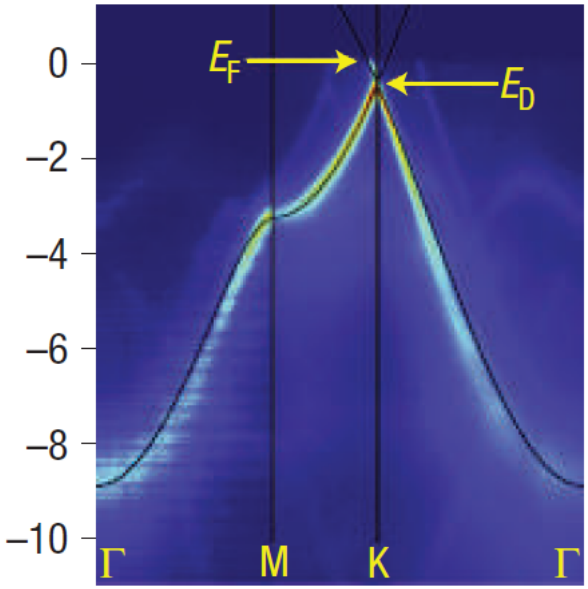
Ohtomo/Hwang, Nature ***427****, 423 (2004)*

Strange electrons in simple materials: graphene





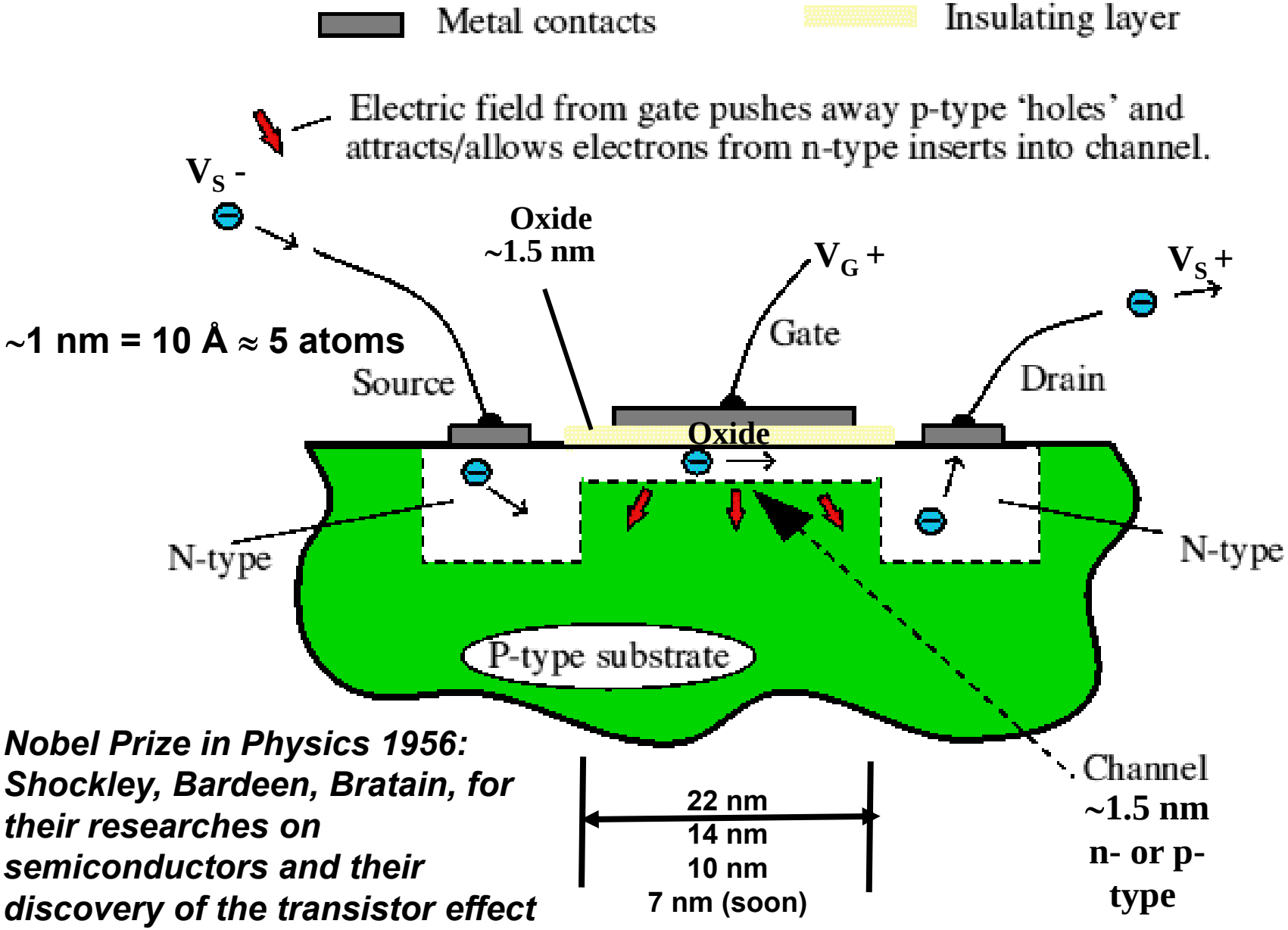
Photoelectron spectroscopy



The Nobel Prize in Physics 2010: Geim, Novoselov, for groundbreaking experiments regarding the two-dimensional material graphene"

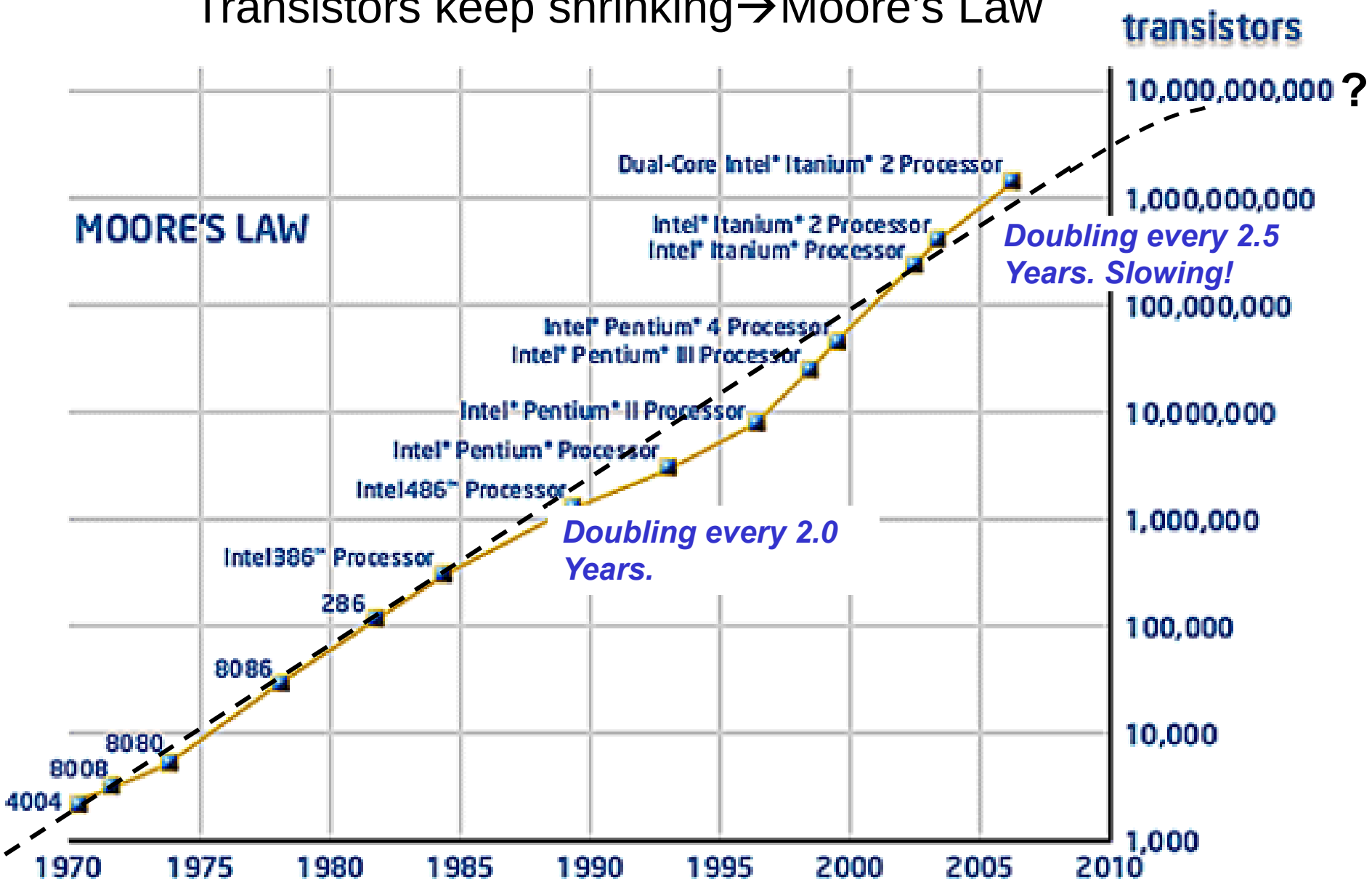
Bostwick et al., Nature Physics 3, 36 - 40 (2007)

The IT workhorse: the metal-oxide-semiconductor field-effect transistor (MOSFET)

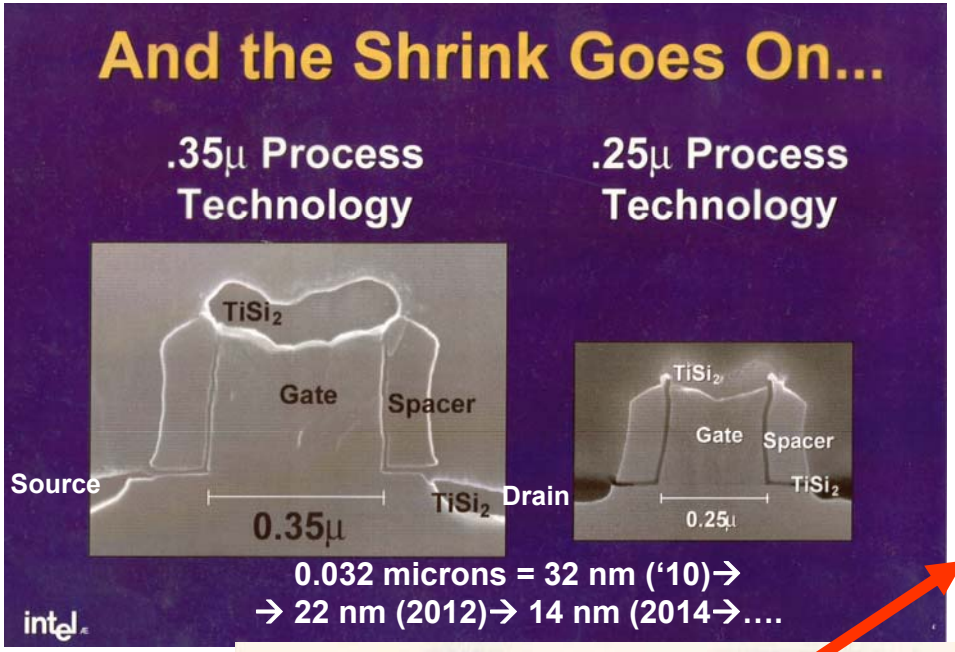


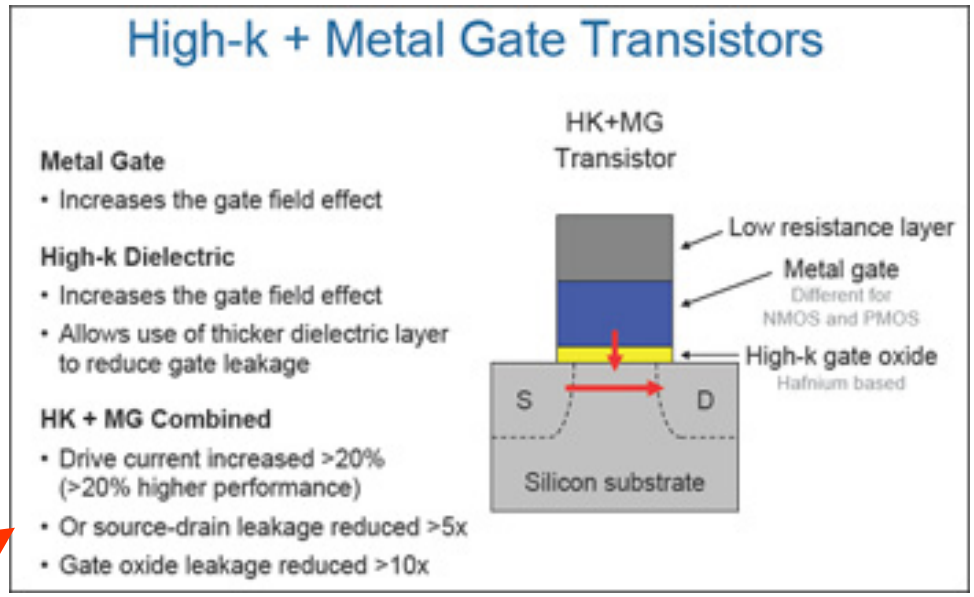
Nobel Prize in Physics 1956: Shockley, Bardeen, Bratain, for their researches on semiconductors and their discovery of the transistor effect

Transistors keep shrinking→Moore's Law



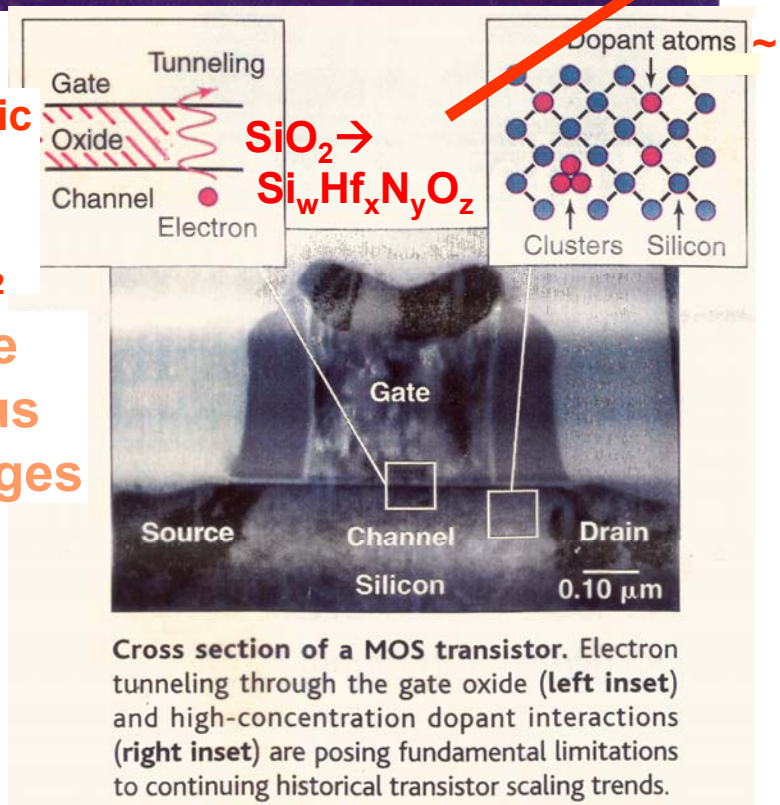
http://www.intel.com/technology/mooreslaw/index.htm





~few atomic layers— currently 15 Å SiO_2

Some serious challenges



Cross section of a MOS transistor. Electron tunneling through the gate oxide (**left inset**) and high-concentration dopant interactions (**right inset**) are posing fundamental limitations to continuing historical transistor scaling trends.

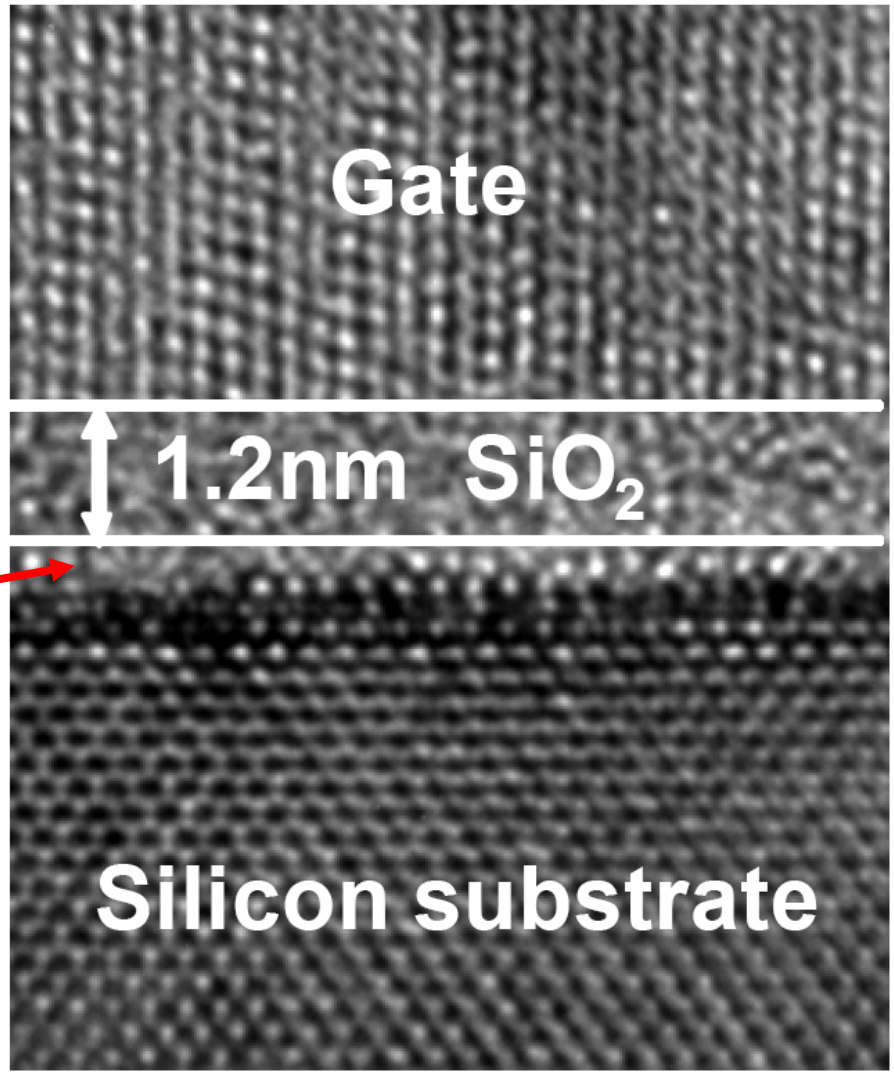
SiO_2→ $Si_wHf_xN_yO_z$

~1 %

- 10 μm — 1971
- 3.0 μm — 1975
- 1.5 μm — 1982
- 1.0 μm — 1985
- 800 nm — 1989
- 600 nm — 1994
- 350 nm — 1995
- 250 nm — 1997
- 180 nm — 1999
- 130 nm — 2002
- 90 nm — 2004
- 65 nm — 2006
- 45 nm — 2008
- 32 nm — 2010
- 22 nm — 2012
- 14 nm --- 2014
- 10 nm — 2016
- 7 nm — est. 2018
- 5 nm — est. 2020

Current SiO_2 gate oxide thicknesses in the 1 nm range → with high-k dielectrics, $Si_wHf_xN_yO_z$,… a few nm or more

