Physics of Molecules

- Quantum Mechanics of Bonding [how electrons distribute themselves to hold several atoms together?] (annotation over "how electrons distribute themselves": wavefunction?)

Hamiltonian (molecule) $\xrightarrow{(\approx)}$ Hamiltonian for electrons + nuclei motion

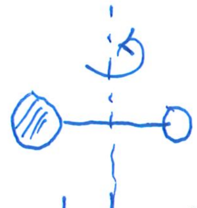
Hamiltonian for electrons →

eigenstates [molecular orbitals]
fill electrons by Pauli Exclusion Principle

→ Bonding (equilibrium bond length)

nuclei motion →

Vibration+



rotation+

+ Harmonic Oscillator and rigid rotor QM will be used

It is a harder problem than atoms!

For the electrons:

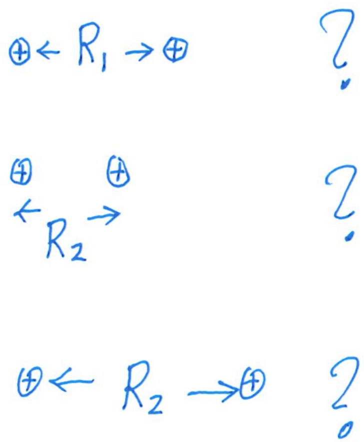
What to do (what is $\psi(\vec{r}_1, \cdots, \vec{r}_N)$) multiple electron

to achieve lower energy?

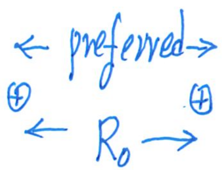
(to form bonds)

But all questions can be handled by Quantum Mechanics

For the two (or more) nuclei



Where should be the preferred separation?



⇒ Vibration

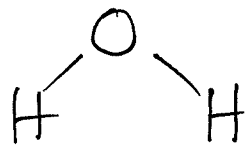
⇒ rotation

A. Let's meet some molecules

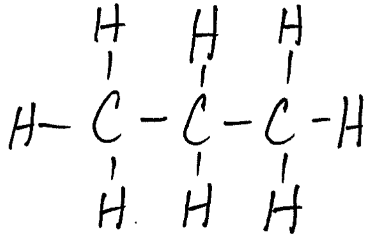
- O = C = O

  $[CO_2]$

  [What are double bonds?]



$[H_2O]$



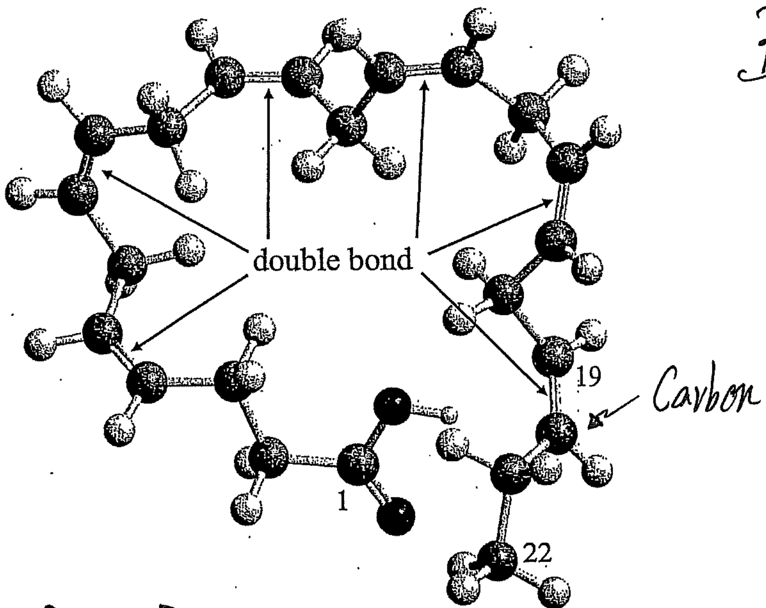
$[C_3H_8]$ (Propane)

$[C_6H_6]$ (Benzene)

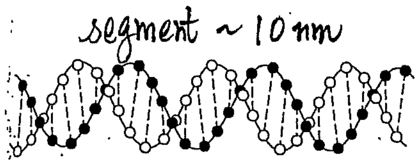
[What does symbol mean?]

