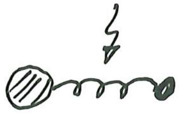
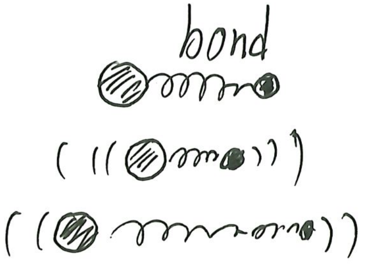
# Physics of Molecules

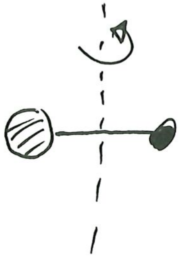
[Q: what is this spring/bond?]



- "Old Physics": Quantum Mechanics of Bonding
  - Electrons under influence of several ions/nuclei
  - Schrödinger Equation → One-electron problem (effectively)
  - Fill electrons into molecular orbitals using Pauli Principle
- New Physics
  - Molecules have internal motions



Vibrational Motion of Nuclei



rotational Motion

Need Background on...

- Schrödinger Eq. $\psi = a_1\phi_1 + a_2\phi_2$ turns TISE into $\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{vmatrix} = 0$
- QM of harmonic oscillator (Vibrational Motion)
- QM of rotor (rotational motion)
- Transitions governed by [electric dipole moment]

$$\int \psi^*_{final} \left(-\vec{\mu}\cdot\vec{\mathcal{E}}\right) \psi_{initial}\, d^3r$$

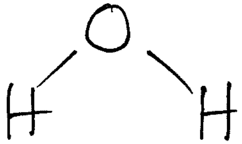
(selection rules)

# A. Let's see some molecules

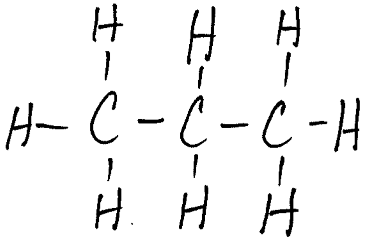
- $O=C=O$

  [$CO_2$]

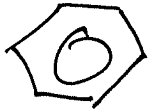
  [What are double bonds?]



[$H_2O$]



[$C_3H_8$] (Propane)

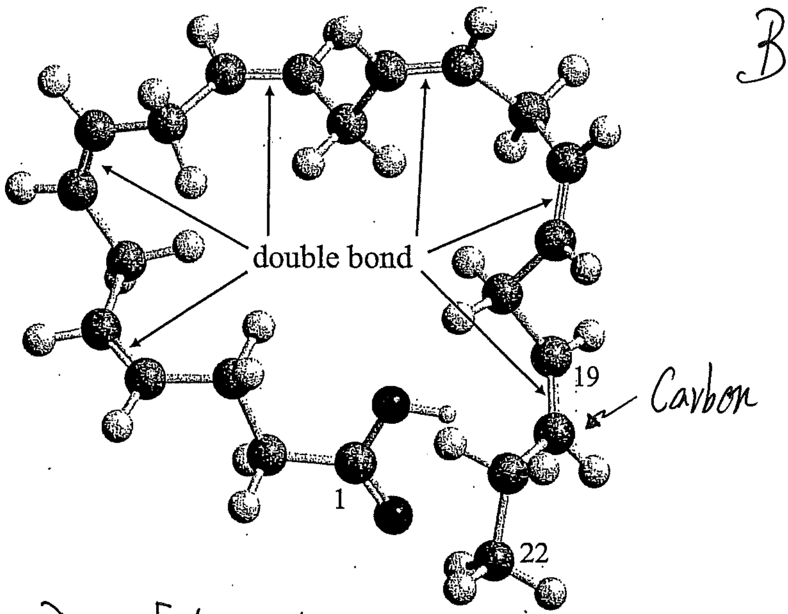


[$C_6H_6$] (Benzene)

[What does symbol mean?]