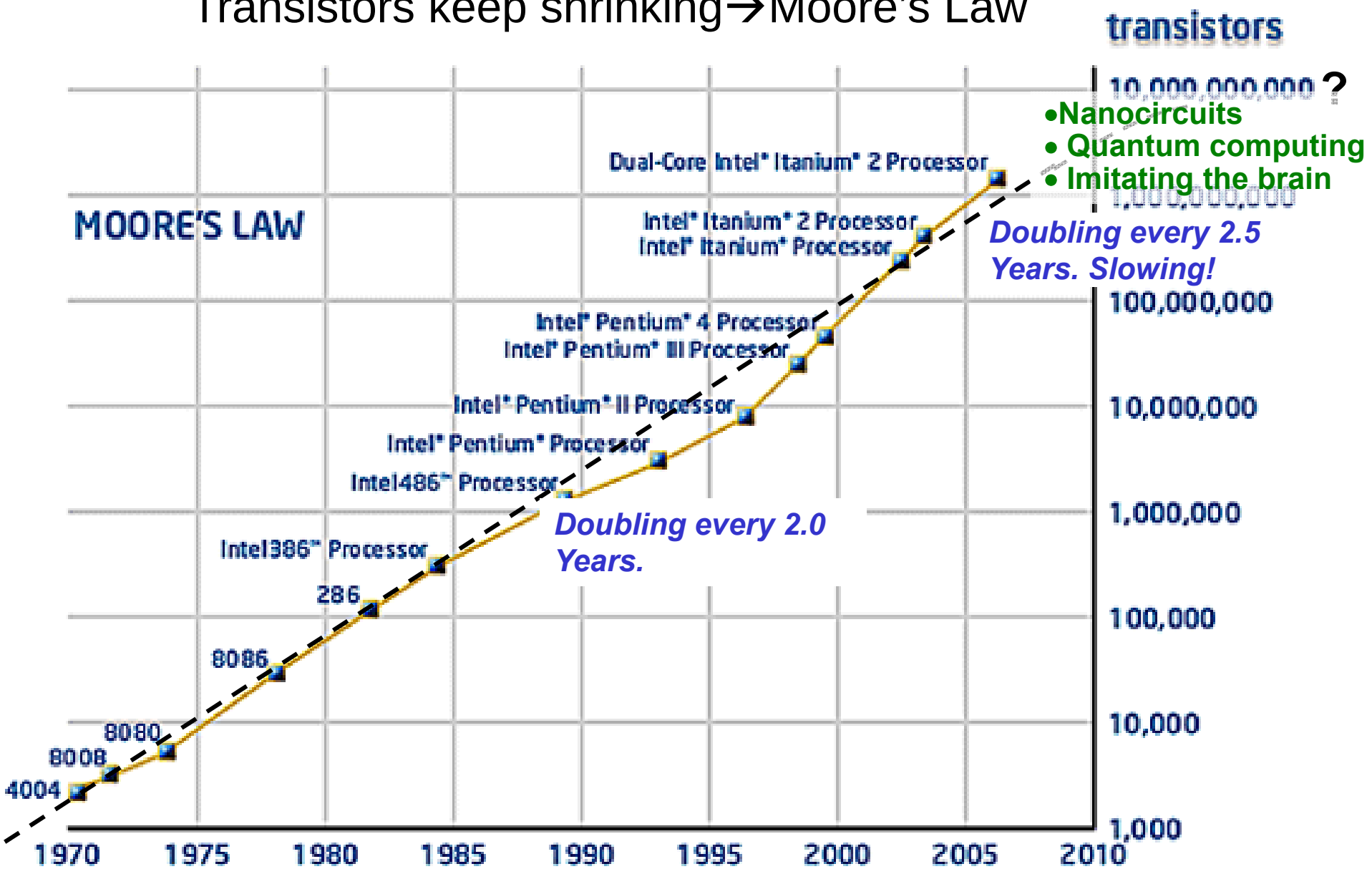
Mixed oxides:
Si^{+1}, Si^{+2}, Si^{+3}, and coord. sites



Chau et al., INTEL

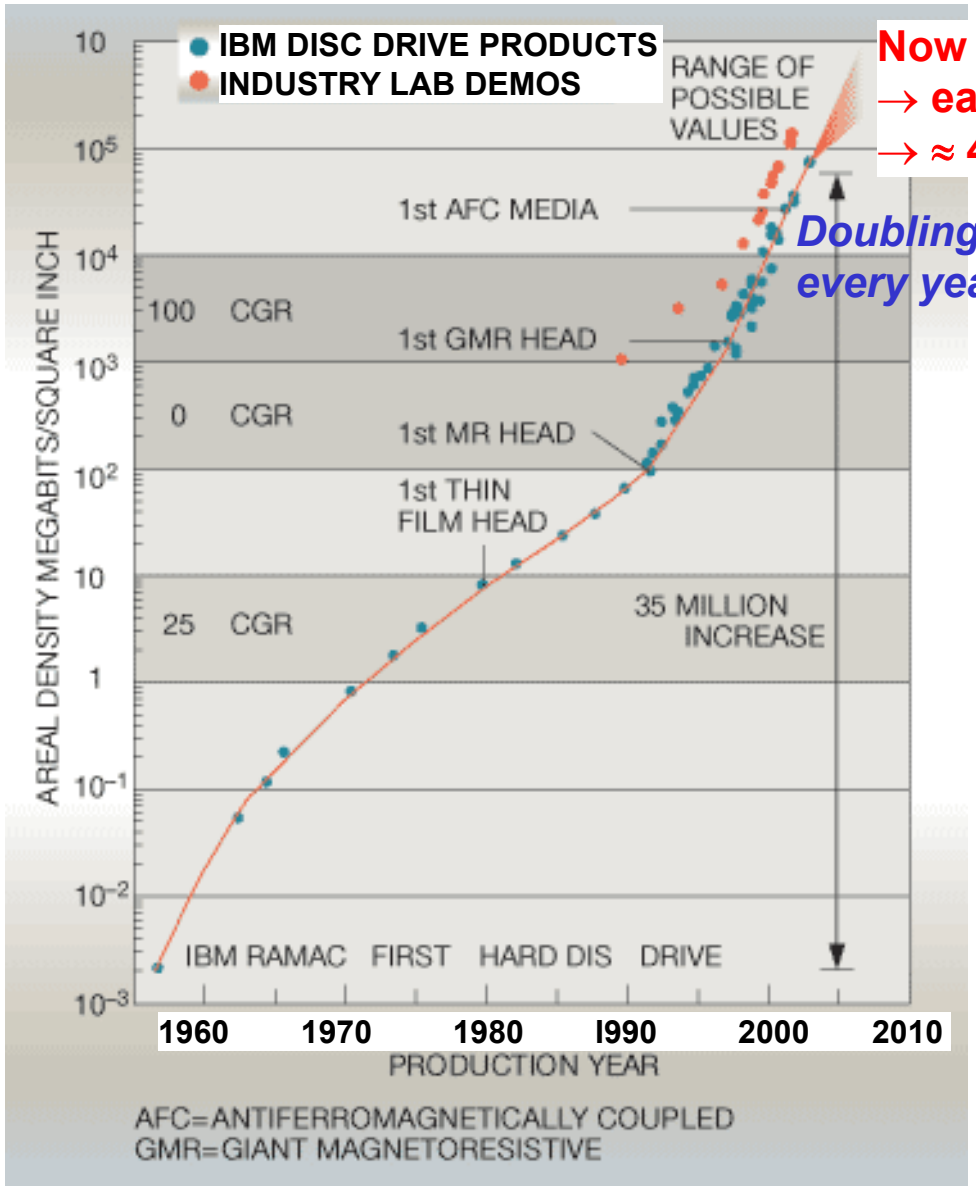
Fig. 2 High resolution TEM cross section of 1.2nm physical SiO_2 gate oxide at the 90nm logic technology node. → 65 nm technology → 45 nm → 32 nm→ 22 nm→14 nm→…

Transistors keep shrinking→Moore's Law



http://www.intel.com/technology/mooreslaw/index.htm

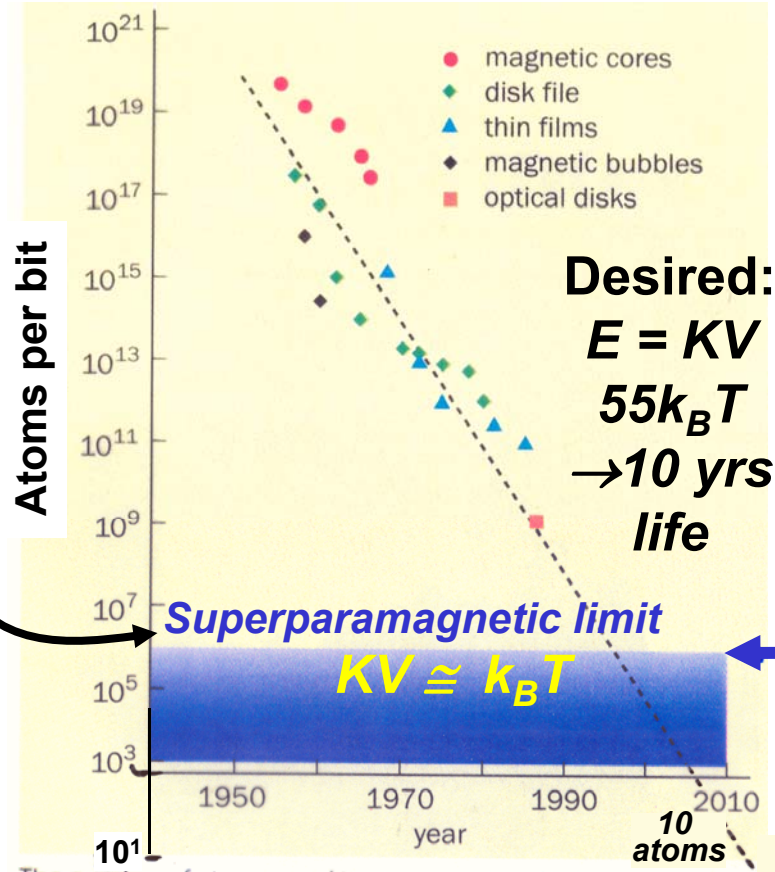
"Moore's Law" for magnetic storage



Doubling every year!

Now 170 Gbits/in^2 = 20 Gbytes/in^2
→ each bit ~14 nm x 30 nm x 210 nm
→ ≈ 4,000,000 atoms, read at GHz rates

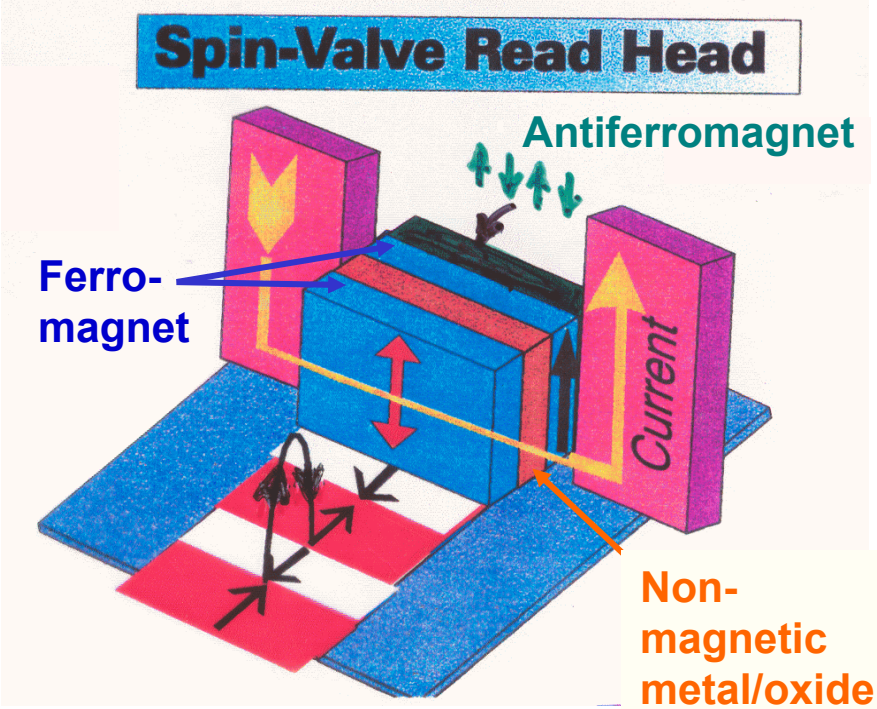
How for can we go?



The number of atoms used to store one bit of information with different forms of magnetic or optical storage has reduced over the years. The blue region indicates the superparamagnetic regime, below which thermal fluctuations at room temperature could alter the orientation of magnetic bits.

http://www.research.ibm.com/journal/sj/422/grochowski.html

Harris, Awschalom Physics World, Jan. '99

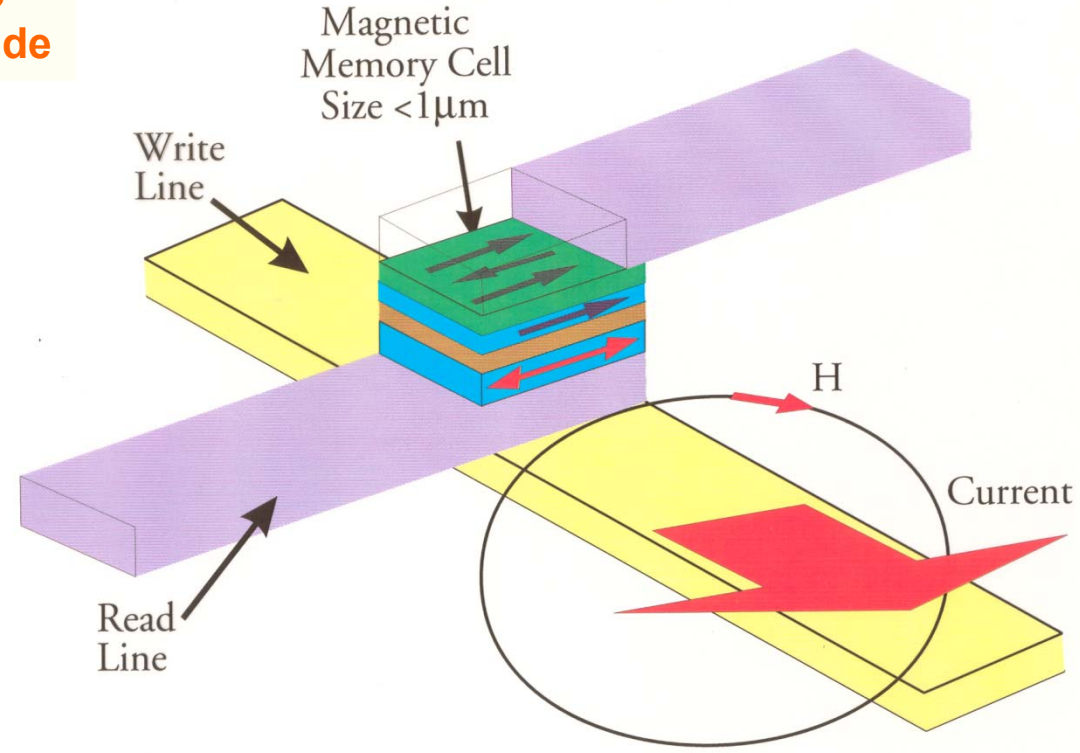


Some key elements in Spintronics/Semiconductors/ Sensors—multilayer nanostructures

Giant change in resistance→ much smaller read heads

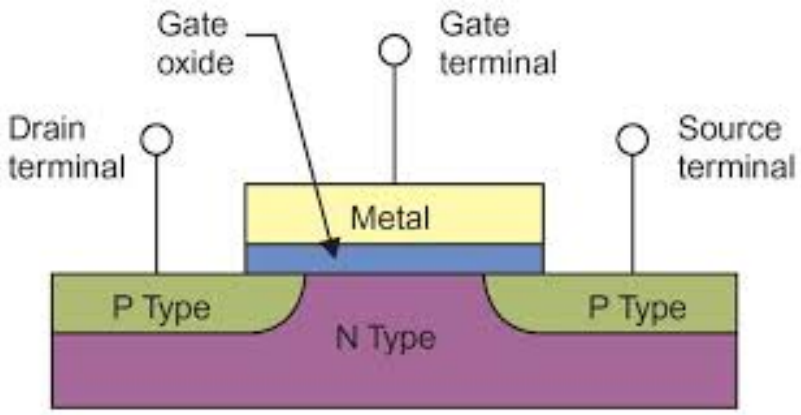
Nobel Prize in Physics 2007: Fert and Grünberg: for the discovery of Giant Magnetoresistance

Magnetic Random Access Memory (MRAM-Non Volatile)