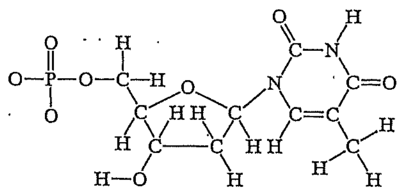
- Diatomic Molecules [Simpler] : H_2 , O_2 , CO

- Big & Complicated



DHA [docasahexaenoic acid] (Taken from Fayer, "Absolutely Small")





A, G, C, T

"•" Thymine "T"

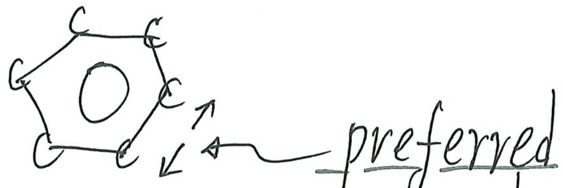
[From Taylor et al., "Modern Physics"]

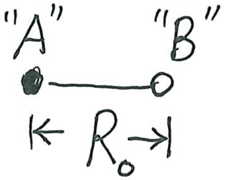
DNA [Deoxyribonuclei acid]

- There exists preferred (equilibrium) separation between atoms

$O = C = O$

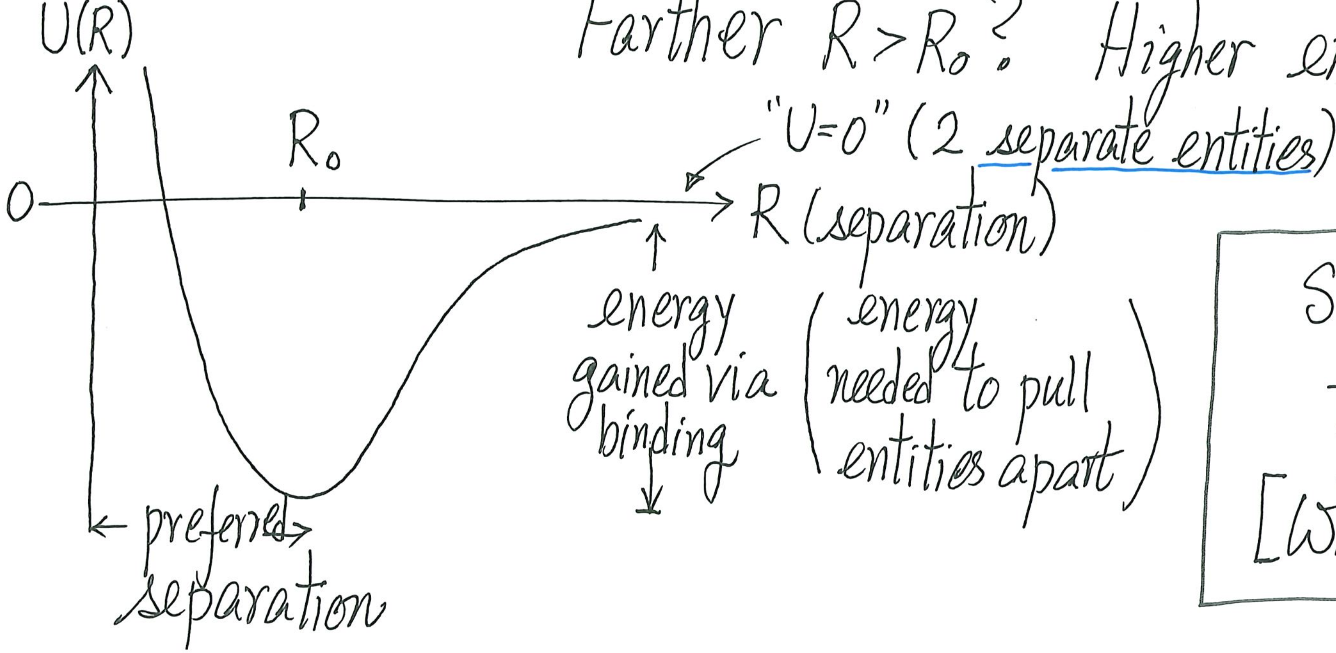
Some preferred separation (bond length)