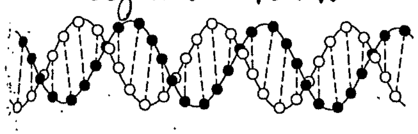
- Diatomic Molecules [Simpler] : $H_2$ , $O_2$ , $CO$

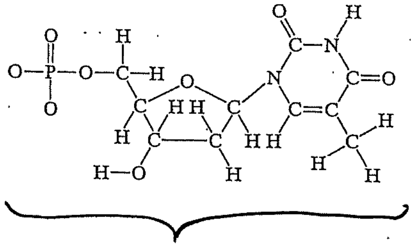
- Big & Complicated



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

segment ~ 10 nm





= "•" Thymine "T"

A, G, C, T

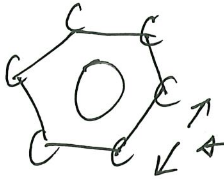
[From Taylor et al., "Modern Physics"]

DNA [Deoxyribonuclei acid]

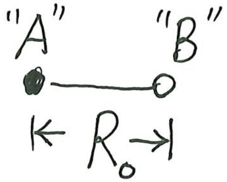
- There exists preferred (equilibrium) separation between atoms

$O = C = O$

Some preferred separation (bond length)



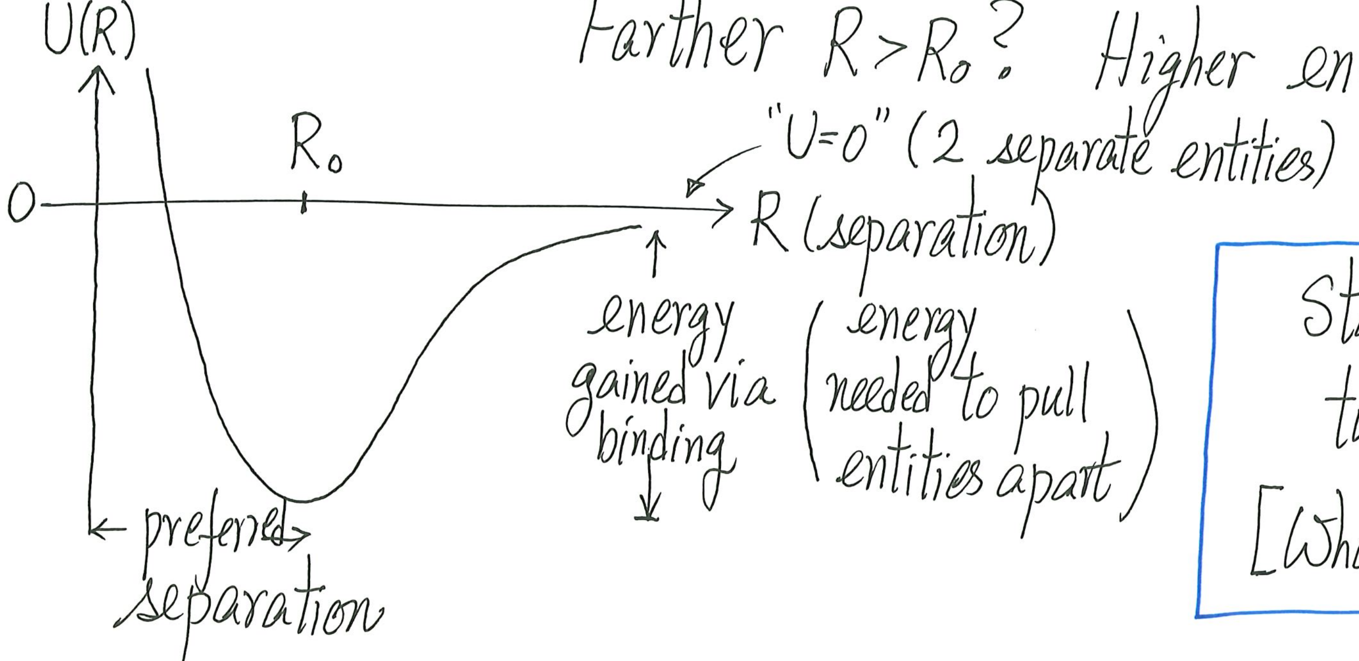
preferred separation



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?]

