Physics of Molecules

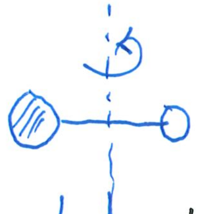
- Quantum Mechanics of Bonding [$\overbrace{\text{how electrons distribute themselves}}^{\text{wavefunction?}}$ to hold several atoms together?]

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

$$\boxed{\begin{array}{c}\text{eigenstates [molecular orbitals]}\\ \text{fill electrons by Pauli Exclusion Principle}\end{array}}$$

→ Bonding (equilibrium bond length)

Vibration$^+$



rotation$^+$

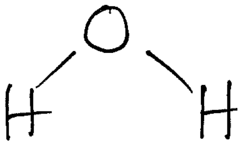
$^+$ Harmonic Oscillator and rigid rotor QM will be used

A. Let's meet some molecules

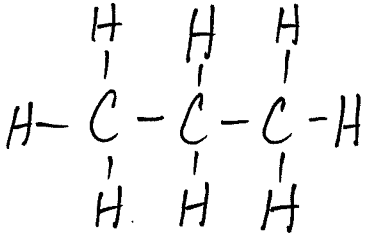
- $O=C=O$

  [CO_2]

  [What are double bonds?]



[H_2O]



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

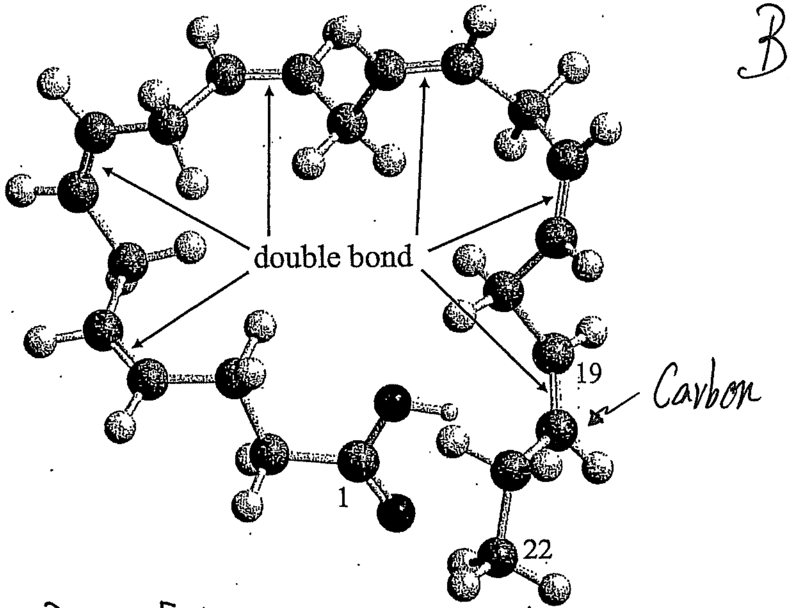
[C_3H_8] (Propane)

[C_6H_6] (Benzene)

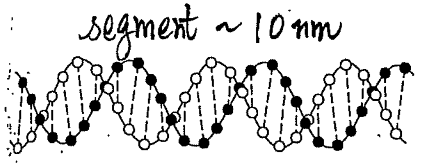
[What does symbol mean?]

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

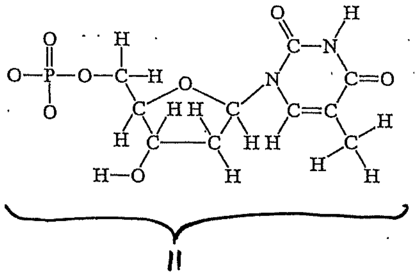
- Big & Complicated



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



A, G, C, T

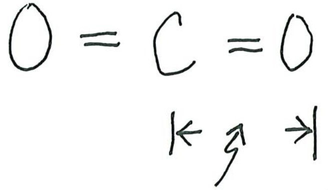


"■" Thymine "T"

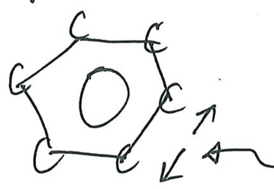
[From Taylor et al., "Modern Physics"]

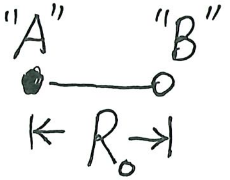
DNA [Deoxyribonuclei acid]

- There exists preferred (equilibrium) separation between atoms



Some preferred separation (bond length)