Closer $R < R_0$? Higher energy
Farther $R > R_0$? Higher energy

R_0 is the preferred separation

- 

Standard U(R) when two entities bind!
[What is its origin?]

Why do {electrons and nucleus / several atoms / protons and neutrons} bind into {atom / molecule / nucleus}?

Why do	electrons and nucleus	bind into	atom	?
	several atoms		molecule	
	protons and neutrons		nucleus	

Energy is lowered!

- For atoms forming molecule

  $R_0 \sim \underline{1-2\,\text{Å}}$ (0.1 nm − 0.2 nm) (typical)

  Binding energy $B \sim \dfrac{e^2}{4\pi\varepsilon_0 R_0}$ (rough estimate) ← electrostatic in nature

  $\sim \underline{7\text{ eV}}$ for ($R_0 \sim 2\,\text{Å}$)

  a few eV (typical)

  Trick: $\boxed{\dfrac{e^2}{4\pi\varepsilon_0} = 1.44\text{ eV}\cdot\text{nm}}$ ← a useful number

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Remark: Same $U(R)$ form works for nucleons (protons/neutrons) binding into nucleus

But $R_0 \sim 10^{-15}\,\text{m} \sim \underline{10^{-6}\,\text{nm}}$

$B \sim$ Many MeV

} but the interaction is due to nuclear force [different from Coulombic]

[Typical scales in Nuclear Physics]

- Phenomenology...

(stronger bonds) • ionic bond • covalent bond • metallic bond (solids/metals)

(weaker bonds) • hydrogen bond • van der Waals bond

[all related to <u>how electrons distribute themselves</u>[+] to attain minimum in $U(R)$]

- R_0 = bond length (equilibrium separation)

  B = Binding energy = Energy needed to separate molecule into <u>neutral atoms</u>
  [Dissociation Energy]

[+] Quantum Mechanically, this is related to the $|\text{wavefunction}|^2$ — electron density distribution

Typical R_0 and B for Ionic and Covalent Bonds

Molecule	R_0 (nm)	B (eV)[†]	Bond
KCl	0.27	4.3	Ionic
LiF	0.16	5.9	Ionic
NaBr	0.25	3.7	Ionic
NaCl	0.24	4.2	Ionic
H_2	0.074	4.5	Covalent
HCl	0.13	4.4	Covalent
N_2	0.11	9.8	Covalent
O_2	0.12	5.1	Covalent

Note: Ionic and covalent bondings involve binding energies of the Same order of magnitude [few eV]

[†] Note: B is also given in kJ/mole by multiplying N_A (Avogadro's #)

Ionic? Covalent?

- QM thinking: All that matters is $|\text{wavefunction(electrons)}|^2$ — Schrödinger Equation
- $|\text{wavefunction}|^2$ give preference to one atom (more near atom A than Atom B, then "Atom A" looks like an anion A^-, and atom B looks like a cation B^+, then "ionic".
- $|\text{wavefunction}|^2$ doesn't prefer A OR B, but has appreciable value between A and B, then "covalent".

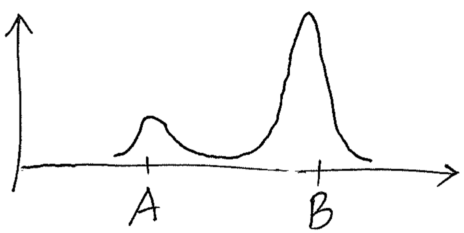
QM puts bondings under one roof!