- For atoms forming molecule

  $R_0 \sim \underline{1-2\,\mathring{A}}$ (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 ($R_0 \sim 2\,\mathring{A}$)

  a few eV (typical)

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

- Same U(R) form works for nucleons (protons/neutrons) binding into nucleus

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

  $B \sim \underline{\text{Many}}\ \underline{\text{MeV}}$

  } 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</u> <u>atoms</u>
  [Dissociation Energy]

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

# Typical $R_0$ and B for Ionic and Covalent Bonds

| Molecule | $R_0$ (nm) | $B$ (eV)$^{\dagger}$ | 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 <u>Same order of magnitude</u> [<u>few eV</u>]

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

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

Energy is lowered!

# B. Ionic Bonding : Energetics

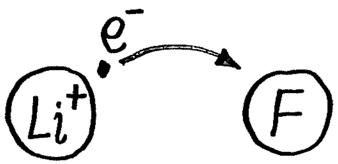
- usually involve atoms in 1st (2nd) and 7th (6th) columns in periodic table

Eg. Li and F

Same for NaCl

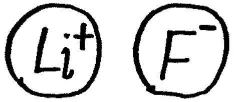
(a) Widely separated:

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



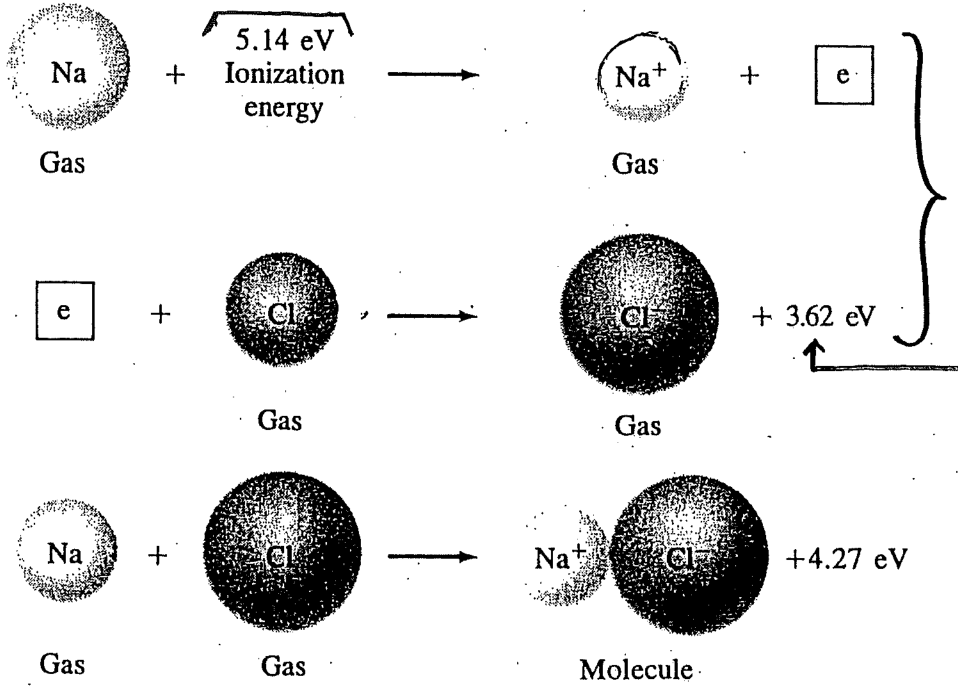
(Needs energy to do this?)

(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 1.52eV [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.