Closer $R < R_0$? Higher energy

Farther $R > R_0$? Higher energy

R_0 is the preferred separation

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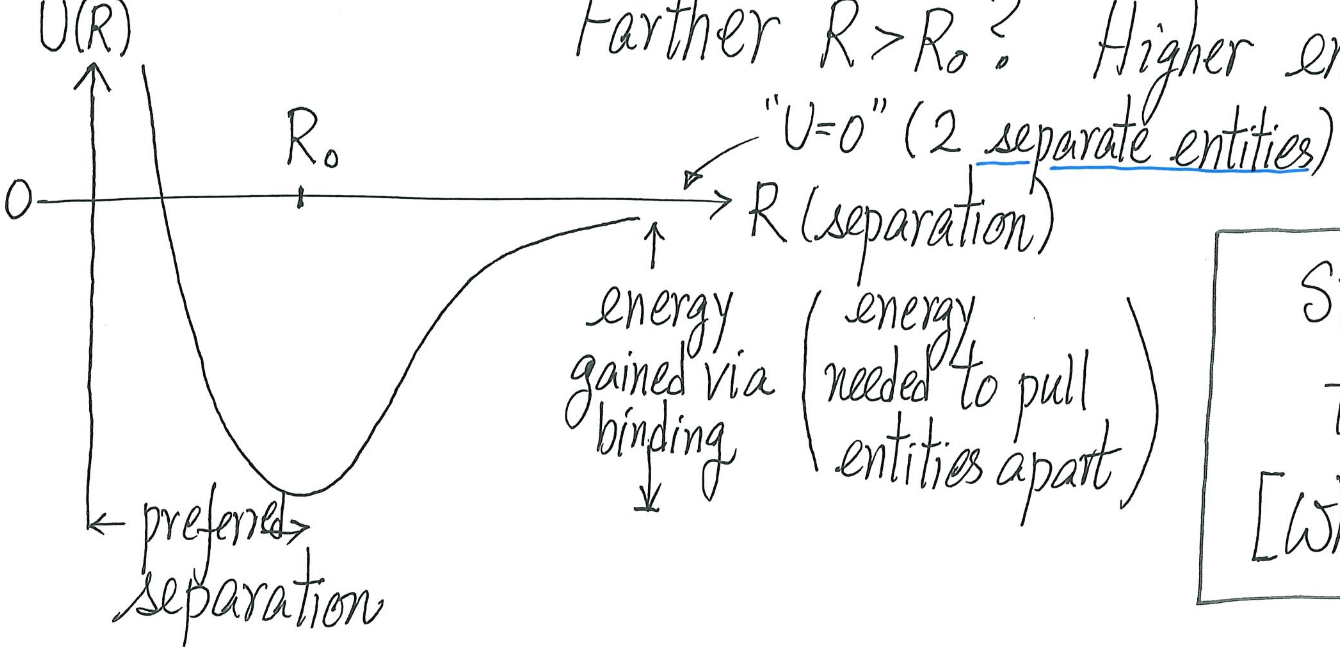

Standard U(R) when two entities bind!
[What is its origin?]

$$\text{Why do} \left\{\begin{array}{l}\text{electrons and nucleus}\\ \text{several atoms}\\ \text{protons and neutrons}\end{array}\right\} \text{bind into} \left\{\begin{array}{l}\text{atom}\\ \text{molecule}\\ \text{nucleus}\end{array}\right\} ?$$

Energy is lowered!

■ For atoms forming molecule

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

electrostatic in nature

Binding energy $B \sim \dfrac{e^2}{4\pi\varepsilon_0 R_0}$ (rough estimate) $\sim \underline{7\,\text{eV}}$ for ($R_0 \sim 2\,\text{Å}$)

<u>a few eV</u> (typical)

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

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

$$\left.\begin{array}{l} \text{But } R_0 \sim 10^{-15}\,\text{m} \sim \underline{10^{-6}\,\text{nm}} \\ B \sim \underline{\text{Many}}\ \underline{\text{MeV}} \end{array}\right\}$$

but the interaction is due to nuclear force

[Typical scales in Nuclear Physics]

[different from Coulombic]

- Phenomenology...

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

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

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

- R_0 = bond length (equilibrium separation)

B = Binding energy [Dissociation Energy] = Energy needed to separate molecule into neutral atoms

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

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	
NaBr	0.25	3.7	
NaCl	0.24	4.2	
H_2	0.074	4.5	Covalent
HCl	0.13	4.4	
N_2	0.11	9.8	
O_2	0.12	5.1	

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

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

Ionic? Covalent?

- QM thinking: All that matters is $\underbrace{|\text{wavefunction(electrons)}|^2}_{\underline{\text{Schrödinger Equation}}}$

- $|\text{wavefunction}|^2$ 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!