The fact is:

- Usually, covalent with some ionic character
- or ionic with some covalent character

They are just descriptions of extreme cases

e.g. $|\psi|^2$



ionic? covalent?

It is all QM in work!

B. Ionic Bonding : Energetics

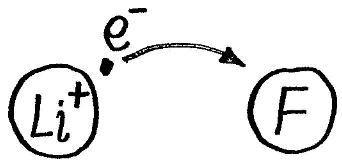
- usually involve atoms in 1^{st} (2^{nd}) and 7^{th} (6^{th}) columns in periodic table

Eg. Li and F

Same for NaCl

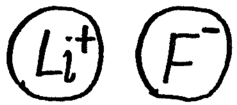
(a) Widely separated:

(b) Approach one another, an electron can transfer from lithium to fluorine



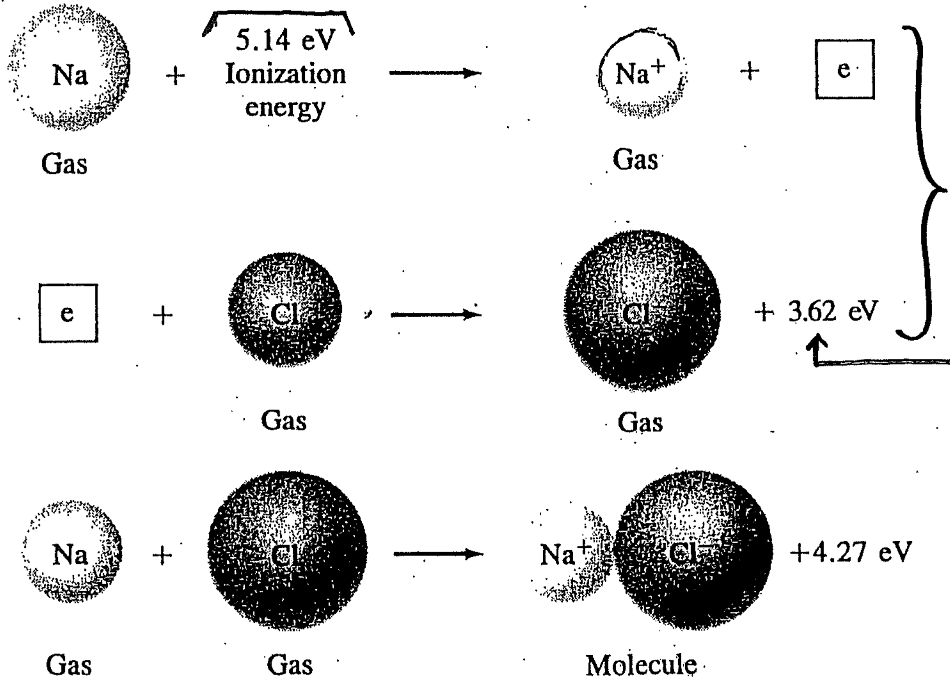
(Needs energy to do this?)

(c) Charged ions are strongly attracted and form a stable LiF molecule



(Gain energy (Coulombic))

e.g. NaCl



Transfer of electron from sodium to chlorine requires 1.52 eV net [Ionization energy]$^{+}$

electron affinity^{+}

At equilibrium separation, gain energy due to electrostatic attraction between Na^{+} and Cl^{-}

$^{+}$ Remark: Ionization energy can be calculated by QM, as Na atom and Na^{+} ion treated as two QM problems (see many-electron atoms). A similar approach for Cl atom and Cl^{-} ion gives the electron affinity.