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

= Ionization energy of sodium − Electron affinity of chlorine

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

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

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

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

$$E(R) = \text{total energy at separation } R$$
$$= \Delta E \quad - \frac{e^2}{4\pi\varepsilon_0 R} \qquad \text{[Competing terms]}$$

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

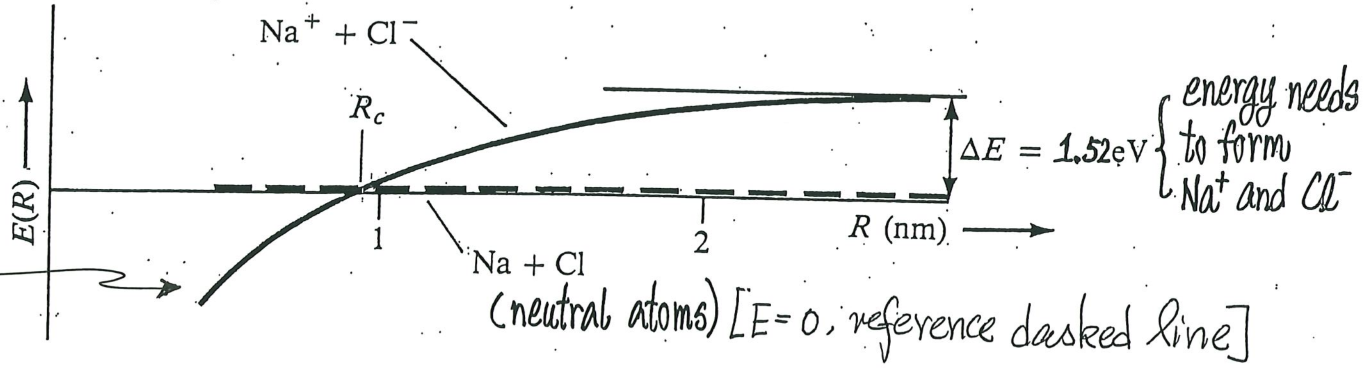
Note: • For $R > R_c = 0.95$ nm, $E > 0$

• For $R < R_c = 0.95$ nm, $E < 0$ $\Big[\underbrace{\text{lower energy}}_{}$ than two neutral atoms$\Big]$

electrostatic attraction wins $R < R_c$

Close-up of E(R)

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



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.

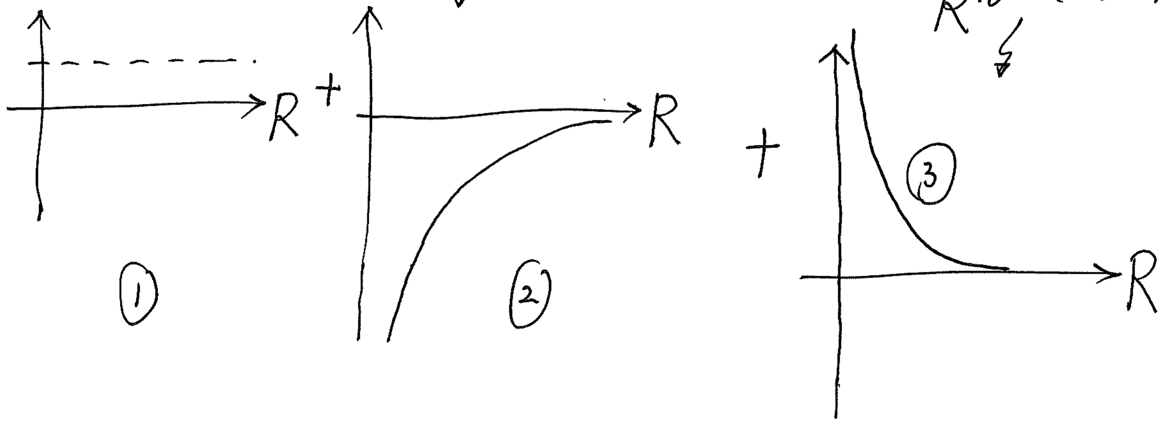
[From Taylor et al., "Modern Physics"]