B. Ionic Bonding : Energetics

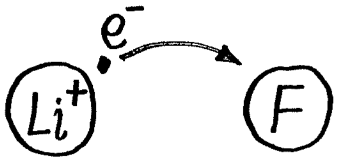
- usually involve atoms in 1st (2nd) and 7th (6th) columns in periodic table

Eg. Li and F

(a) Widely separated:

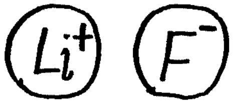
Same for NaCl

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



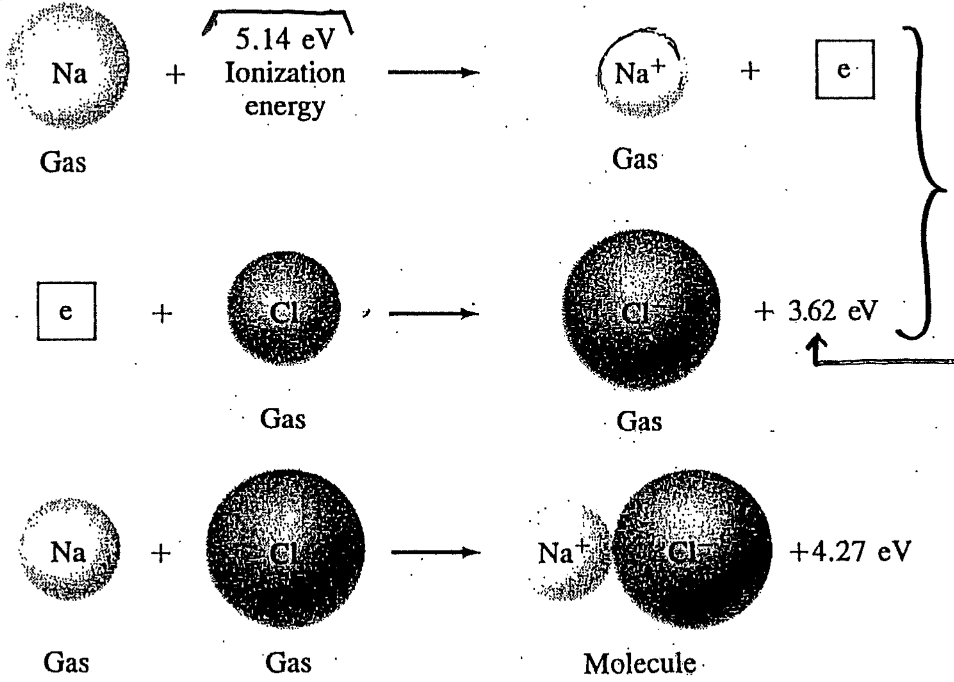
(Needs energy to do this?)

(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 1.52eV net [Ionization energy][+]

electron affinity[+]

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

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[+] 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.

$$\Delta E = \text{Energy required for transferring an electron from sodium to chlorine}$$

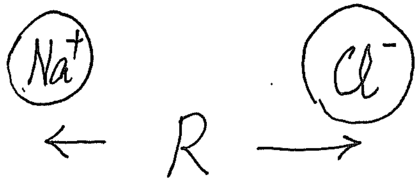
$$= \text{Ionization energy of sodium} - \text{Electron affinity of chlorine}$$

$$= 5.14\,\text{eV} - 3.62\,\text{eV} = \underbrace{1.52\,\text{eV}}_{\text{Need energy to form Na}^{+}\text{ and Cl}^{-}}$$

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

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

$$\begin{matrix}\text{electrostatic energy}\\ \text{due to attraction}\end{matrix} = \frac{-e^2}{4\pi\varepsilon_0 R}$$



E(R) = total energy at separation R

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

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

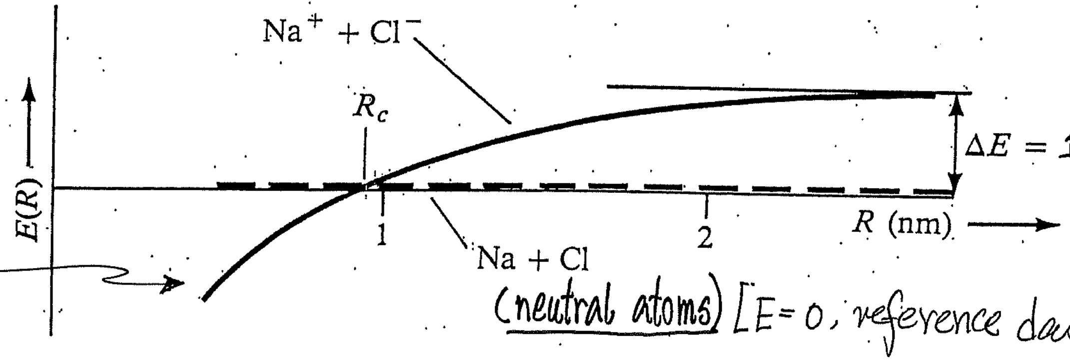
Note: • For $R > R_c = 0.95$ nm, $E > 0$