ΔE = Energy required for transferring an electron from sodium to chlorine

= Ionization energy of sodium − Electron affinity of chlorine

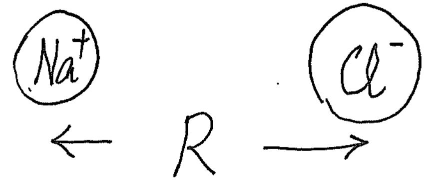
$= 5.14\ \text{eV} - 3.62\ \text{eV} = \underbrace{1.52\ \text{eV}}$

Need energy to form Na^+ and Cl^-

∴ Spontaneous electron transfer between well-separated atoms will not occur

- But forming ions gains back electrostatic energy when atoms get closer

electrostatic energy due to attraction $= \dfrac{-e^2}{4\pi\varepsilon_0 R}$



$E(R)$ = total energy at separation R

$$= \Delta E - \frac{e^2}{4\pi\varepsilon_0 R} \quad \text{[Competing terms]}$$

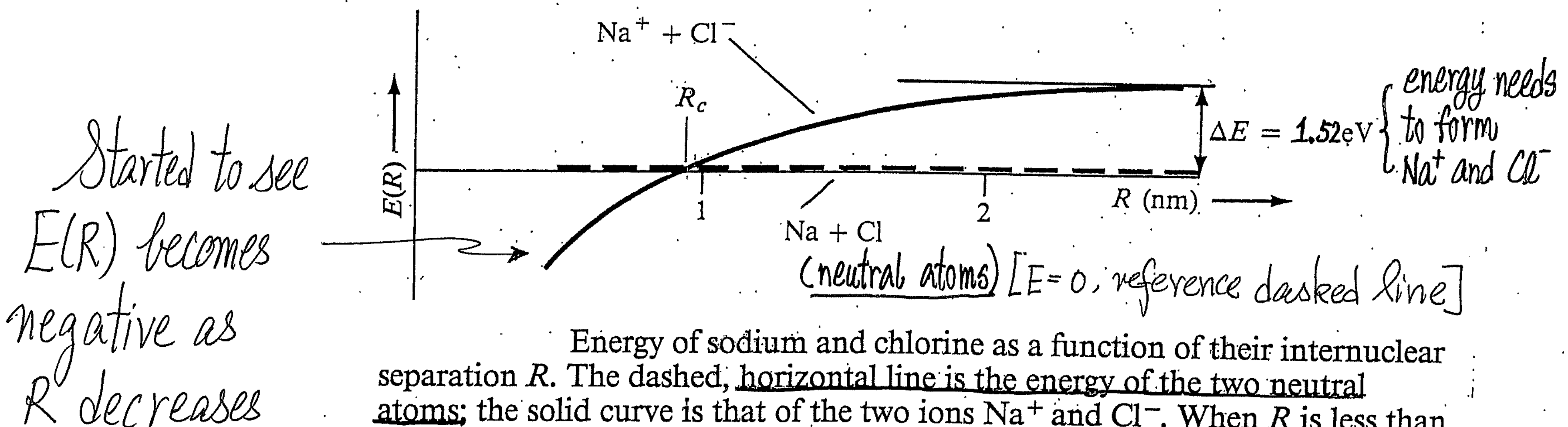
[Note: $E=0$ refers to two neutral atoms]

Note: • For $R > R_c = 0.95$ nm, $E > 0$

• For $R < R_c = 0.95$ nm, $E < 0$ [lower energy than two neutral atoms]

electrostatic attraction wins $R < R_c$

Close-up of $E(R)$



Energy of sodium and chlorine as a function of their internuclear separation R. The dashed, horizontal line is the energy of the two neutral atoms; the solid curve is that of the two ions Na^+ and Cl^-. When R is less than R_c, the two ions have lower energy than the two netural atoms.

[From Taylor et al., "Modern Physics"]