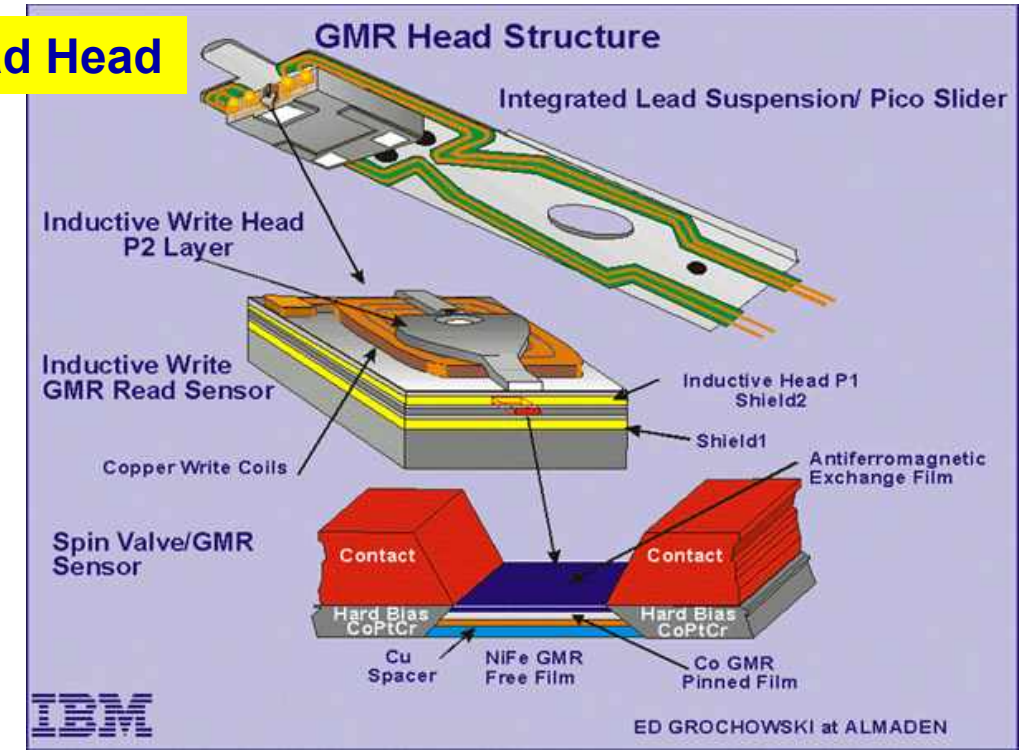


Multilayers and interfaces in information and energy technology

Transistor

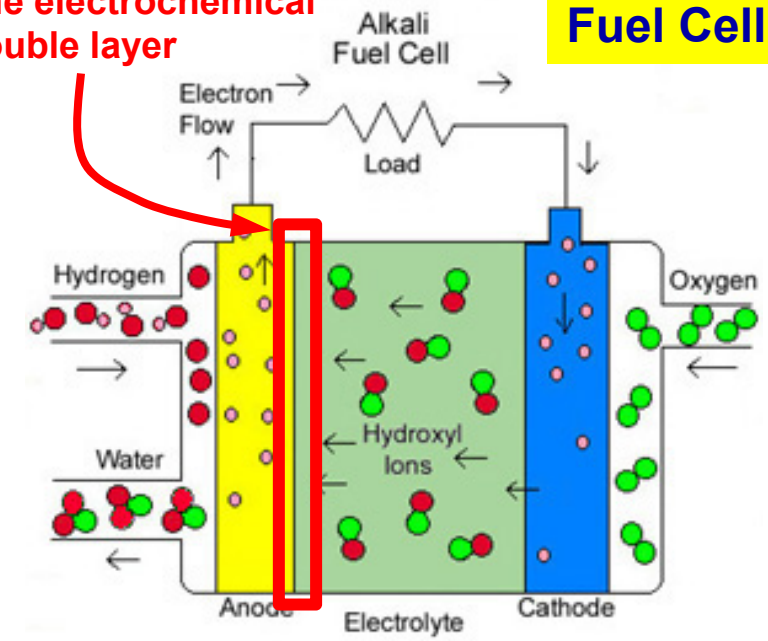


Hard Drive Read Head



Fuel Cell

The electrochemical double layer



Photovoltaic Cell

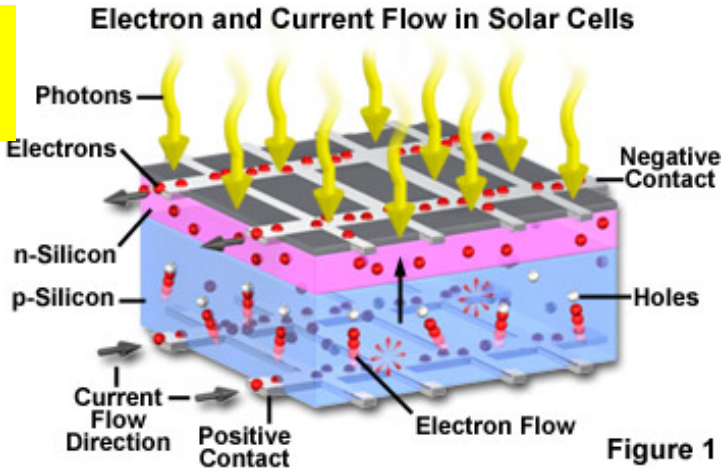
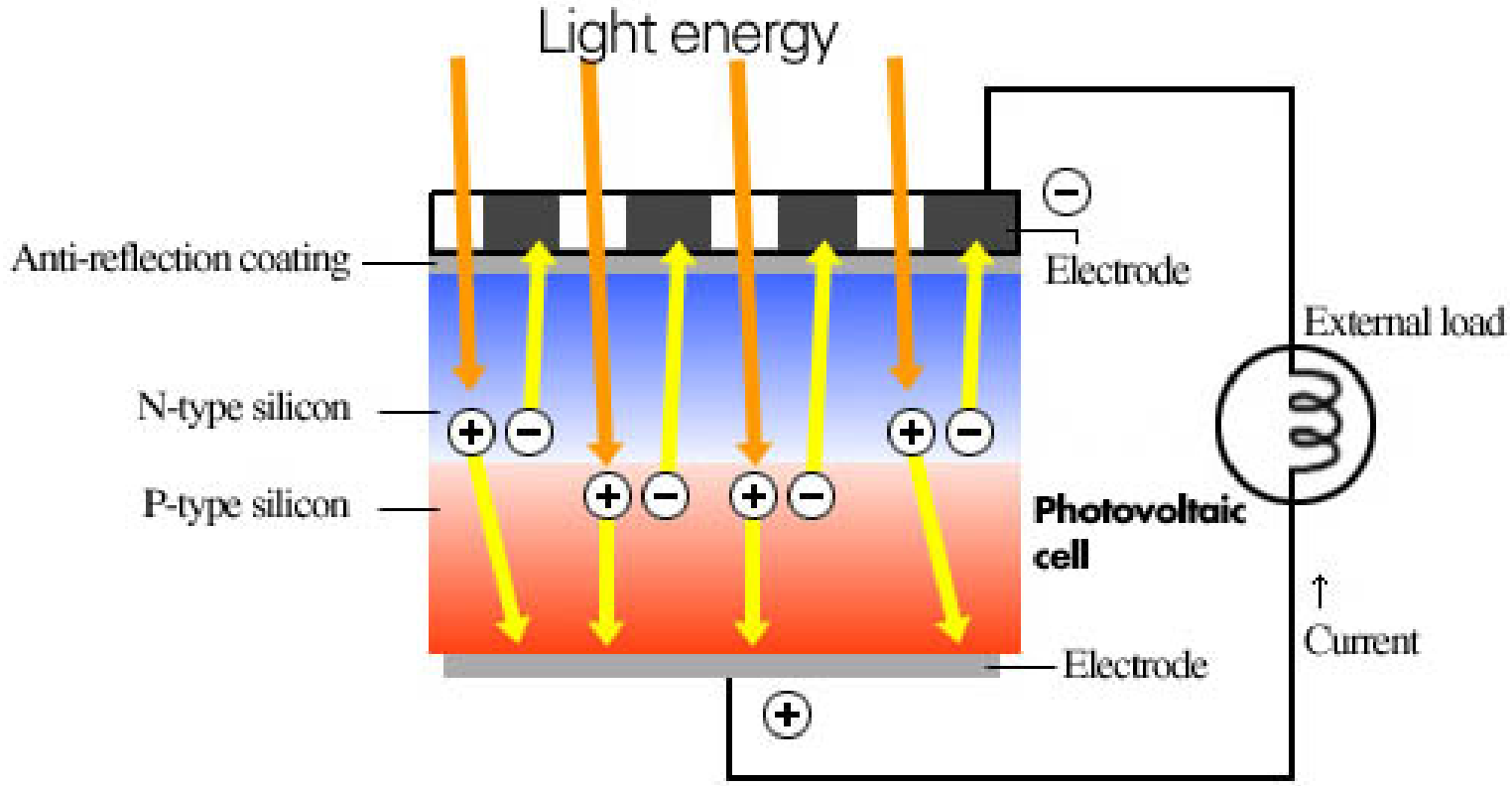
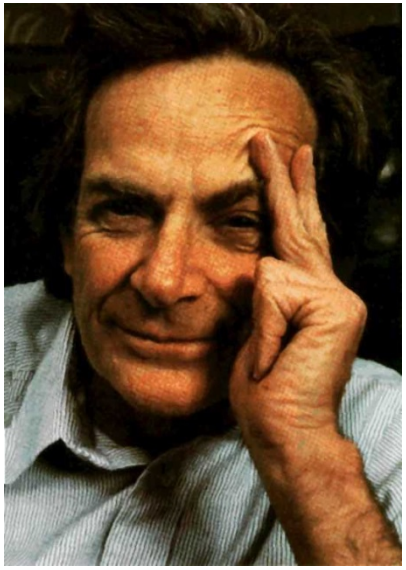


Figure 1

The photovoltaic cell

A photovoltaic cell generates electricity when irradiated by sunlight.





1959 — Richard P. Feynman "There's plenty of room at the bottom"

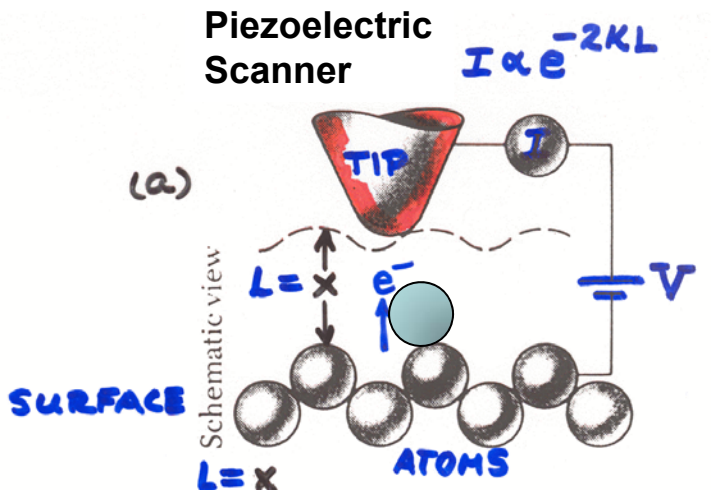
"Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?"

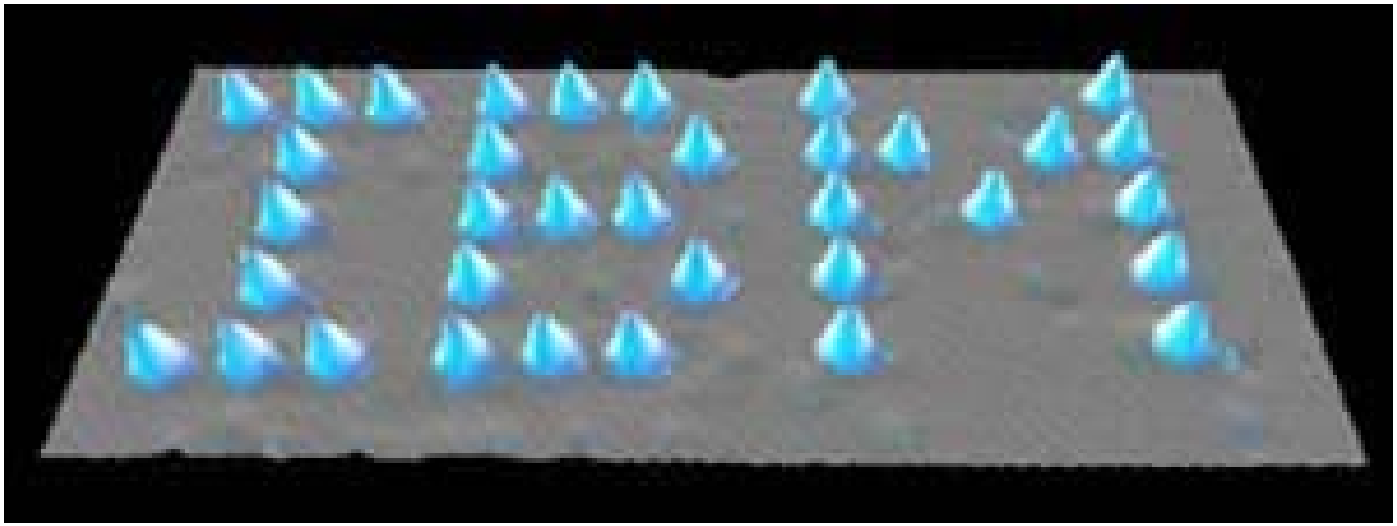
It would be possible if you could print it with dots (= bits) that are 8 nanometers or about 32 metal atoms across, containing about 1000 atoms, or a cube 10 x 10 x 10 atoms

+ Many visionary ideas:

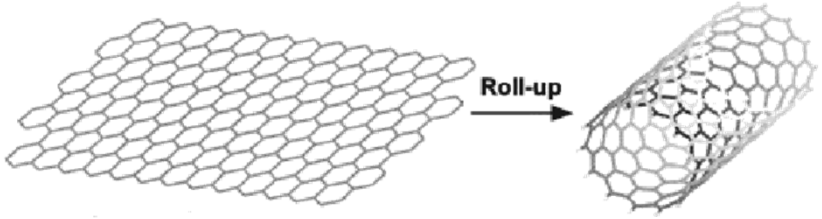
Miniaturization of computers
Imaging and manipulation of single atoms or molecules →→
http://www.zyvex.com/nanotech/feynman.html

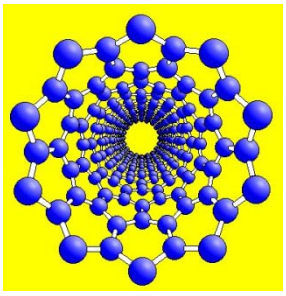
Writing with single atoms—30 years later



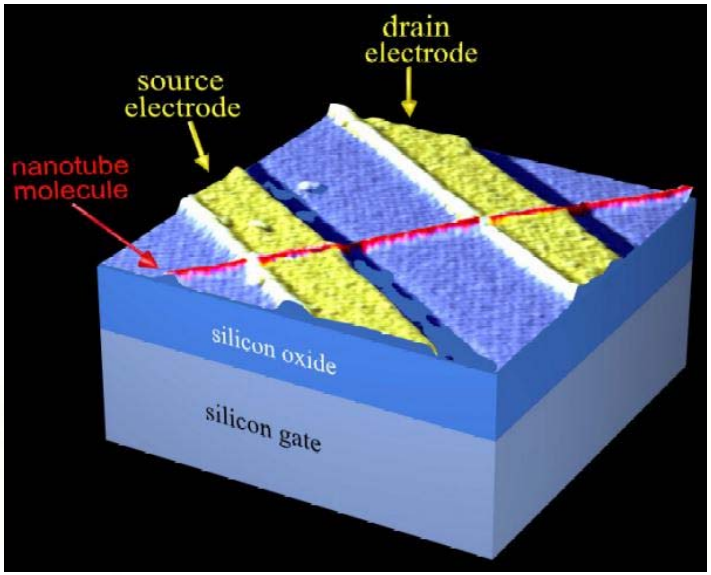


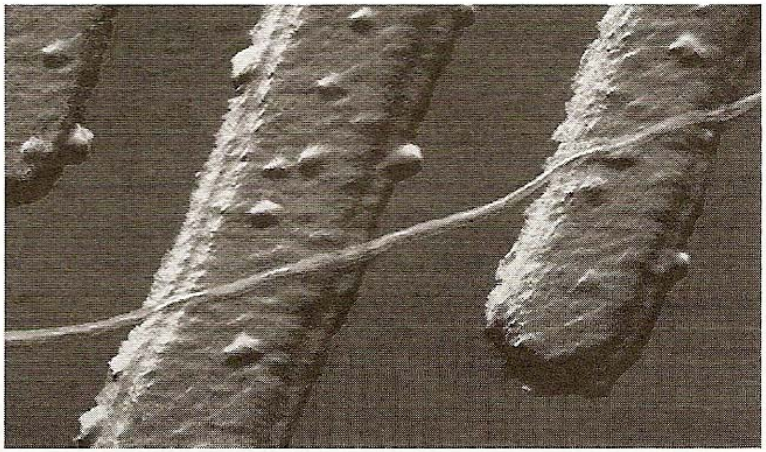
1989--IBM, written with single xenon atoms, using a scanning tunneling microscope, but too slow for real data storage—so far

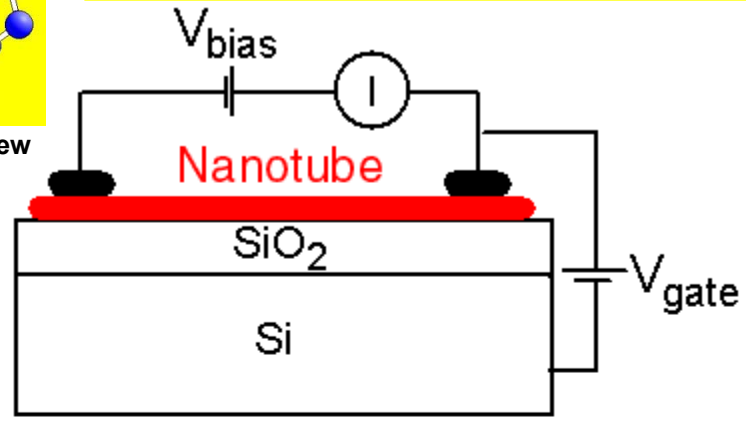


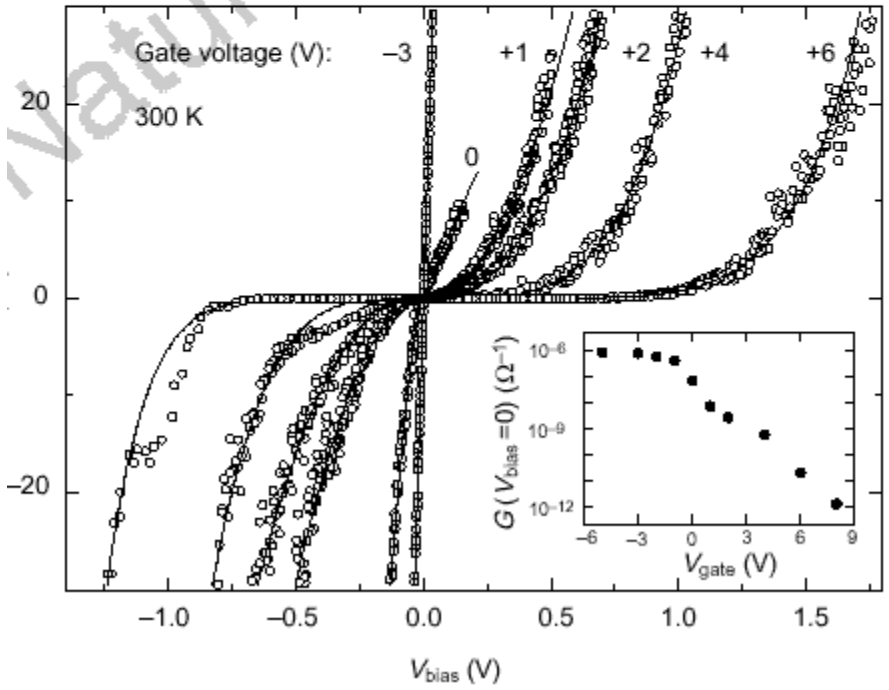


A carbon nanotube transistor



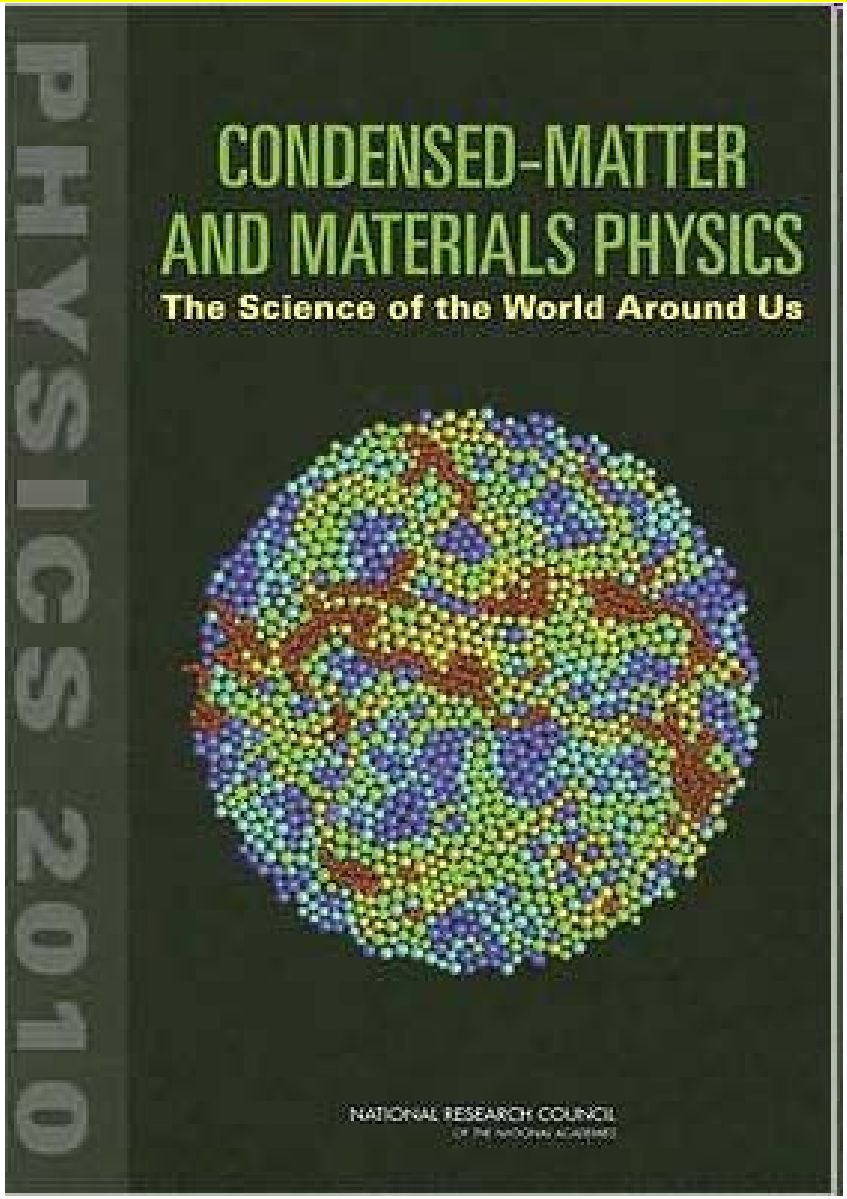






http://ipn2.epfl.ch/CHBU/images/NTtransistir.gif

A Look at the Future--
Condensed Matter Physics—The Science of the World Around Us

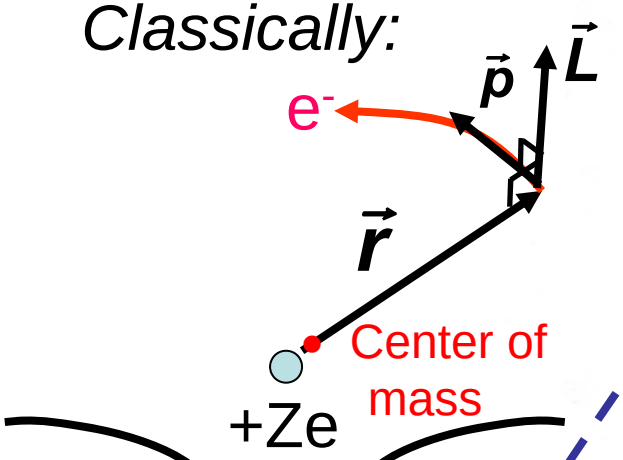


- ***How Do Complex Phenomena Emerge from Simple Ingredients?→***
  Strongly correlated materials
- ***How Will the Energy Demands of Future Generations Be Met?→***
  Solar cells, fuel cells,…
- ***What New Discoveries Await Us in the Nanoworld?→***
  Surfaces and interfaces, novel nanodevices
- ***How Will the Information Technology Revolution Be Extended?→***
  Nanoscale logic and memory, spin electronics =”spintronics”
- ***What Happens Far from Equilibrium and Why?→ Many nanoscale systems***
- ***What Is the Physics of Life?→ Biophysics***

Publisher: National Academies Press
Pub. Date: December 2007
ISBN-13: 9780309109697, 286pp