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

$\underbrace{\text{lower energy}}_{}$ electrostatic attraction wins $R < R_c$

Close-up of E(R)

Started to see E(R) becomes negative as R decreases



energy needs to form Na$^+$ and Cl$^-$

(neutral atoms) [E = 0, reference dashed line]

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.

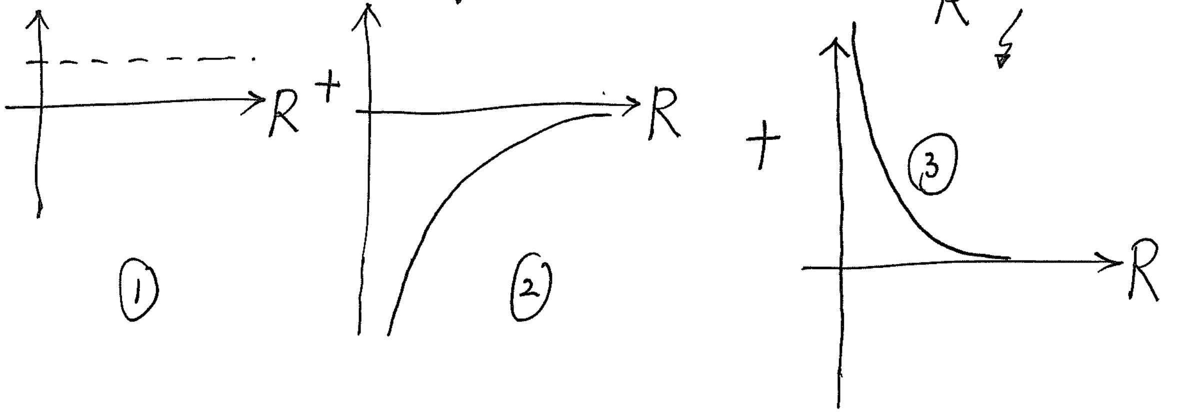
[From Taylor et al., "Modern Physics"]

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

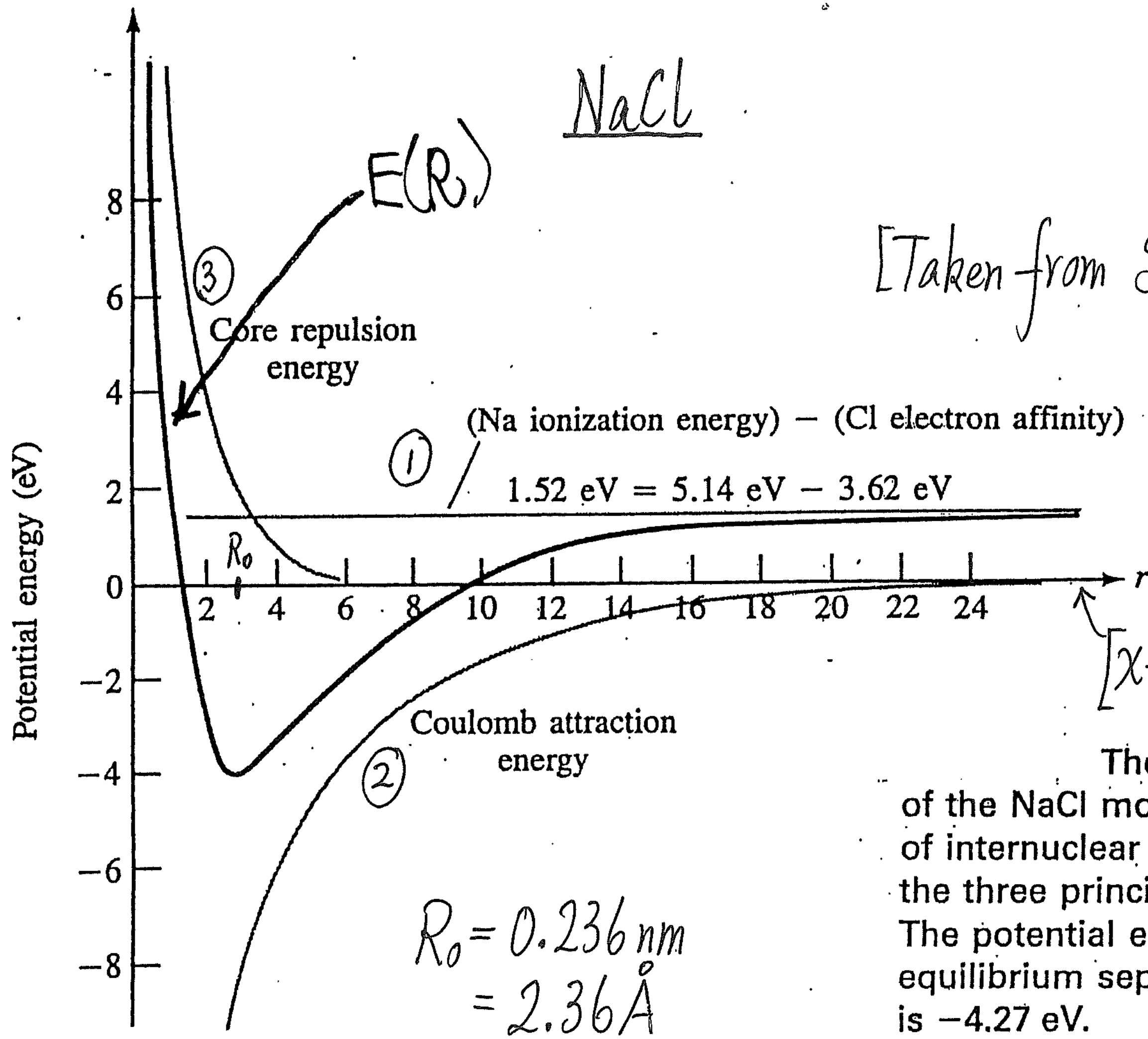
$$E(R) = \Delta E - \frac{e^2}{4\pi\varepsilon_0 R} + \underbrace{\text{Core repulsion energy}}_{\sim + \frac{b}{R^n}}$$