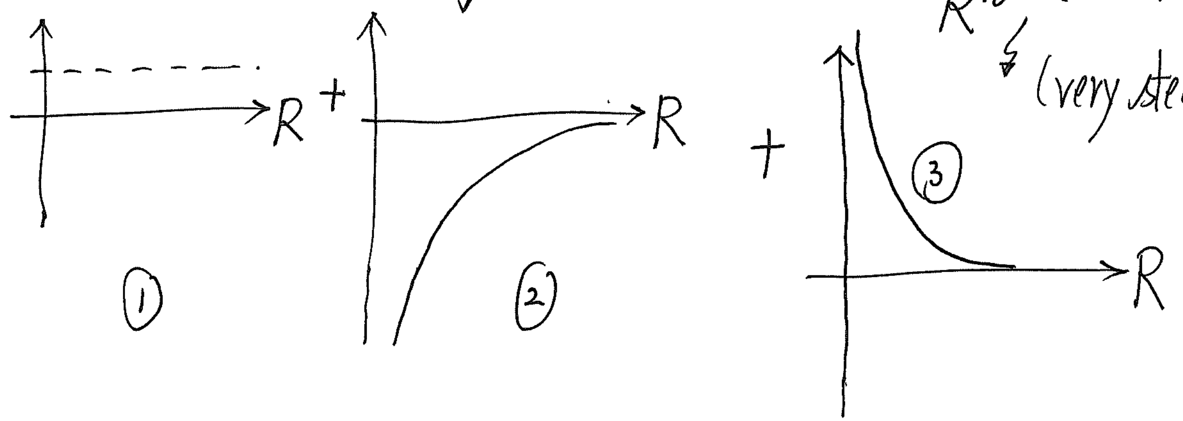
- **Strong Repulsion at small R : "Core Repulsion"**
  - Repulsion between two nuclei, and
  - Pauli Principle (Quantum effect) [more important]
    - electrons avoid each other
    - must fill in states (molecular) of progressively higher energies

$$E(R) = \Delta E - \frac{e^2}{4\pi\varepsilon_0 R} + \underbrace{\text{Core repulsion energy}}_{\sim + \frac{b}{R^n}}$$

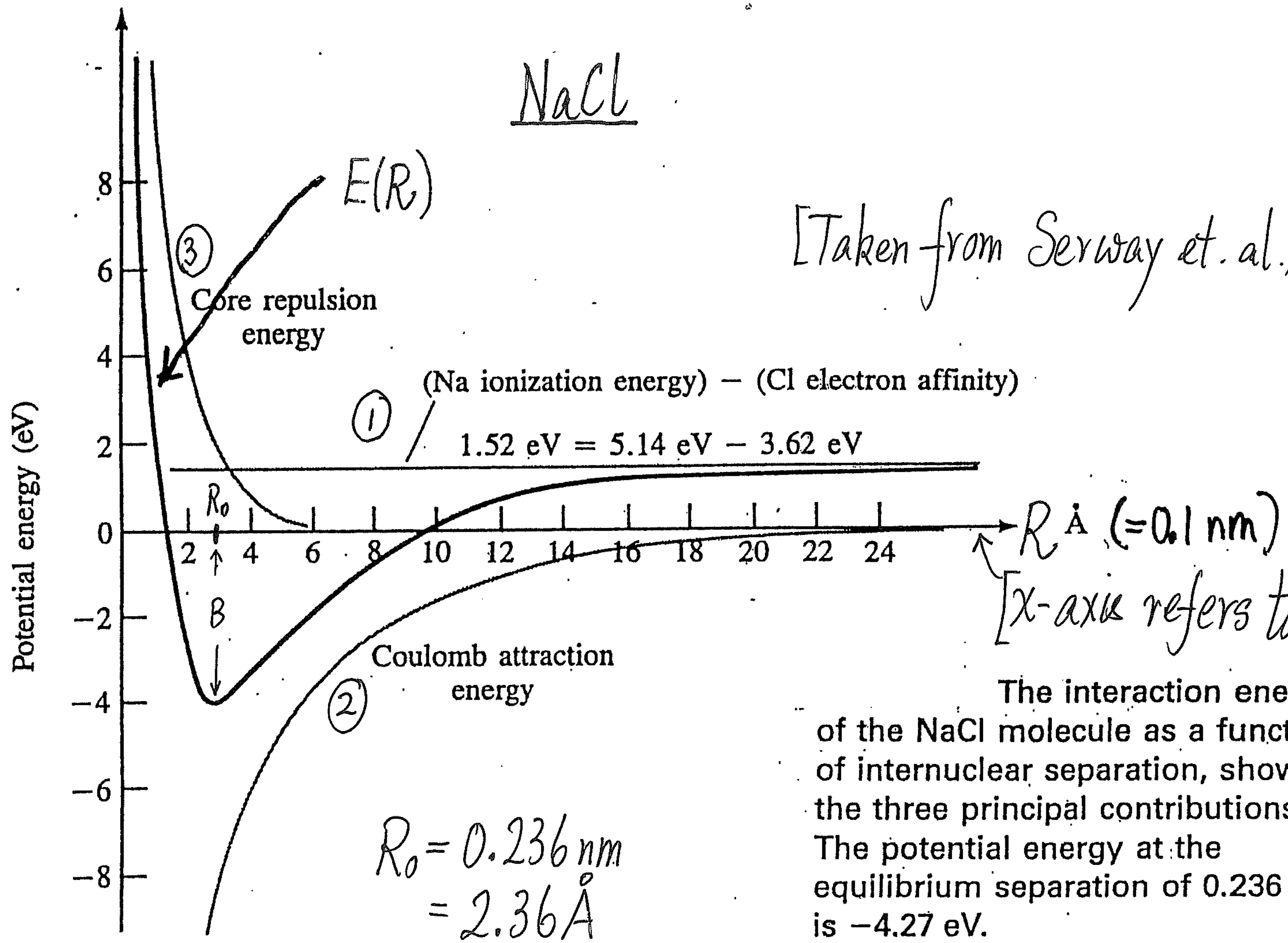
$\sim + \frac{b}{R^n}$ (n = high power) (phenomenological)