The Hydrogenic Atom Schroedinger Equation: Spherical Polar Coordinates

Classically:



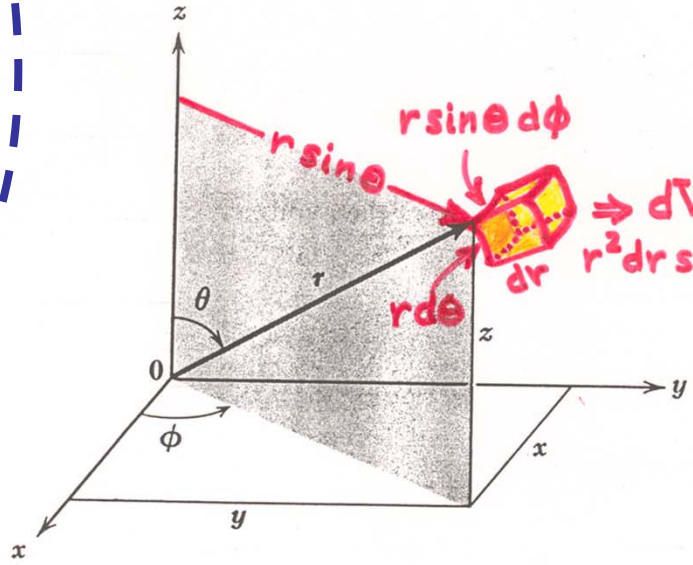
$V(r) = -Ze^2/4\pi\varepsilon_0 r$

$\vec{L} = \vec{r} \times \vec{p}$ **is conserved**

$\mu =$ **reduced mass**

$$= \frac{m_e}{1 + \frac{m_e}{M_n}}$$

Quantum mechanically:



$\Rightarrow dV = r^2 dr \sin\theta d\theta d\phi$

$\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi =$

$-\cos\theta\,|_0^{\pi} \times 2\pi = 4\pi$

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

Polar angle = θ = arc cos(z/r)

Azimuthal angle = ϕ = arc tan(y/x)

Converting to new coordinates

$$\therefore \hat{K} = -\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

$$= -\frac{\hbar^2}{2\mu}\cdot\frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] + \left[\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$= \frac{\hat{p}_r^2}{2\mu}$ $\qquad$ $= \frac{\hat{L}^2}{2\mu r^2}$

$\Rightarrow$ H-ATOM SCH. EQN. IS:

$$\hat{H}\psi(r,\theta,\phi) = \hat{K}\psi(r,\theta,\phi) - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$\rightarrow Z_{eff}(r)$ IN MANY-e ATOM

• USE SEPARATION OF VARIABLES:

$$\Psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$$ [$\Theta(\theta) \equiv f(\theta)$ & $\Phi(\phi) \equiv g(\phi)$ in text]

– ASSUMED FORM –

• SUBSTITUTE, REARRANGE →

ϕ: $\frac{d^2\Phi}{d\phi^2} + C_\phi^2\Phi = 0 \Rightarrow \Phi(\phi) = A e^{\pm i C_\phi \phi}$

$C_\phi = m_\ell = 0, \pm 1, \cdots$ $\quad \boxed{\Phi_{m_\ell}(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i m_\ell \phi}}$ – COMPLEX (1)

θ: $\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left[C_\theta - \frac{m_\ell^2}{\sin^2\theta}\right]\Theta = 0$ (2)

$C_\theta = \ell(\ell+1)$ → $Z_{eff}(r)$ IN MANY e^- ATOM

R: $\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{\ell(\ell+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]R = ER$ (3)

A "RADIAL SCHROEDINGER EQN."

$\hat{H}_{radial} R = ER \Rightarrow$ $\boxed{E = E_n = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0}\cdot\frac{1}{n^2}, \quad n = 1,2,3,\cdots}$ **The Bohr Formula!**

• SOLVING FOR Θ WITH (2) ⇒

$\boxed{\Theta_{\ell m_\ell}(\theta) = \text{ASSOC. LEGENDRE POLYNOMIALS IN } (\cos\theta) - \text{REAL}}$

$\ell = 0, 1, 2, 3, \cdots (n-1)$

$m_\ell = -\ell, -\ell+1, \cdots 0 \cdots +\ell-1, +\ell$ $\quad (2\ell+1)$

The same for many-e⁻ atoms

SOLVING FOR R WITH (3) ⇒

$\boxed{R_{n\ell}(r) = \text{ASSOC. LAGUERRE FUNCTIONS} = (\text{POLYNOMIAL IN } r)\cdot e^{-Zr/a_0}}$ ALSO – REAL

Changes for many-e⁻ atoms

The atomic orbitals:

$Y_{\ell m_\ell}(\theta,\phi) =$ **" spherical harmonics"**

But we can make them real for convenience

COMPLEX, IF $m \neq 0$

TABLE 6.1

NORMALIZED WAVE FUNCTIONS OF THE HYDROGEN ATOM FOR $n = 1, 2,$ AND 3* ($Z=1$ = HYDROGEN)

$\psi_{n\ell m_\ell}(r,\theta,\phi) = \Phi_{m_\ell}\,\Theta_{\ell m_\ell}\,R_{n\ell}$

n	ℓ	m_ℓ	$\Phi_{m_\ell}(\phi)$	$\Theta_{\ell m_\ell}(\theta)$	$R_{n\ell}(r)$	$\psi_{n\ell m_\ell}(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\cos\theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\cos\theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}(3\cos^2\theta-1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.3 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

IS SAME FOR MANY e^- ATOMS

CHANGES FOR MANY e^- ATOMS

$e^{-r/na_0} \rightarrow e^{-Zr/na_0}$ for hydrogenic

$Z \rightarrow Z_{eff}(r)$ in many-e^- atoms

And for a **hydrogenic** atom: atomic no. Z, one electron

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta$$

$$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi}$$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$$

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\cos\theta$$

$$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\sin\theta\, e^{\pm i\phi}$$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$$

$$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$$

$$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$$

These are written in terms of the parameter

$$a_0 \equiv \frac{\hbar^2}{\mu e^2} = 0.529 \times 10^{-8}\ \text{cm}$$

$$\mu = \text{reduced mass} = \frac{m_e}{1 + \frac{m_e}{M_{nucleus}}}$$

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}, n = 1,2,3,...$$

$$\langle r_{nl} \rangle = \frac{n^2 a_0}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{\ell(\ell+1)}{n^2}\right)\right]$$

$$= \frac{n^2 a_0}{Z}\left[\begin{array}{l} \textit{1.5 for 1s, 1.5 for 2s,} \\ \textit{1.25 for 2p, ... converging} \\ \textit{to 1.0 for very large n and } \ell_{max} = n-1 \\ \textit{(Correspondence Principle limit)} \end{array}\right]$$

$$r_{Bohr} = \frac{n^2 a_0}{Z}$$

MAKING THE ATOMIC ORBITALS REAL (E.G., FOR CHEMICAL BONDING):

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\,\frac{1}{\sqrt{2\pi}}\,e^{i m_\ell \phi}$$

- $\psi_{n\ell m_\ell}$: COMPLEX
- $R_{n\ell}(r)$: REAL
- $\Theta_{\ell m_\ell}(\theta)$: REAL
- $\frac{1}{\sqrt{2\pi}}e^{i m_\ell \phi}$: COMPLEX IF $m_\ell \neq 0$

SO JUST TAKE COMB. OF $\pm m_\ell$ AS:

$$\psi_{n\ell(-)}(r,\theta,\phi) = \begin{cases} \frac{1}{2}\left[\psi_{n\ell m_\ell} + \psi_{n\ell -m_\ell}\right] \propto R_{n\ell}\,\Theta_{\ell m_\ell}\cos m_\ell\phi \\ \frac{1}{2i}\left[\psi_{n\ell m_\ell} - \psi_{n\ell -m_\ell}\right] \propto R_{n\ell}\,\Theta_{\ell m_\ell}\sin m_\ell\phi \end{cases}$$

REAL

EXAMPLE: 2p ORBITALS

$\psi_{210} = \psi_{2p_0} = \psi_{2p_z} \propto r\cos\theta = z$ (ALREADY REAL)

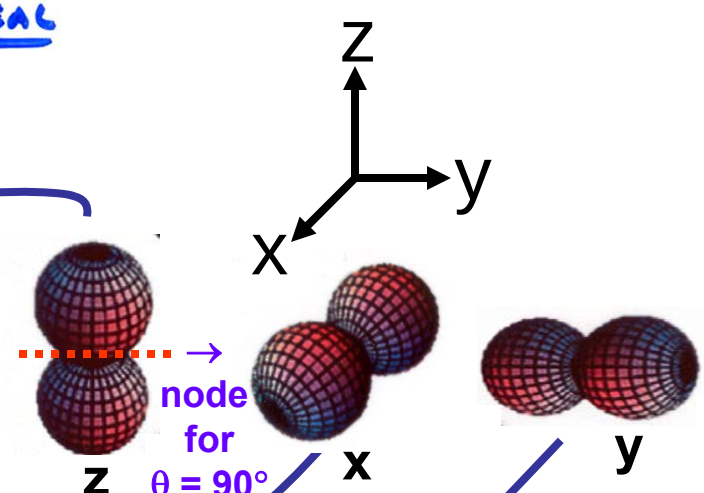
$\psi_{211} = \psi_{2p_{+1}} \propto r\sin\theta\, e^{i\phi} = r\sin\theta[\cos\phi + i\sin\phi]$

$\psi_{21-1} = \psi_{2p_{-1}} \propto r\sin\theta\, e^{-i\phi} = r\sin\theta[\cos\phi - i\sin\phi]$

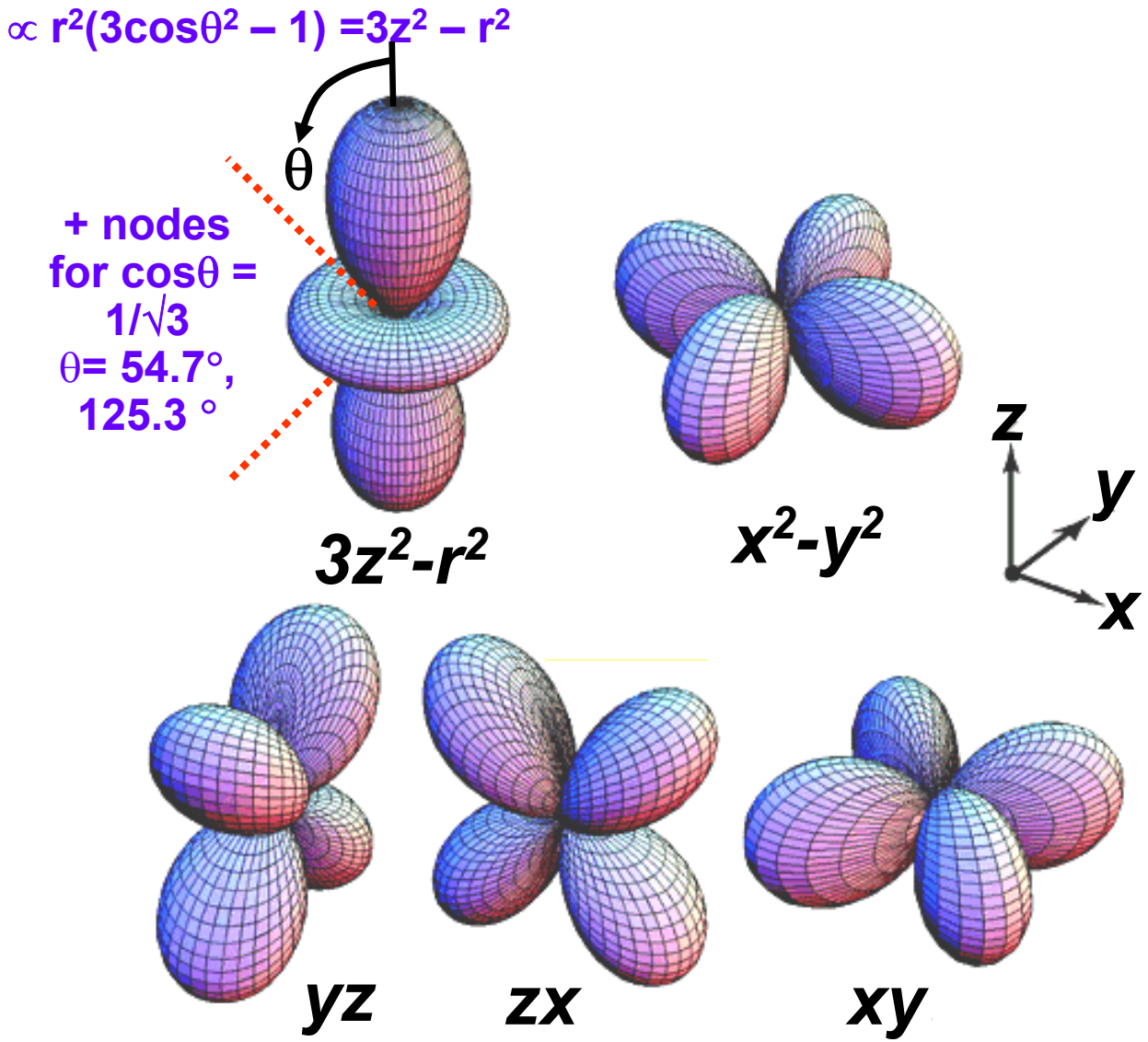
$\therefore$

$\frac{1}{2}[\psi_{2p_{+1}} + \psi_{2p_{-1}}] = \psi_{2p_x} \propto r\sin\theta\cos\phi = x$

$\frac{1}{2i}[\psi_{2p_{+1}} - \psi_{2p_{-1}}] = \psi_{2p_y} \propto r\sin\theta\sin\phi = y$



And the same thing for the d orbitals:



The real atomic orbitals, through 3d

$$\psi_{1s} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$\psi_{2s} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2-\frac{Zr}{a}\right)e^{-Zr/2a}$$

$$\psi_{2p_z} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\cos\theta$$

$$\psi_{2p_x} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\cos\varphi$$

$$\psi_{2p_y} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\sin\varphi$$

$$\psi_{3s} = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(27-18\frac{Zr}{a}+2\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}$$

$$\psi_{3p_z} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6-\frac{Zr}{a}\right)re^{-Zr/3a}\cos\theta$$

$$\psi_{3p_x} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6-\frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\cos\varphi$$

$$\psi_{3p_y} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6-\frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\sin\varphi$$

$$\psi_{3d_{z^2}} = \frac{1}{81(6\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}(3\cos^2\theta-1)$$

$$\psi_{3d_{xz}} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\cos\varphi$$

$$\psi_{3d_{yz}} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\sin\varphi$$

$$\psi_{3d_{x^2-y^2}} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\cos 2\varphi$$

$$\psi_{3d_{xy}} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\sin 2\varphi$$

$\Psi_{n\ell m_\ell m_s}(r,\theta,\varphi,spin) = \Psi_{n\ell m_\ell}(r,\theta,\varphi) x [\alpha(\uparrow) \text{ or } \beta(\downarrow)]$

With spin

$Y_{\ell m_\ell}(\theta,\phi) =$ "spherical harmonics"

The atomic orbitals:

COMPLEX, IF $m \neq 0$

But we can make them real for convenience

TABLE 6.1

NORMALIZED WAVE FUNCTIONS OF THE HYDROGEN ATOM FOR n = 1, 2, AND 3* (Z=1 = HYDROGEN)

$\Psi_{n\ell m_\ell}(r,\theta,\phi) = \Phi_{m_\ell} \Theta_{\ell m_\ell} R_{n\ell}$

n	ℓ	m_ℓ		$\Phi_{m_\ell}(\phi)$	$\Theta_{\ell m_\ell}(\theta)$	$R_{n\ell}(r)$	$\Psi_{n\ell m_\ell}(r,\theta,\phi)$
1	0	0	1s	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	2s	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$2p_0$	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$ → node for $\theta = 90°$
2	1	±1	$2p_{\pm1}$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$
3	0	0	3s	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$3p_0$	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos\theta$ → node for $r = 6a_0$
3	1	±1	$3p_{\pm1}$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin\theta\, e^{\pm i\phi}$
3	2	0	$3d_0$	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3\cos^2\theta - 1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2\theta - 1)$ → nodes for $\cos^2\theta = 1/3$
3	2	±1	$3d_{\pm1}$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin\theta\cos\theta\, e^{\pm i\phi}$ → θ= 54.7°, 125.3 °
3	2	±2	$3d_{\pm2}$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.3 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

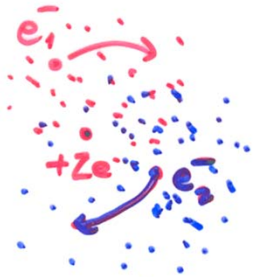
IS SAME FOR MANY e⁻ ATOMS

CHANGES FOR MANY e⁻ ATOMS

$e^{-r/na_0} \rightarrow e^{-Zr/na_0}$ for hydrogenic

$Z \rightarrow Z_{eff}(r)$ in many-e⁻ atoms

What properties do wave functions of overlapping (thus indistinguishable) particles have?—electrons as example:



$\psi = \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)$, *including spin of both electrons*

But labels can't affect any measurable quantity.

E.g. – probability density :

$$\left|\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)\right|^2 = \left|\psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1)\right|^2$$

Therefore

$$\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \pm 1\psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1)$$
$$\equiv \hat{P}_{12}\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)$$

with $\hat{P}_{12}$ = *permutation operator* $\rightarrow \vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2$

and eigenvalues of ± 1

Finally, all particles in two classes :

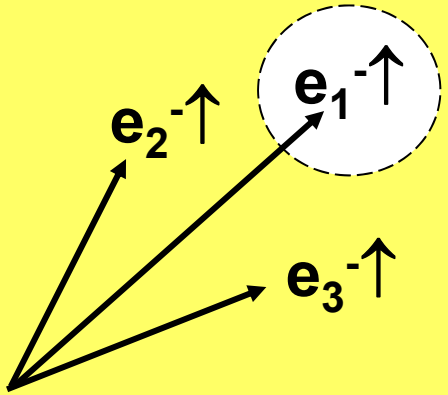
FERMIONS : (incl. e^-*'s) :* ψ *antisymmetric*

$s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ldots$ $\qquad \hat{P}_{12}\psi = -1\psi$

BOSONS : (incl. photons) : ψ *symmetric*

$s = 0, 1, 2, \ldots$ $\qquad \hat{P}_{12}\psi = +1\psi$

Probability of finding two electrons at the same point in space with the same spin (↑↑ or ↓↓) is zero: "the Fermi Hole"



→the Exchange Interaction

→Hund's 1st rule & magnetism

The Fermi hole or Exchange/Correlation Hole as seen in theory-silicon atom:

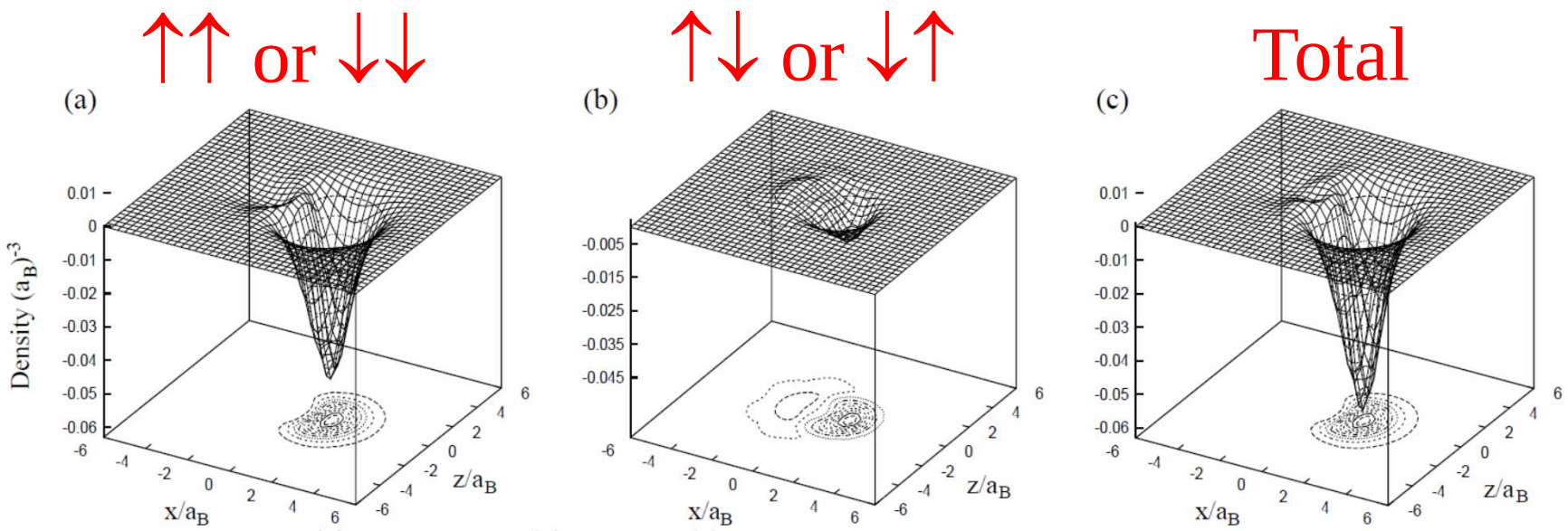


FIG. 1. The same spin (a), opposite spin (b) and total (c) exchange-correlation hole about a spin-up particle located at 1.4 a_B from the atom center on the x axis (parallel to the p orbitals) for the ground state of the Si atom in the $L_z = 0$ projection. The surface plot shows the change in density along a plane cutting through the origin along the x and z axes.