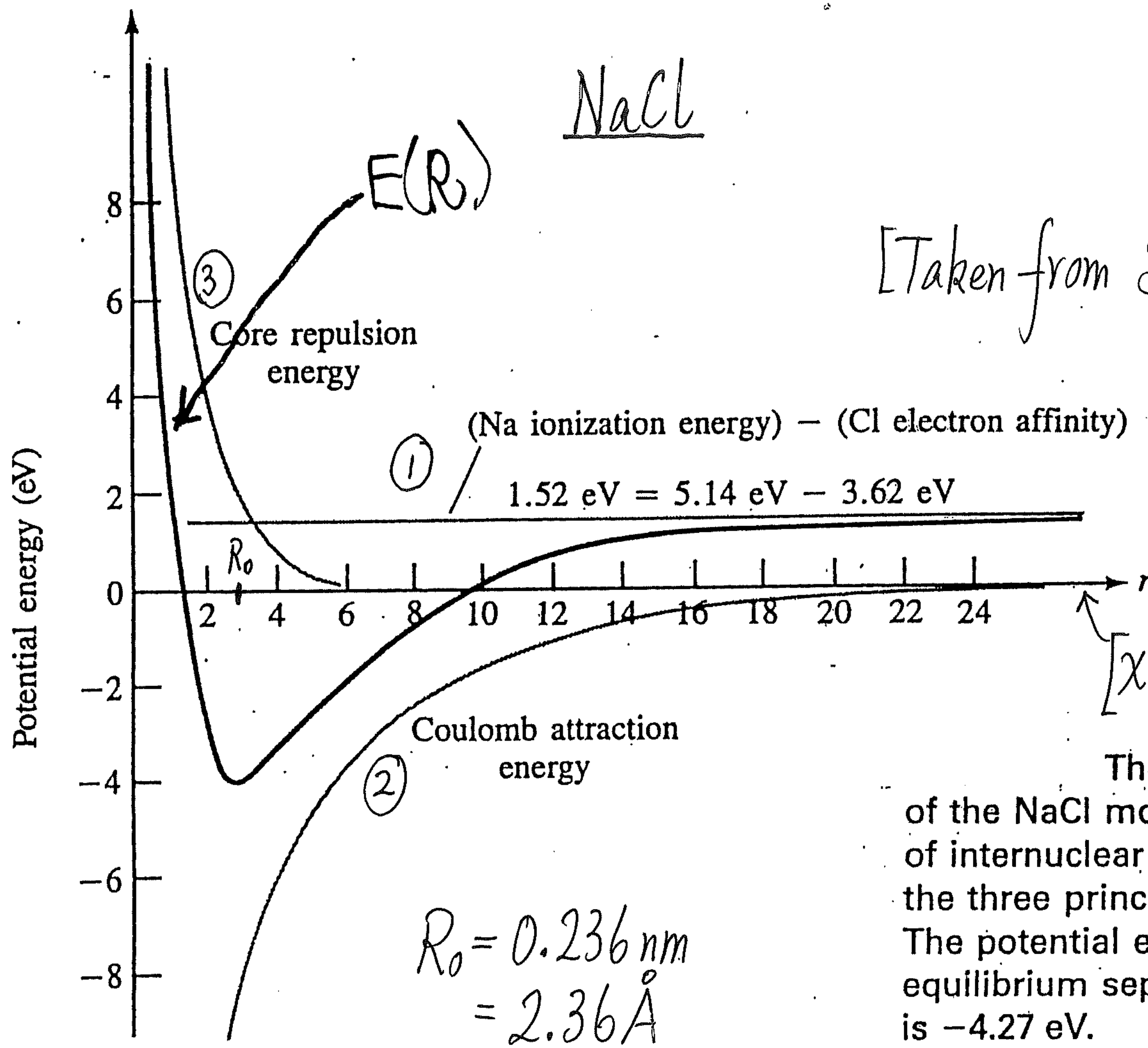
- Strong Repulsion at small R : "Core Repulsion"
  - Repulsion between two nuclei
  - Pauli Principle (Quantum effect) [more important]
    - electrons avoid each other
    - must fill in states (molecular) of progressively higher energies

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

(n = high power) (phenomenologically)

E(R) =





(=0.1 nm)

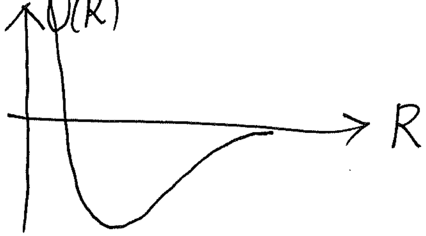
[Taken from Serway et. al., "Modern Physics"]

[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.