(very steep)

E(R) =



NaCl



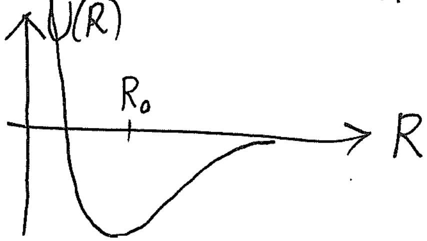
[Taken from Serway et. al., "Modern Physics"]

[x-axis refers to neutral atoms]

The interaction energy of the NaCl molecule as a function of internuclear separation, showing the three principal contributions. The potential energy at the equilibrium separation of 0.236 nm is −4.27 eV.

$R_0 = 0.236\,nm$
$= 2.36\,Å$
$B \cong 4.2\,eV$

∴ Electrons re-distribution and Core Repulsion (including Nuclei Repulsion) give



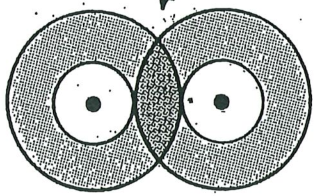
typical of binding (forming bonds)

Covalent Bond
(Baby level)

(a)

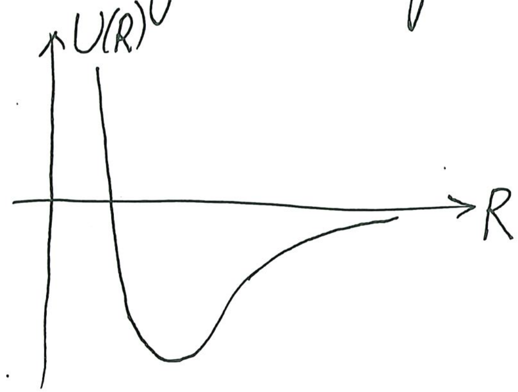
high probability of finding electrons

Q: What does such a picture mean quantum mechanically?



(b)

Right Distribution of electrons facilitates binding, thus gives



Schematic plot of the distribution of the outer electrons in two atoms that bond covalently. **(a)** The two separate atoms. **(b)** When the atoms form a covalent molecule, the wave functions for the outer electrons interfere constructively and produce a concentration of charge in the region between the two nuclei. The two dots show the positions of the two nuclei, and for clarity the distribution of inner electrons is omitted entirely.

QM explanation for chemical Bonds?