Fong (UC Davis) et al., Phys. Rev. A 62, 062507

Antisymmetry and the Pauli Exclusion Principle:

Try Helium, 2 electrons in ground state 1s wave functions, "$1s^2$"

Simple normalized antisymmetric trial wave function is

$$\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\vec{s}_2)$$

$$= \frac{1}{\sqrt{2}}\left[\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)\varphi_{1s}(\vec{r}_2,\vec{s}_2=\downarrow) - \varphi_{1s}(\vec{r}_1,\vec{s}_1=\downarrow)\varphi_{1s}(\vec{r}_2,\vec{s}_2=\uparrow)\right]$$

interchanging labels via permutation operator $\hat{P}_{12}$ gives

$$\hat{P}_{12}\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\vec{s}_2) \equiv \psi(\vec{r}_2,\vec{s}_2;\vec{r}_1,\vec{s}_1)$$

$$= \frac{1}{\sqrt{2}}\left[\varphi_{1s}(\vec{r}_2,\vec{s}_2=\uparrow)\varphi_{1s}(\vec{r}_1,\vec{s}_1=\downarrow) - \varphi_{1s}(\vec{r}_2,\vec{s}_2=\downarrow)\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)\right]$$

$$= -\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\vec{s}_2)\text{, as required}$$

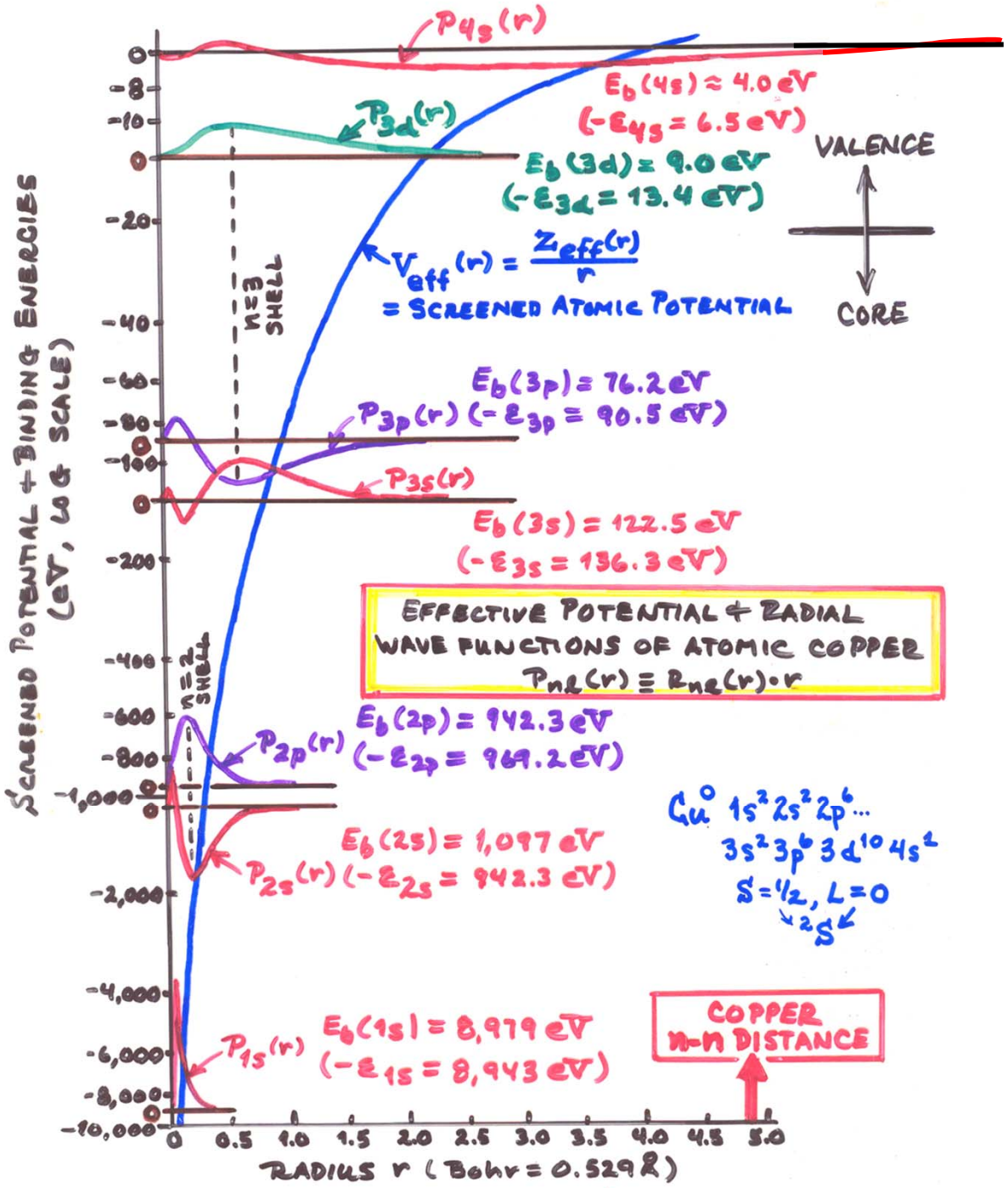
Can't tell which electron is spin up--indistinguishable

Also, if we try to put both electrons in 1s with spin-up (↑), first term always cancels second term, and $\psi = 0$! Therefore, we have the Pauli Exclusion Principle !!!→

Intraatomic electron screening in many-electron atoms--a self-consistent Q.M. calculation

Plus radial one-electron functions:

$$P_{n\ell}(r) \equiv rR_{n\ell}(r)$$



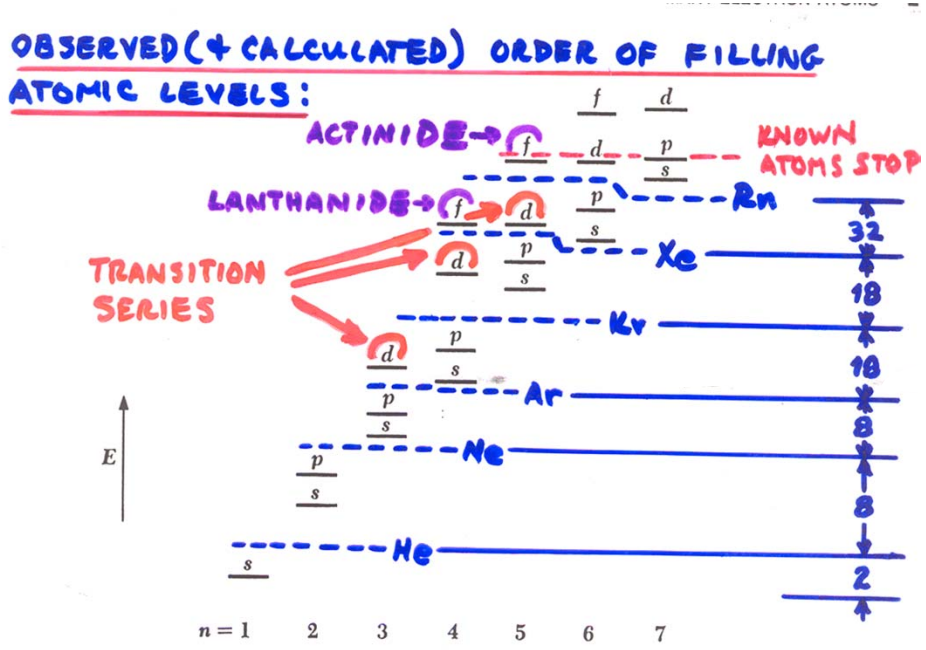
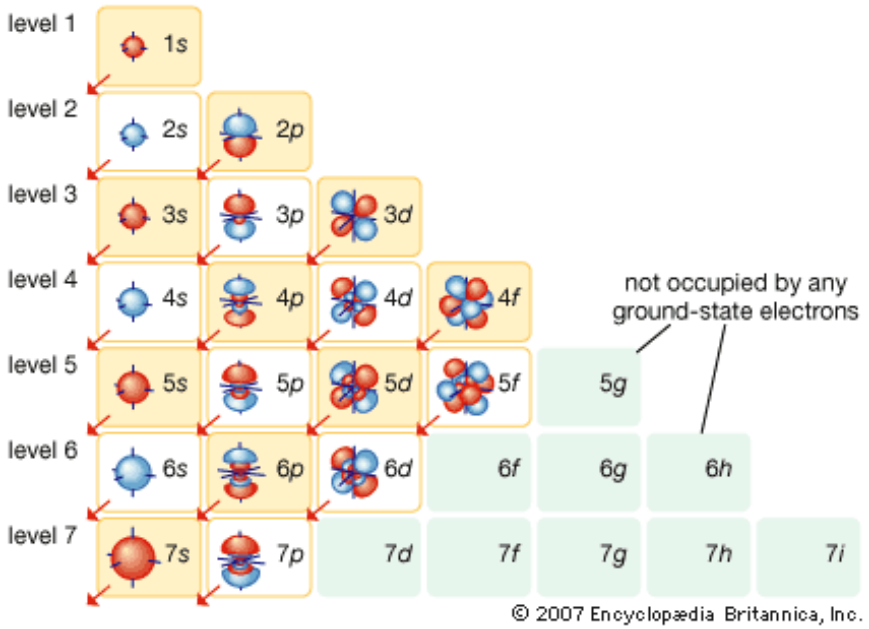


FIGURE 7.13 The sequence of quantum states in an atom. Not to scale.



TRANSITION METALS

Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters s, p, d, . . . signify electrons having orbital angular momentum 0, 1, 2, . . . in units $\hbar$; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

H^{1} $1s$																	He^{2} $1s^2$
Li^{3} $2s$	Be^{4} $2s^2$											B^{5} $2s^22p$	C^{6} $2s^22p^2$	N^{7} $2s^22p^3$	O^{8} $2s^22p^4$	F^{9} $2s^22p^5$	Ne^{10} $2s^22p^6$
Na^{11} $3s$	Mg^{12} $3s^2$											Al^{13} $3s^23p$	Si^{14} $3s^23p^2$	P^{15} $3s^23p^3$	S^{16} $3s^23p^4$	Cl^{17} $3s^23p^5$	Ar^{18} $3s^23p^6$
K^{19} $4s$	Ca^{20} $4s^2$	Sc^{21} $3d$ $4s^2$	Ti^{22} $3d^2$ $4s^2$	V^{23} $3d^3$ $4s^2$	Cr^{24} $3d^5$ $4s$	Mn^{25} $3d^5$ $4s^2$	Fe^{26} $3d^6$ $4s^2$	Co^{27} $3d^7$ $4s^2$	Ni^{28} $3d^8$ $4s^2$	Cu^{29} $3d^{10}$ $4s$	Zn^{30} $3d^{10}$ $4s^2$	Ga^{31} $4s^24p$	Ge^{32} $4s^24p^2$	As^{33} $4s^24p^3$	Se^{34} $4s^24p^4$	Br^{35} $4s^24p^5$	Kr^{36} $4s^24p^6$
Rb^{37} $5s$	Sr^{38} $5s^2$	Y^{39} $4d$ $5s^2$	Zr^{40} $4d^2$ $5s^2$	Nb^{41} $4d^4$ $5s$	Mo^{42} $4d^5$ $5s$	Tc^{43} $4d^6$ $5s$	Ru^{44} $4d^7$ $5s$	Rh^{45} $4d^8$ $5s$	Pd^{46} $4d^{10}$ –	Ag^{47} $4d^{10}$ $5s$	Cd^{48} $4d^{10}$ $5s^2$	In^{49} $5s^25p$	Sn^{50} $5s^25p^2$	Sb^{51} $5s^25p^3$	Te^{52} $5s^25p^4$	I^{53} $5s^25p^5$	Xe^{54} $5s^25p^6$
Cs^{55} $6s$	Ba^{56} $6s^2$	La^{57} $5d$ $6s^2$	Hf^{72} $4f^{14}$ $5d^2$ $6s^2$	Ta^{73} $5d^3$ $6s^2$	W^{74} $5d^4$ $6s^2$	Re^{75} $5d^5$ $6s^2$	Os^{76} $5d^6$ $6s^2$	Ir^{77} $5d^9$ –	Pt^{78} $5d^9$ $6s$	Au^{79} $5d^{10}$ $6s$	Hg^{80} $5d^{10}$ $6s^2$	Tl^{81} $6s^26p$	Pb^{82} $6s^26p^2$	Bi^{83} $6s^26p^3$	Po^{84} $6s^26p^4$	At^{85} $6s^26p^5$	Rn^{86} $6s^26p^6$
Fr^{87} $7s$	Ra^{88} $7s^2$	Ac^{89} $6d$ $7s^2$															

Ce^{58} $4f^2$ $6s^2$	Pr^{59} $4f^3$ $6s^2$	Nd^{60} $4f^4$ $6s^2$	Pm^{61} $4f^5$ $6s^2$	Sm^{62} $4f^6$ $6s^2$	Eu^{63} $4f^7$ $6s^2$	Gd^{64} $4f^7$ $5d$ $6s^2$	Tb^{65} $4f^8$ $5d$ $6s^2$	Dy^{66} $4f^{10}$ $6s^2$	Ho^{67} $4f^{11}$ $6s^2$	Er^{68} $4f^{12}$ $6s^2$	Tm^{69} $4f^{13}$ $6s^2$	Yb^{70} $4f^{14}$ $6s^2$	Lu^{71} $4f^{14}$ $5d$ $6s^2$
Th^{90} – $6d^2$ $7s^2$	Pa^{91} $5f^2$ $6d$ $7s^2$	U^{92} $5f^3$ $6d$ $7s^2$	Np^{93} $5f^5$ $7s^2$	Pu^{94} $5f^6$ $7s^2$	Am^{95} $5f^7$ $7s^2$	Cm^{96} $5f^7$ $6d$ $7s^2$	Bk^{97}	Cf^{98}	Es^{99}	Fm^{100}	Md^{101}	No^{102}	Lr^{103}

s^1 s^2 p^1 p^2 p^3 p^4 p^5 p^6

d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

4f1 ... 4f(5d) FILLING ... 4f14

... 5f(6d) FILLING ...

RARE EARTHS

ACTINIDES

* □ = EXCEPTIONS

□ = EXCEPTIONS

→ d^5 + d^{10} : ½ FILLED / FILLED MORE STABLE

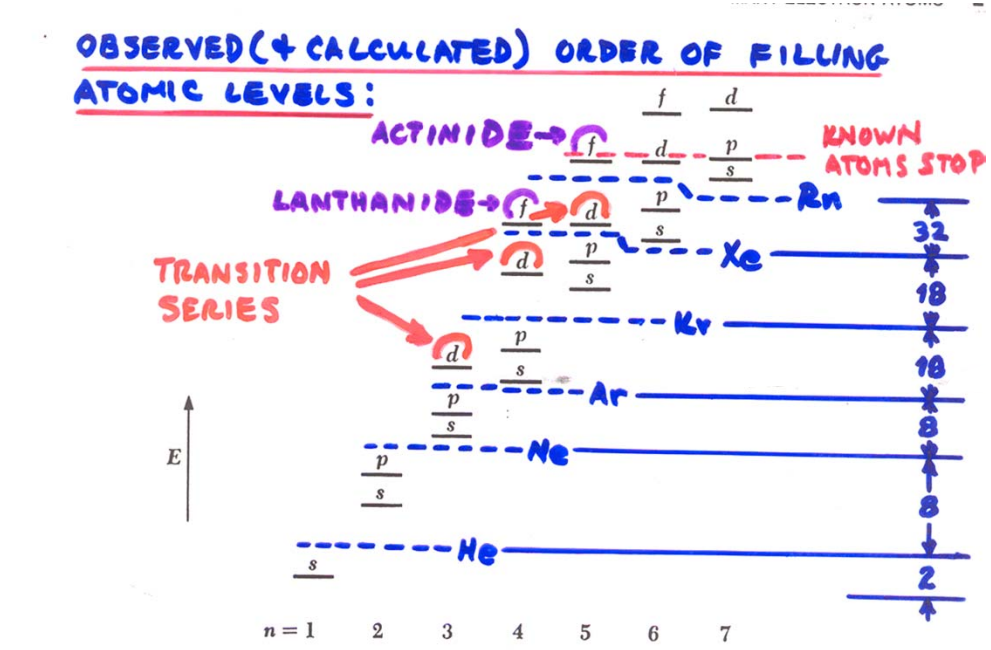
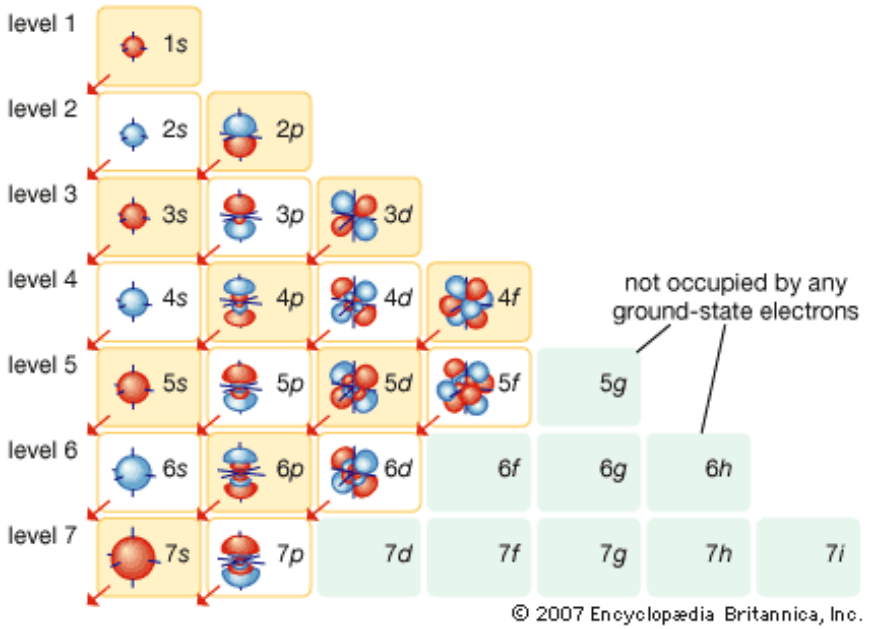


FIGURE 7.13 The sequence of quantum states in an atom. Not to scale.



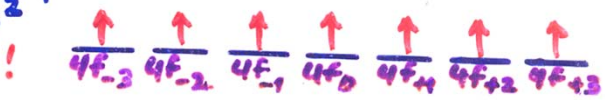
EXAMPLE CONFIGURATIONS:

Z	ATOM	CONFIG.
8	O	$1s^2 2s^2 2p^4$
26	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
63	Eu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7 6s^2$

GROUND-STATE OPEN SHELL COUPLING?

⇒ LARGE μ_{3d} + MAGNETISM

ALSO MAGNETIC!



Exchange interaction.
Hund's First Rule:
highest <u>total</u> spin angular momentum

The quantum mechanics of covalent bonding in molecules: H_2^+ with one electron

$\varphi_- = \varphi_{antibonding}$

$\cong \varphi_{1sa} - \varphi_{1sb}$

$\varphi_+ = \varphi_{bonding}$

$\cong \varphi_{1sa} + \varphi_{1sb}$

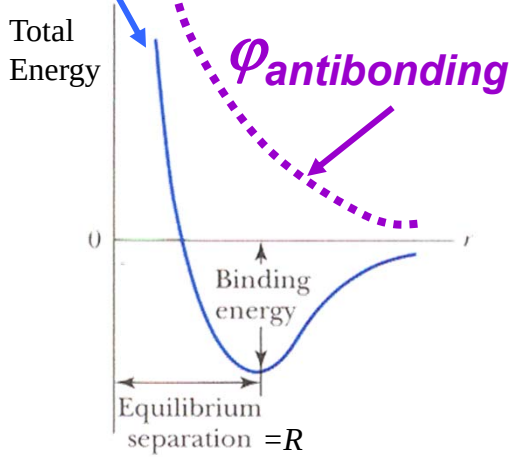


FIGURE 10.2 The net potential energy curve, showing the equilibrium separation and binding energy.