(n = high power) (phenomenological)

$E(R) =$



NaCl



(=0.1 nm)

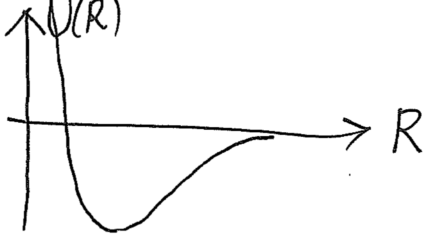
[Taken from Serway et. al., "Modern Physics"]

[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.

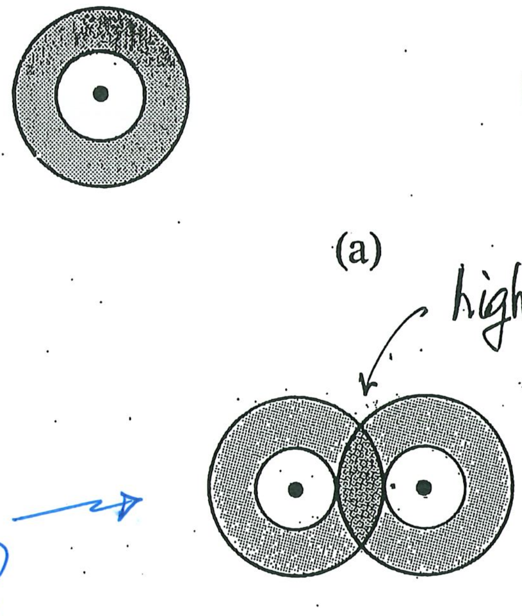
$R_0 = 0.236\,\text{nm}$
$= 2.36\,\text{Å}$
$B \cong 4.2\,\text{eV}$

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



typical of binding (forming bonds)

Covalent Bond
(Baby level)

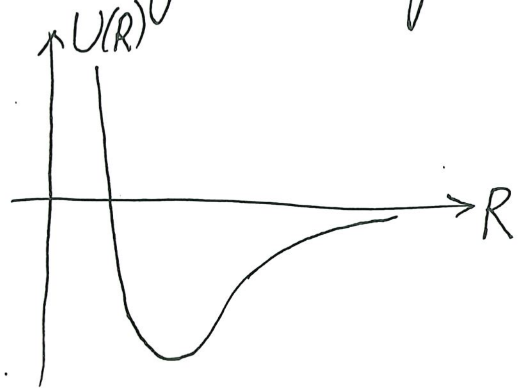


high probability of finding electrons

What does such a picture mean?

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.

Right Distribution of electrons facilitates binding, thus gives



QM explanation for chemical Bonds?