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

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



typical of binding (forming bonds)

Valence (化學價): # electrons an atom gains OR losses in forming a molecule

The nine possible molecules formed by combining the positive ions $Na^+$, $Mg^{2+}$, or $Al^{3+}$ with the negative ions $F^-$, $O^{2-}$, or $N^{3-}$. Numbers in parentheses show the valence of each element concerned.

| | $F^-$ (1) | $O^{2-}$ (2) | $N^{3-}$ (3) |
|---|---|---|---|
| $Na^+$ (1) | $NaF$ | $Na_2O$ | $Na_3N$ |
| $Mg^{2+}$ (2) | $MgF_2$ | $MgO$ | $Mg_3N_2$ |
| $Al^{3+}$ (3) | $AlF_3$ | $Al_2O_3$ | $AlN$ |

Mg losses 2 electrons

→ $Mg^{2+}$ ion

⇒ Mg has valence 2

$Mg_3N_2$ Overall neutral

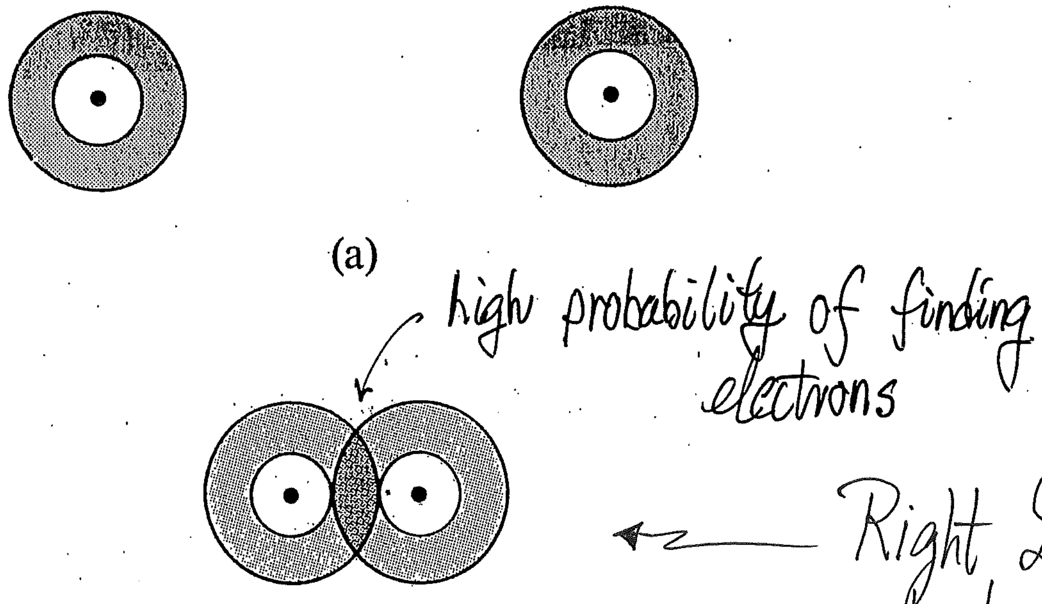
- $Al_2O_3$ OR $Mg_3N_2$, ∘∘∘ ⇒ Definite ratios (2:3 OR 3:2) in chemical reactions

Early evidence of matter having basic units

(Dalton)

atoms

# Covalent Bond
## (Baby level)



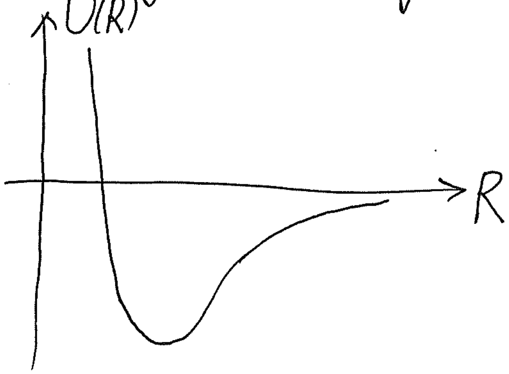
(a)

(b)

high probability of finding electrons

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 ?