Bonding in H_2^+: a linear combination of atomic orbitals (LCAO) or tight-binding (TB) picture

The bonding state

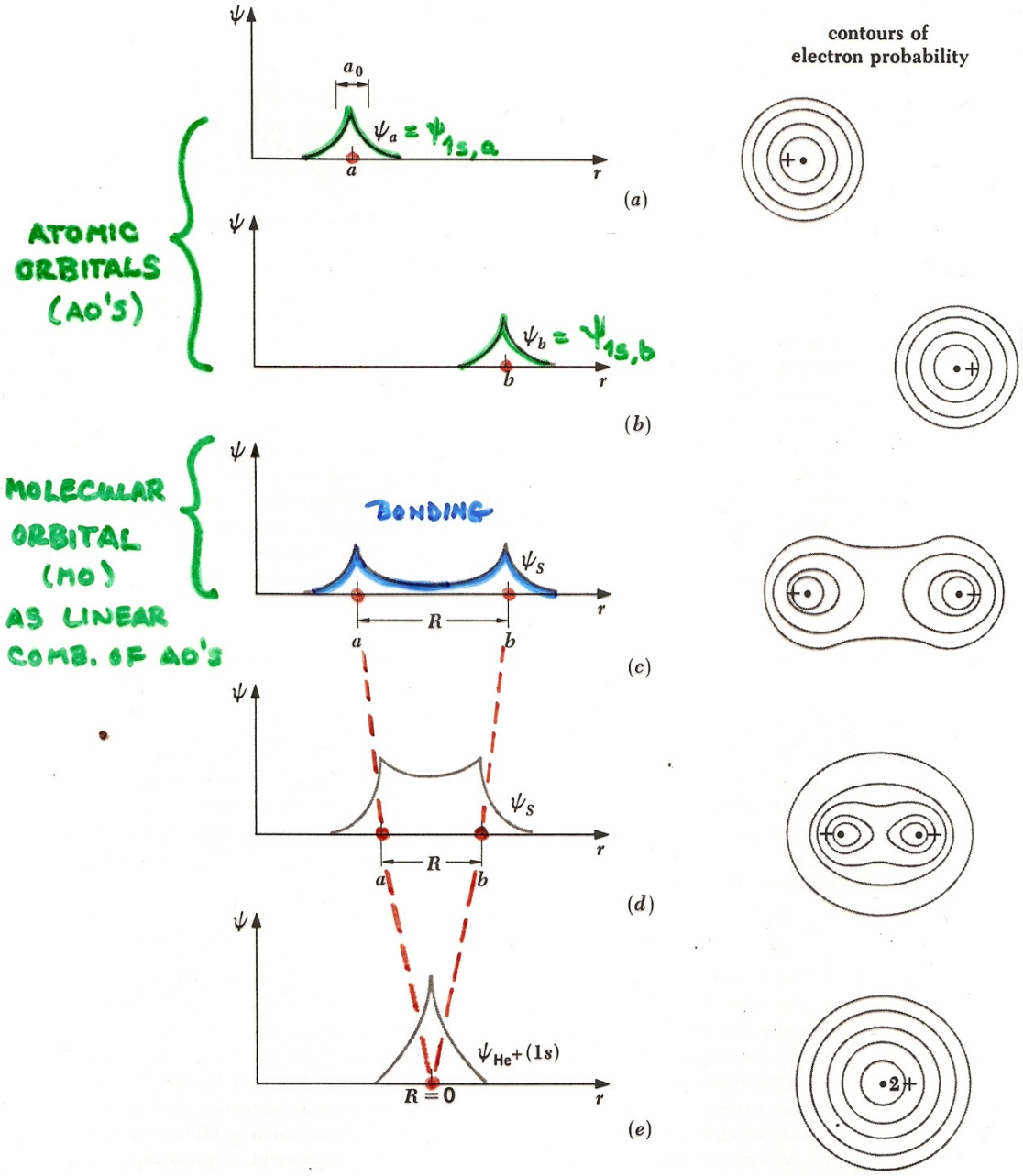


FIGURE 8.5 The combination of two hydrogen-atom 1s wave functions to form the symmetric H_2+ wave function ψ_S.

Bonding in H_2^+: a linear combination of atomic orbitals (LCAO) or tight-binding (TB) picture

The anti-bonding state

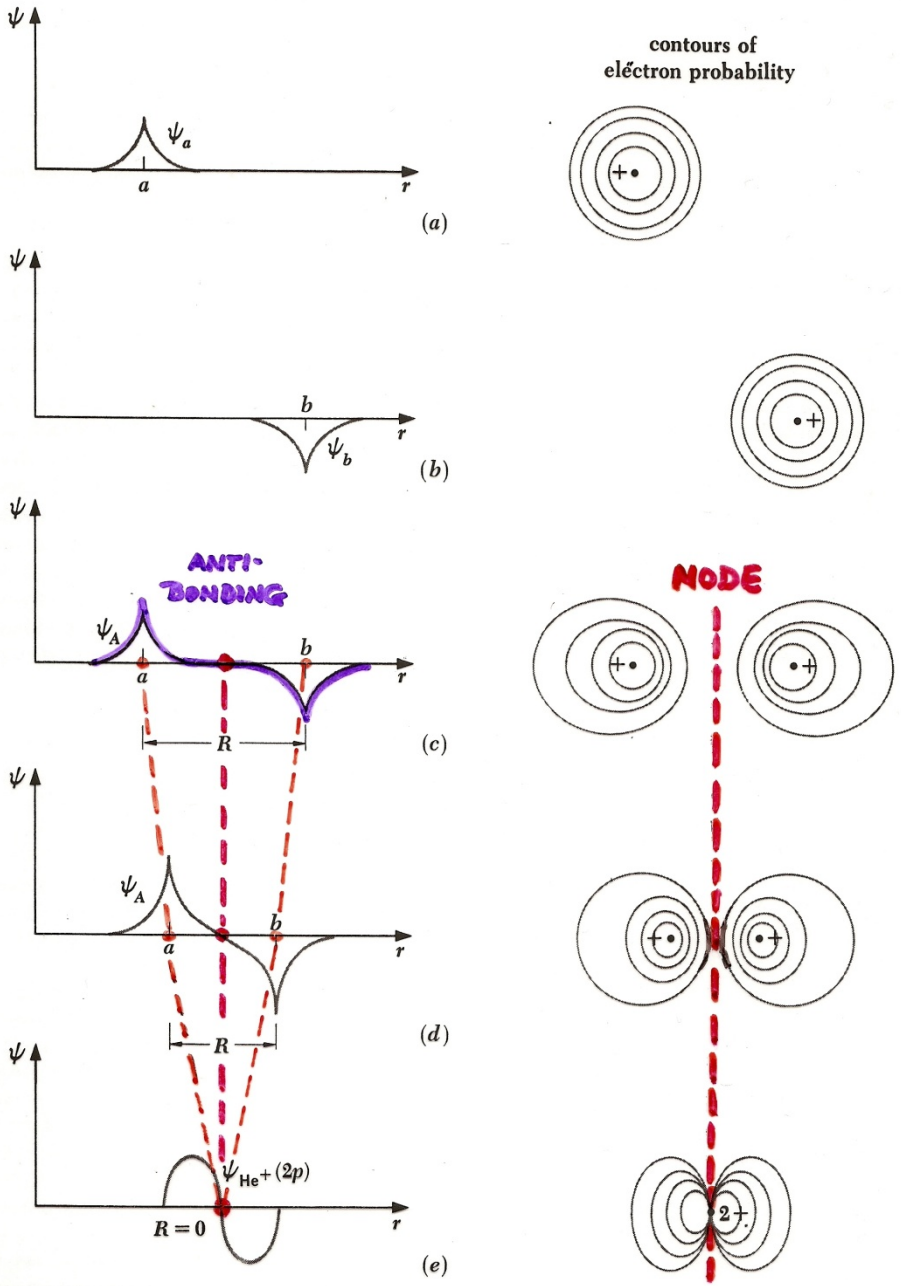


FIGURE 8.6 The combination of two hydrogen-atom 1*s* wave functions to form the antisymmetric H_2+ wave function ψ_A.

Bonding in H_2^+: a linear combination of atomic orbitals (LCAO) or tight-binding (TB) picture

The energies involved

$$V_P = \frac{e^2}{4\pi\varepsilon_0 R} = \frac{14.4}{R(\text{Å})}(\text{eV})$$

$$E(He^+ 2p) = -\frac{(2)^2 e^2}{8\pi\varepsilon_0 a_0 (2)^2} = -13.6\ \text{eV}$$

$$E(He^+ 1s) = -\frac{(2)^2 e^2}{8\pi\varepsilon_0 a_0 (1)^2} = -54.4\ \text{eV}$$

$$E(H1s) = -\frac{(1)^2 e^2}{8\pi\varepsilon_0 a_0 (1)^2} = -13.6\ \text{eV}$$

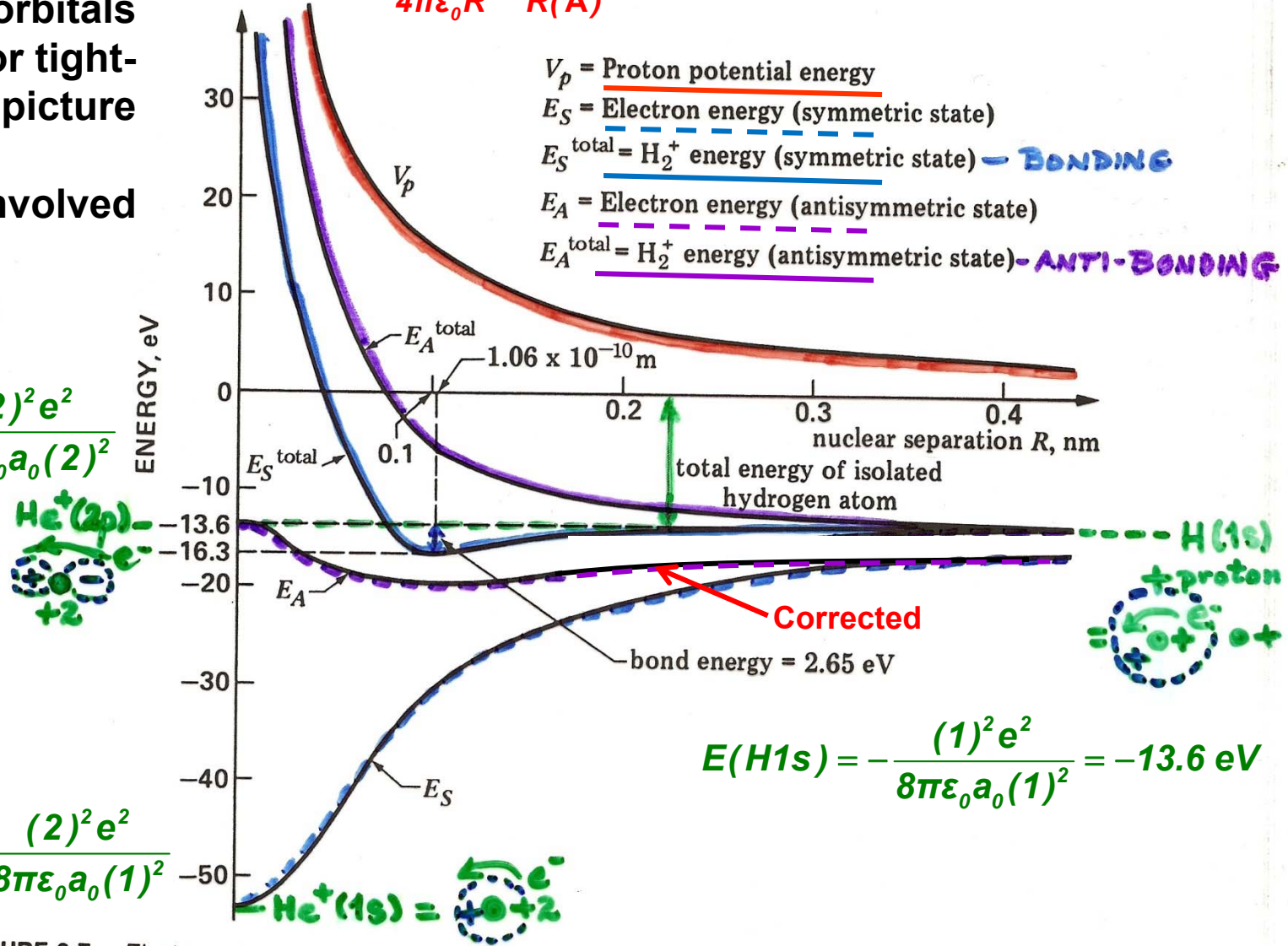
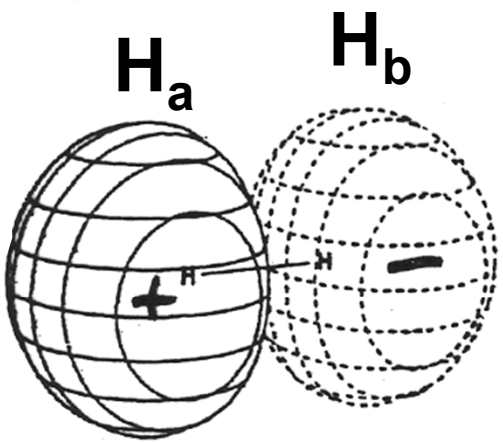


FIGURE 8.7 Electron, proton repulsion, and total energies in H_2+ as a function of nuclear separation R for the symmetric and antisymmetric states. The antisymmetric state has no minimum in its total energy.

2 electrons: The linear combination of atomic orbitals (LCAO-MO) or tight-binding picture for H_2:

III. MOLECULAR ORBITAL DRAWINGS 61

1. Hydrogen Symmetry: $D_{\infty h}$



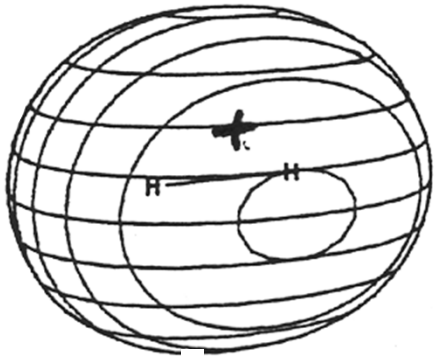
Anti-Bonding

$$\varphi_{anti}^{MO} \cong \varphi_{1sa} - \varphi_{1sa}$$

$1\sigma_u$ ε= 0.2656 a.u. = +7.21 eV

ε *positive (unoccupied)*

ε *negative (occupied)*



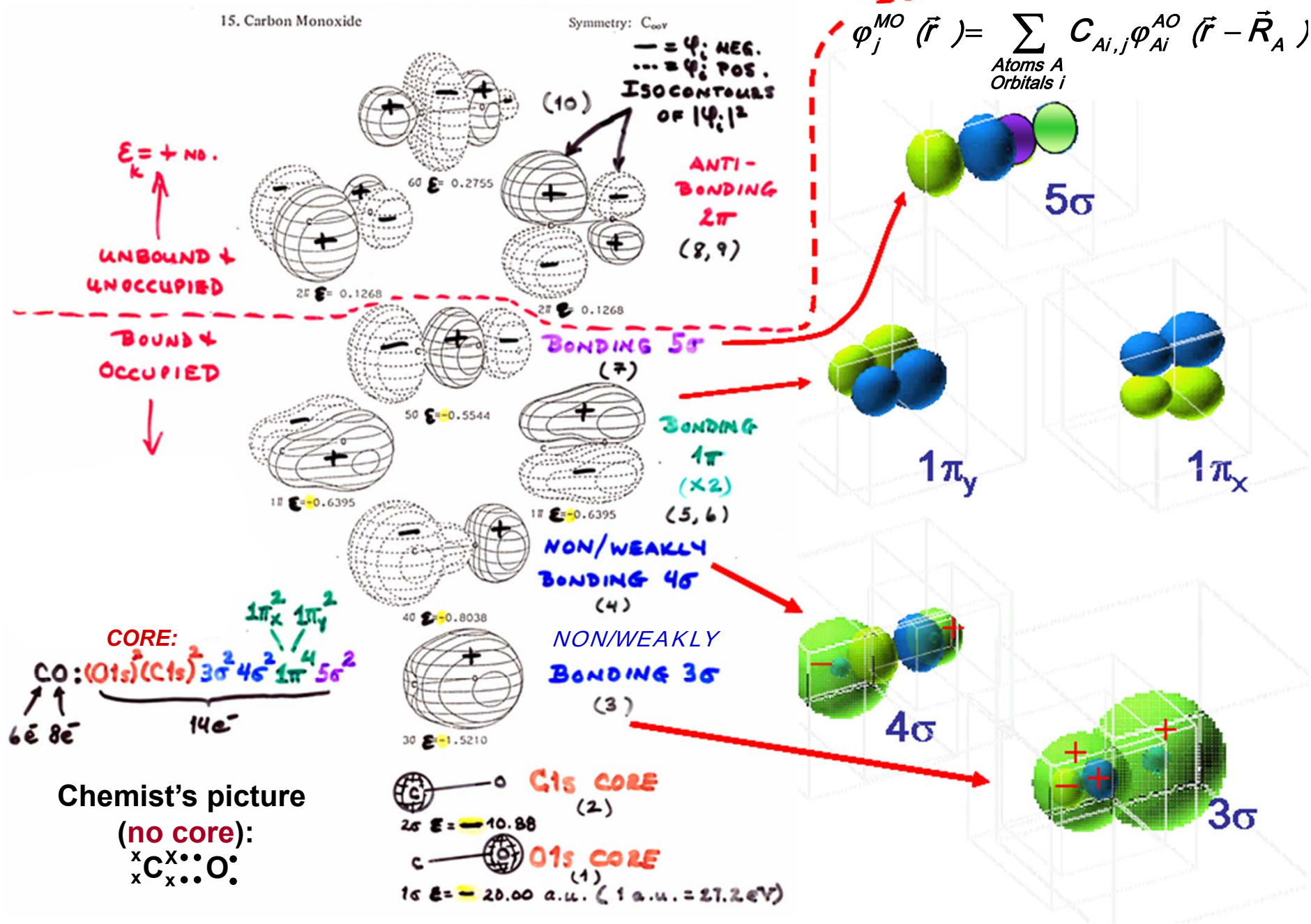
Bonding

$$\varphi_{bonding}^{MO} \cong \varphi_{1sa} + \varphi_{1sa}$$

$1\sigma_g$ ε=-0.5944 a.u. = -16.16 eV

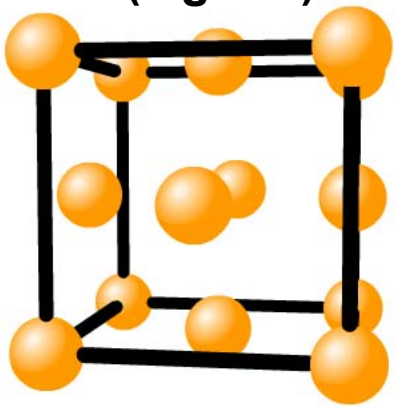
(Compare – 13.61 for H atom 1s)

The LCAO-MO or tight-binding picture for CO:

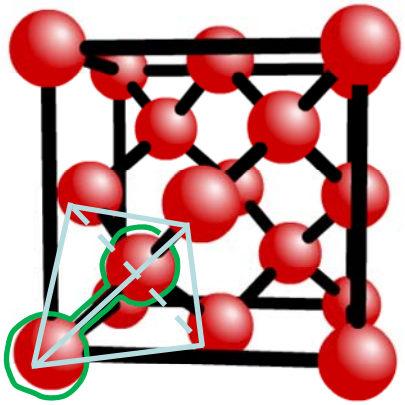


Ordered packing of atoms in solids

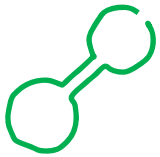
Face-centered cubic (e.g. Cu)



Diamond (e.g., C, Si, Ge)



Basis

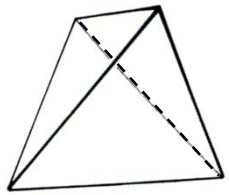


Basis

[Good websites/downloads for simple structures: http://www.dawgsdk.org/crystal/en/library/fcc#0002](http://www.dawgsdk.org/crystal/en/library/fcc#0002)

http://demonstrations.wolfram.com/CrystalViewer/

Tetrahedron

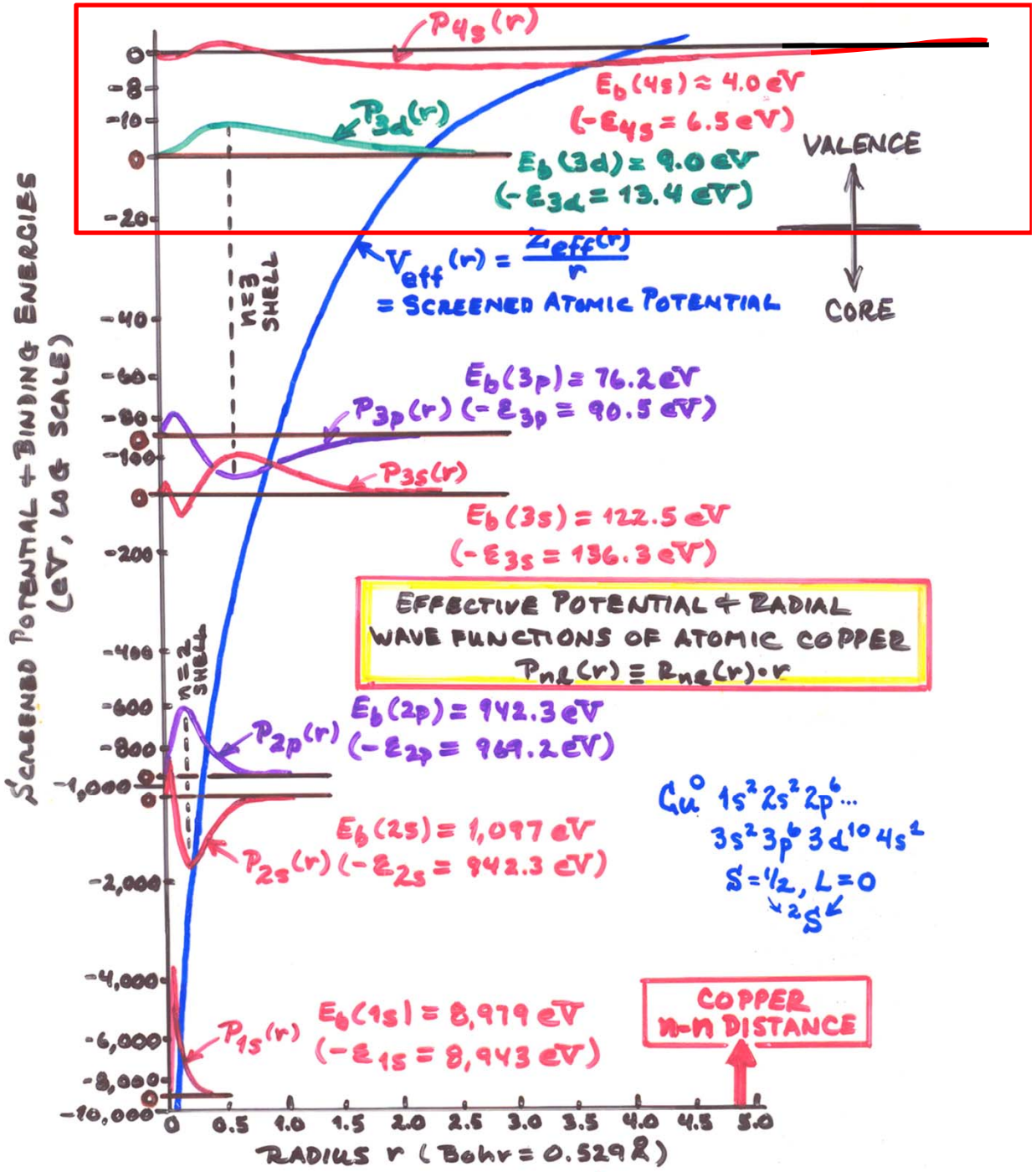


[And another website for various structures, orbitals, etc: http://www.chemtube3d.com/solidstate/_simplecubic(final).htm](http://www.chemtube3d.com/solidstate/_simplecubic(final).htm)

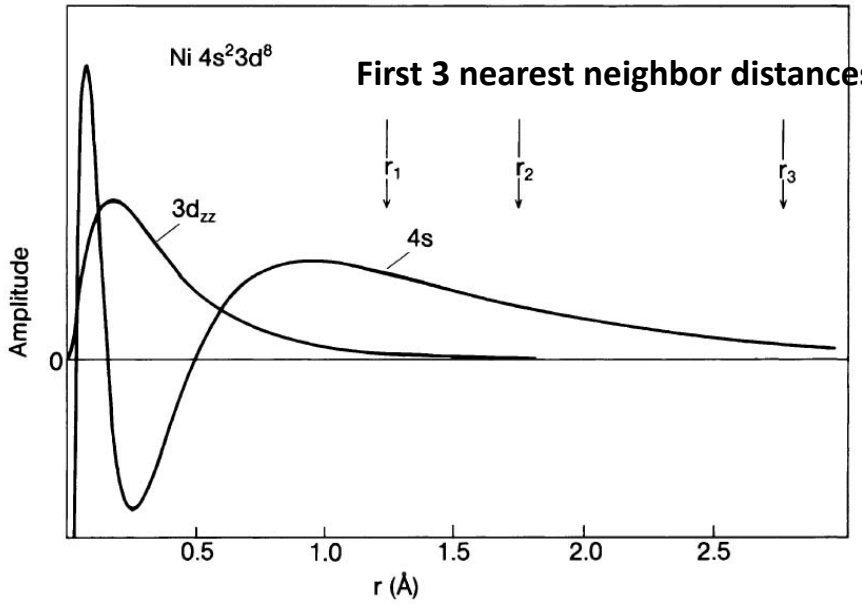
Intraatomic electron screening in many-electron atoms--a self-consistent Q.M. calculation

Plus radial one-electron functions:

$$P_{n\ell}(r) \equiv rR_{n\ell}(r)$$



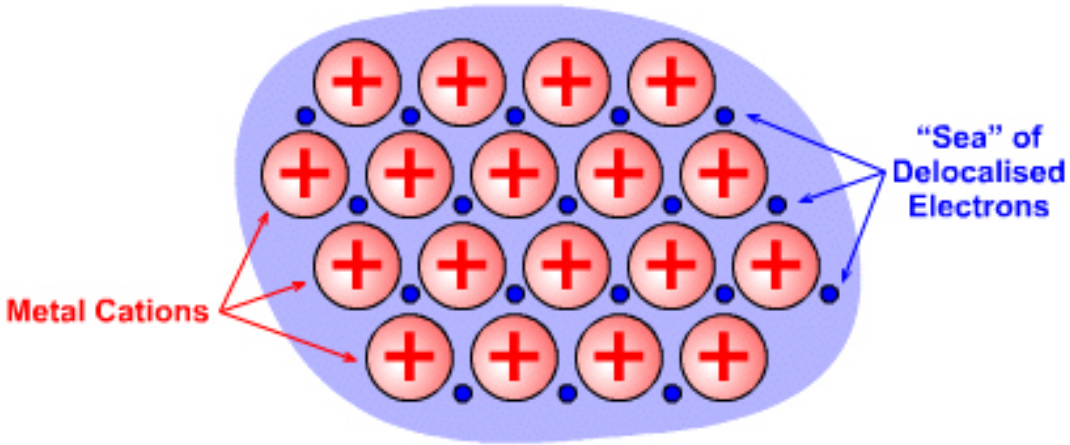
Metallic bonding, e.g. Ni and Cu, with 4s electrons highly delocalized and mobile



$\psi_{4s} \approx C \exp(i\mathbf{k}\bullet\mathbf{r})$

$E_{4s} \approx \hbar^2 k^2/2m_e$

Fig. 1.9. The amplitude of the $3d_{zz}$-wavefunction and the $4s$-wavefunction of Ni [1.4]. The half-distances to the first, second and third nearest neighbors (r_1, r_2 and r_3) are shown for comparison



Electron density in copper

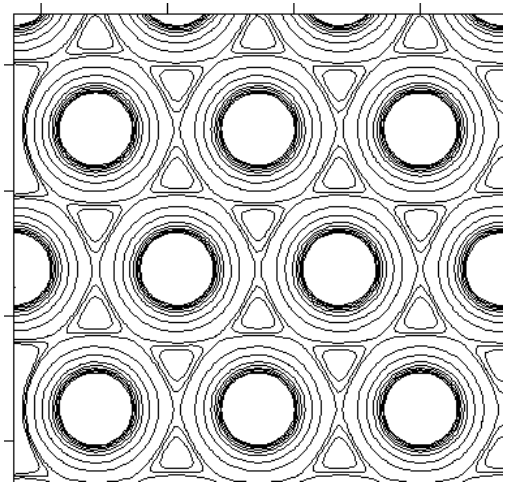


Table 1 Cohesive Energies* of the elements

Energy required to form separated neutral atoms from the solid at 0°K; the values in parentheses are at 298.15°K or at the melting point, whichever temperature is lower. To obtain the energy in J mol^{-1}, multiply the energy in kcal mol^{-1} by $4.184 = 10^3$. To obtain the energy in ergs per atom, multiply the energy in eV per atom by 1.6019×10^{-12}.

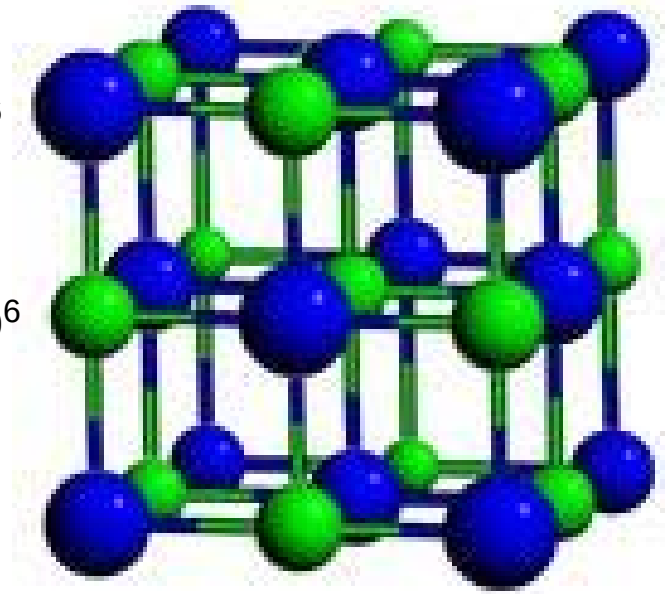
H																	He
4.48																	
103																	
Li	Be											B	C	N	O	F	Ne
1.65	3.33											5.81	7.36				0.02
38.0	76.9											134.	170.	(114)	(60)	(20)	0.45
Na	Mg											Al	Si	P	S	Cl	Ar
1.13	1.53	← eV per atom →										3.34	4.64		2.86		0.080
26.0	35.3	← kcal per mole →										76.9	107	(79.2)	66.1	(32.2)	1.85
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.941	1.825	3.93	4.855	5.30	4.10	2.98	4.29	4.387	4.435	3.50	1.35	2.78	3.87	3.0	2.13	1.22	0.116
21.7	42.1	90.6	112.0	122.	94.5	68.7	98.9	101.2	102.3	80.8	31.1	64.2	89.3	69.	49.2	(28.2)	2.67
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.858		4.387	6.316	7.47	6.810		6.615	5.752	3.936	2.96	1.160	2.6	3.12	2.7	2.0		
19.8	(39.1)	101.2	145.7	172.	157.1		152.6	132.7	90.8	68.3	26.76	59	71.9	62.	46	(25.6)	(3.57)
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.827	1.86	4.491	6.35	8.089	8.66	8.10		6.93	5.852	3.78	(0.694)	1.87	2.04	2.15			
19.1	(42.8)	103.6	146.	186.6	200.	187.	(187)	160.	135.0	87.3	(16.0)	43.2	47.0	49.6	(34.5)		
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4.77	3.9	3.35		2.11	1.80	4.14	4.1	3.1	3.0	3.3	2.6	1.6	(4.4)
110	89	77.2		48.6	41.5	95.4	94	71	70	77	59	36	(102)
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
5.926	5.46	5.405	4.55	4.0	2.6								
136.7	126	124.7	105	92	60								

Ionic solids—another limit: e.g NaCl

Cl^- $1s^2$ $2s^2 2p^6 3s^2 3p^6$

Na^+ $1s^2 2s^2 2p^6$



a = 5.64 Ang.

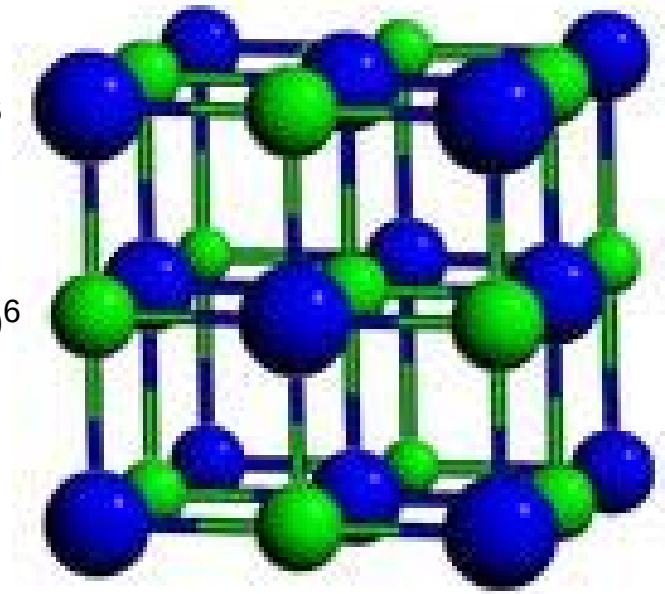
Nobel gas configuration ions, with long-range point-charge Coulomb attraction or repulsion, plus short-range nearest-neighbor repulsion:

$$V = V_{Coul} + V_{Rep} = \sum_{i=1}^{\infty} \frac{(+ \text{ or } -) n_i q_i e^2}{4\pi\varepsilon_o r_i} + \lambda e^{-\frac{r_1}{\rho}} \left[\text{or } B/r^n, n \approx 6, \text{Ibach and Luth} \right]$$

Ionic solids—another limit: e.g NaCl

Cl^- $1s^2\ 2s^2 2p^6 3s^2 3p^6$

Na^+ $1s^2 2s^2 2p^6$



a = 5.64 Ang.

About 5-7 eV per ion pair

Nobel gas configuration ions, with long-range point-charge Coulomb attraction or repulsion, plus short-range nearest-neighbor repulsion:

$$V = V_{Coul} + V_{Rep} = \sum_{i=1}^{\infty} \frac{(+\text{ or }-)n_i q_i e^2}{4\pi\varepsilon_0 r_i} + \lambda e^{-\frac{r_1}{\rho}} \left[\text{or } B/r^n, n \approx 6, \text{Ibach and Luth}\right]$$

as e.g., for NaCl: $\lambda = 1.05 \times 10^{-8}$ *erg,* $\rho = 0.321$ *Angstroms*

$$V = \frac{e^2}{4\pi\varepsilon_0}\left[-\frac{6}{a/2} + \frac{12}{\sqrt{2}a/2} - \frac{8}{\sqrt{3}a/2} \ldots\right] + 1.05e^{-\frac{(a/2)(\text{Ang.})}{0.321}}$$

$$= \frac{e^2}{2\pi\varepsilon_0 a}\left[-6 + \frac{12}{\sqrt{2}} - \frac{8}{\sqrt{3}} \ldots\right] + 1.05e^{-\frac{(a/2)(\text{Ang.})}{0.321}} = -\frac{e^2}{2\pi\varepsilon_0 a}[1.7476] + 1.05e^{-\frac{(a/2)(\text{Ang.})}{0.321}}$$

$= \alpha$ = Madelung constant

Electronegativities of some elements

Table 1.2. The electronegativity of selected elements [1.1]

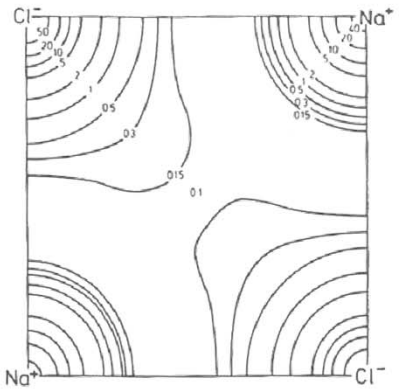
H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.3	Sn 1.8	Sb 1.9	Te 2.1	I 2.5

LEAST

MOST

Charge distributions in ionic and covalent bonding

IONIC :



COVALENT :

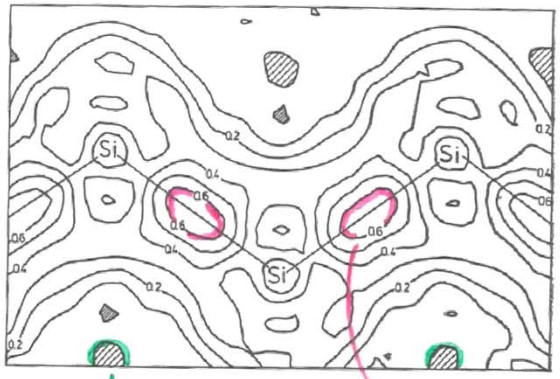


Fig. 1.8. Density of valence electrons in a typical ionic crystal (NaCl) and in a typical covalently bound crystal (Si) [1.2, 3]. One clearly sees the concentration of charge along the bond between Si atoms, whereas in the ionic bonding, the electrons are almost spherically distributed around the ions

LOSS OF e⁻ CHARGE RELATIVE TO ATOMIC DENSITIES

GAIN OF e⁻ CHARGE RELATIVE TO ATOMIC DENSITIES

COVALENT:

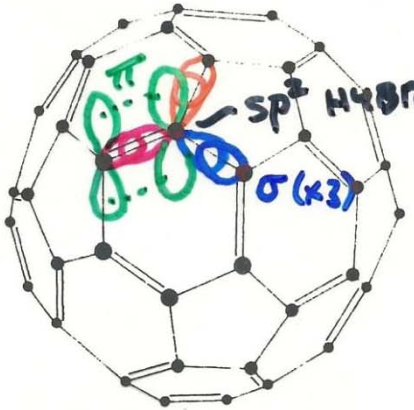


Fig. 1.5. The structure of C_{60}

"buckyball"

"fullerenes"

IONIC:

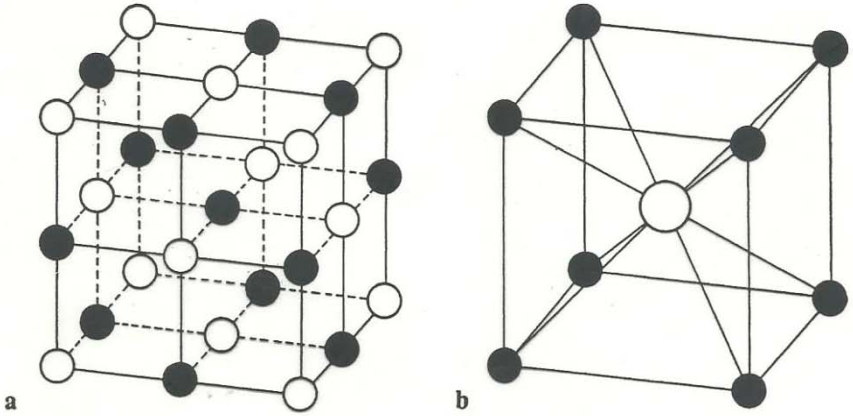
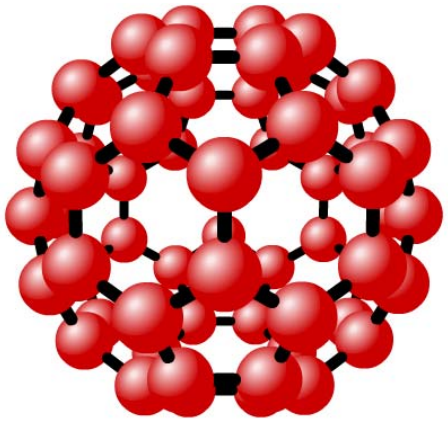
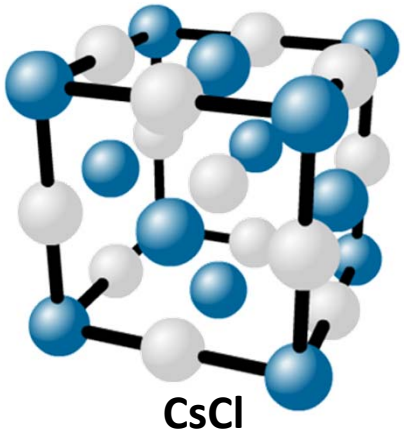


Fig. 1.6. The two structures typical ionic bonding in solids: a NaCl struct b CsCl structure

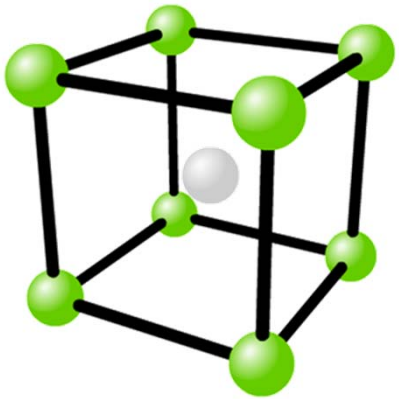
Buckyball



NaCl



CsCl



Covalent and Van der Waals Bonding in Graphite

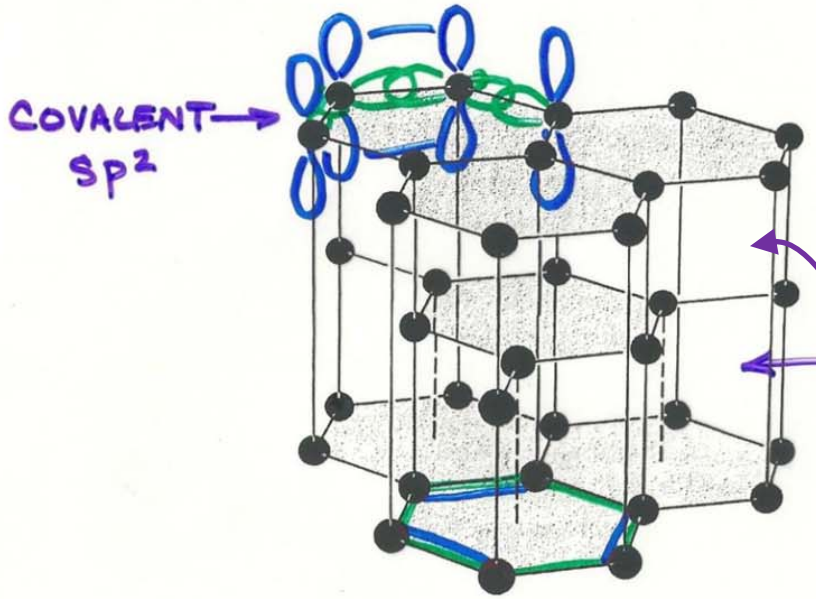


Figure 15.17
Crystal structure of graphite (not to scale). The distance between the top and bottom planes is almost 4.8 times the nearest-neighbor distance within planes.

Covalent and Hydrogen Bonding in Ice

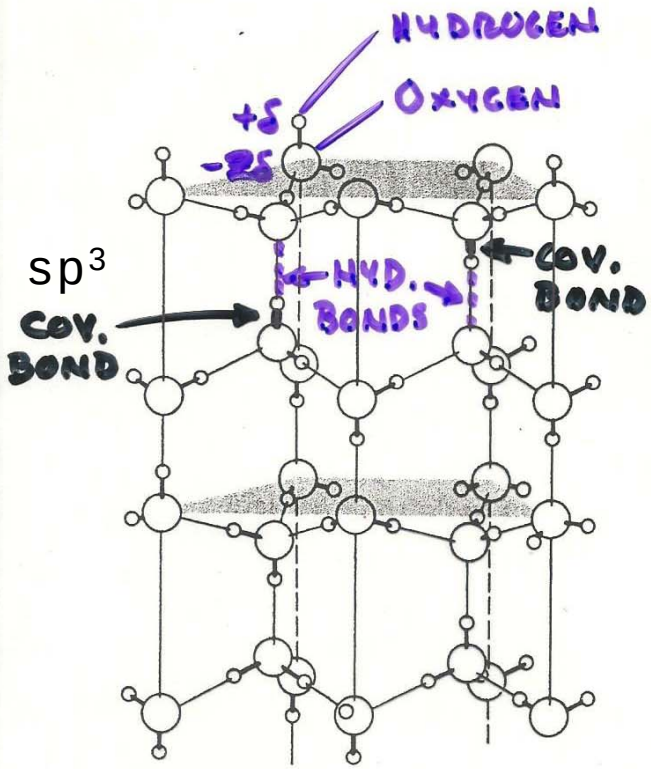
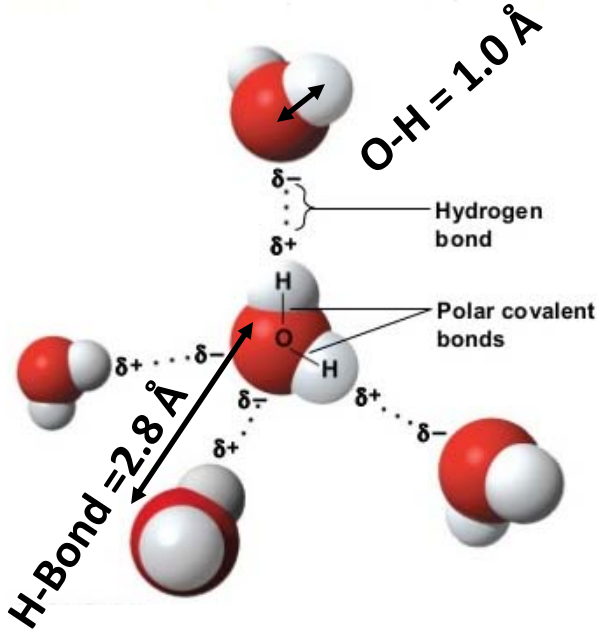
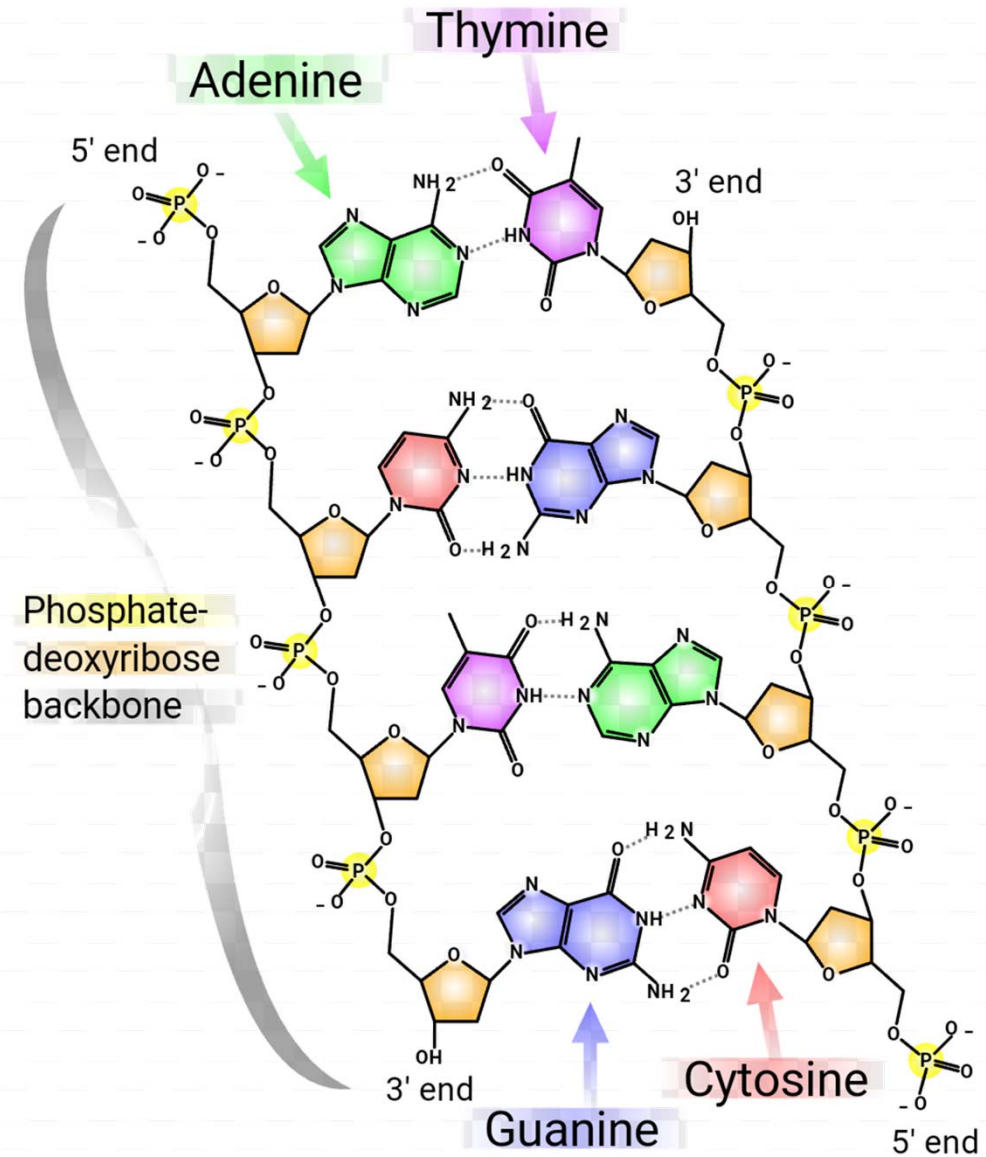


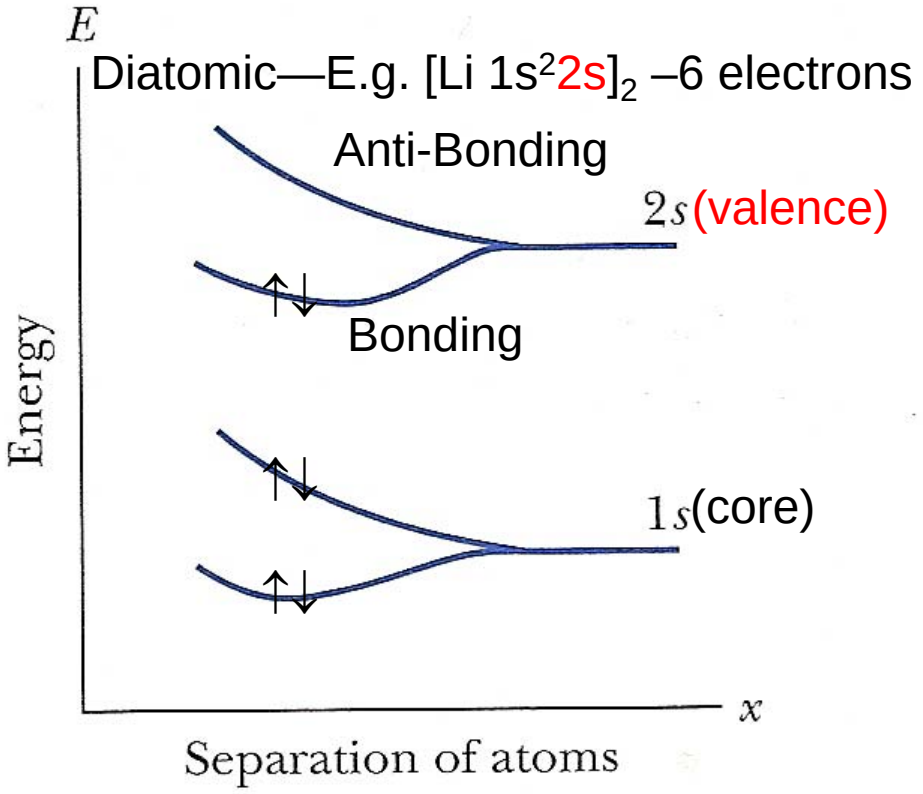
Figure 19.11
The crystal structure of one of the many phases of ice. The large circles are oxygen ions; the small circles are protons. Ice is an example in which hydrogen bonding plays a crucial role. (After L. Pauling, *The Nature of The Chemical Bond*, 3rd. ed., Cornell University Press, Ithaca, New York, 1960.)



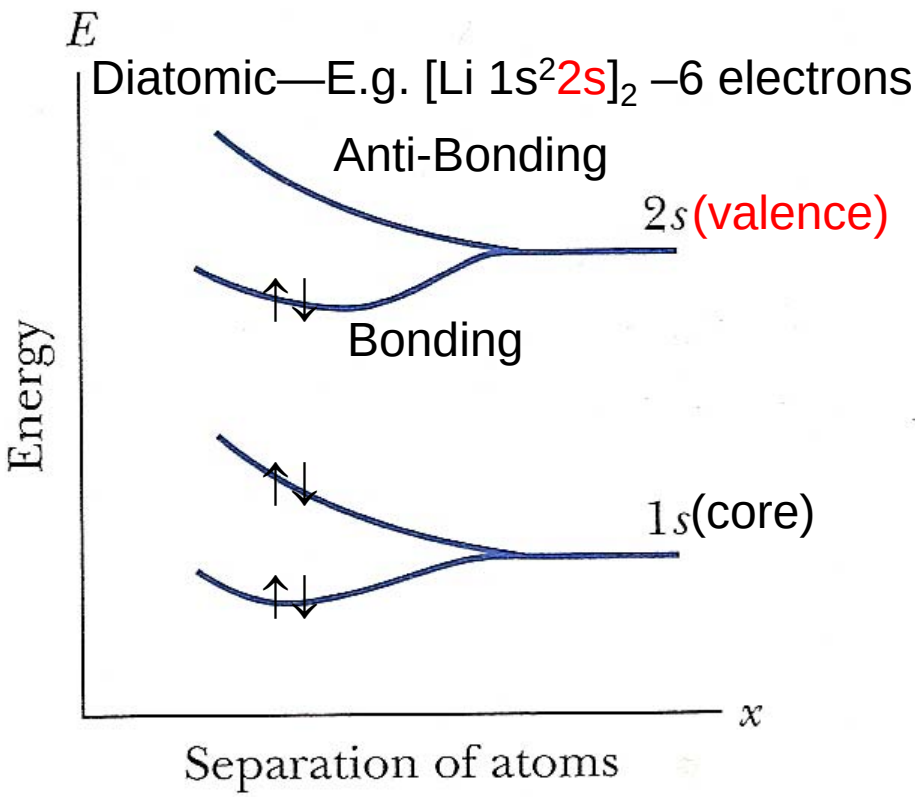
Hydrogen bonding in DNA

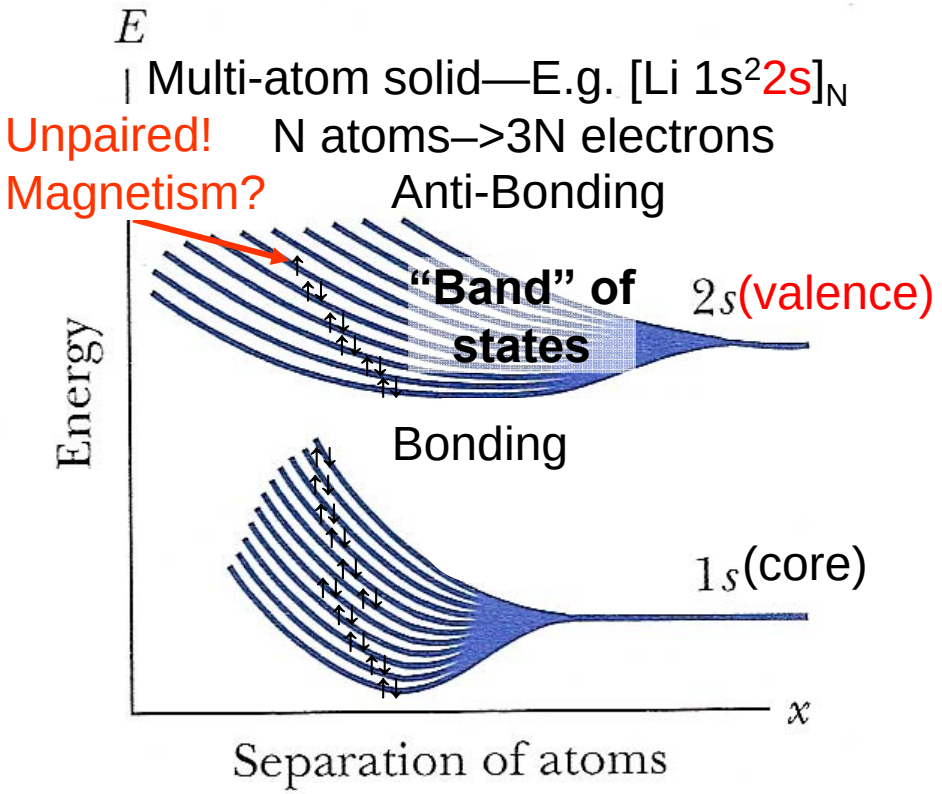


Bonding in solids/solid-state devices as an extension of that in molecules



Bonding in solids/solid-state devices as an extension of that in molecules





Example: N = 11: 22 e^- in 1s-derived
11 e^- in 2s-derived

The types of band structures-by conductive behavior

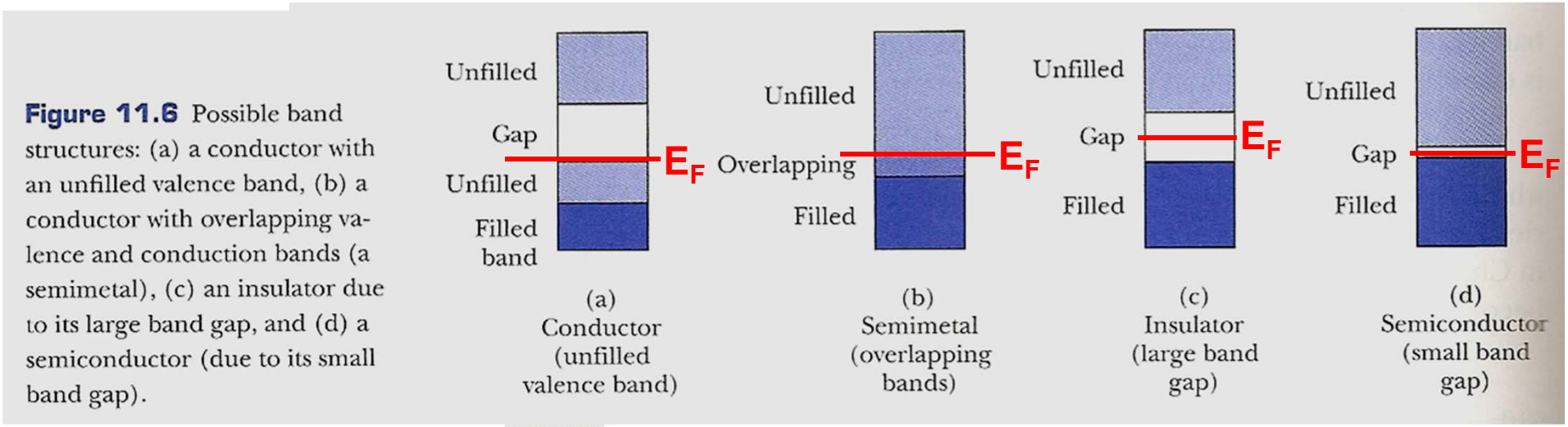
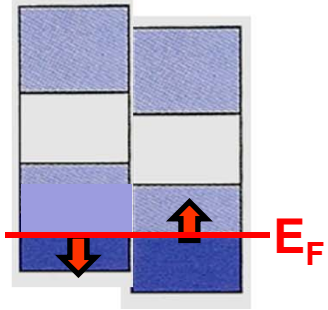
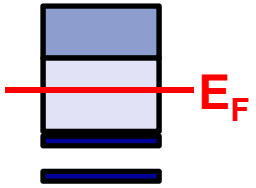


Figure 11.6 Possible band structures: (a) a conductor with an unfilled valence band, (b) a conductor with overlapping valence and conduction bands (a semimetal), (c) an insulator due to its large band gap, and (d) a semiconductor (due to its small band gap).



(e)
Spin-down Spin-up
Ferromagnetic
Conductor
(The exchange interaction)



(f)
Ionic solid:
Very narrow
atomic/ionic
filled bands