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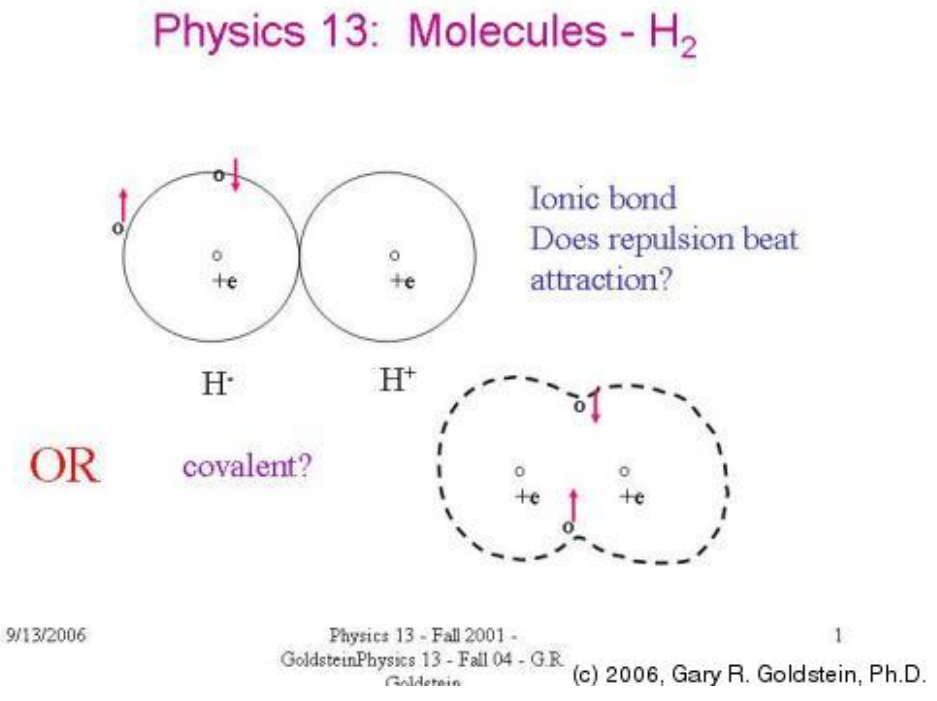
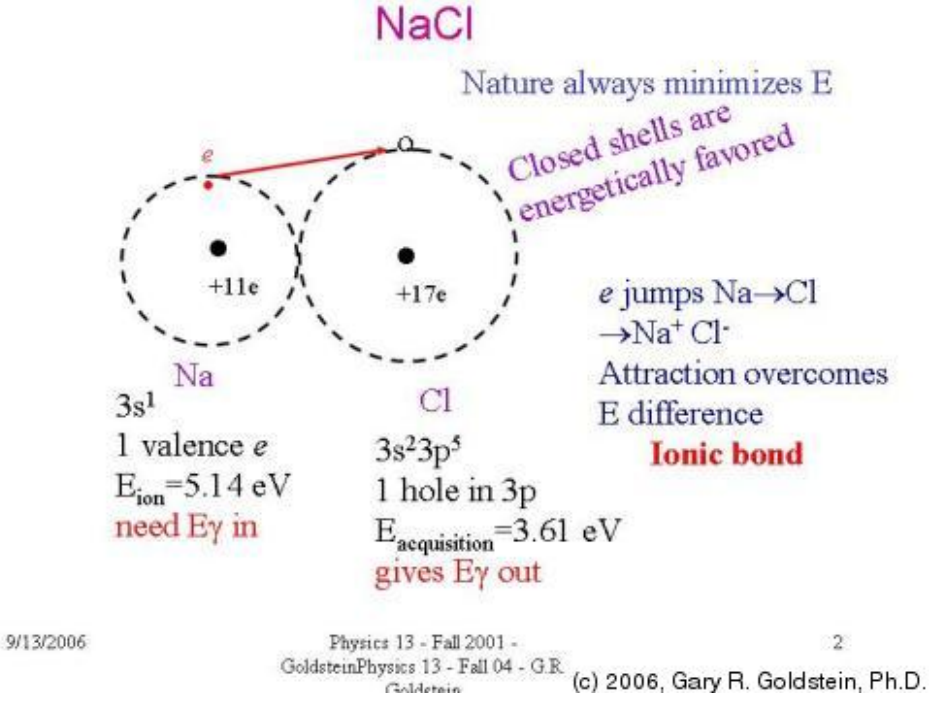
1. Physics 13: Molecules - H2



2. NaCl



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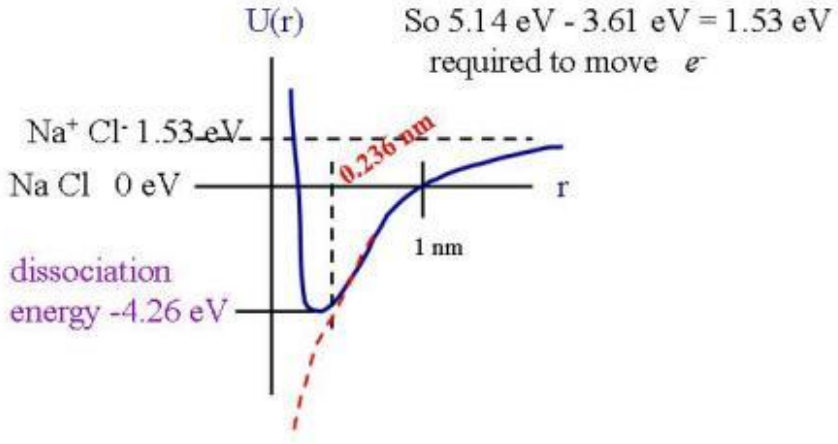
3. NaCl U(r)

NaCl U(r)



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4. NaCl calculation

NaCl calculation

Attraction of form $-\frac{k_{EM}e^2}{r}$ must overcome 1.53 eV

but exclusion principle causes repulsion for small r

when subshell $e's$ start to overlap

$$U(r) = 1.53 \text{ eV} - \frac{k_{EM}e^2}{r} + U^{exclusion}(r)$$

$$\text{Now } -\frac{k_{EM}e^2}{2.36\times10^{-10}m} = -6.09 \text{ eV}$$

$$U(r_{\min}) = -4.26 \text{ eV} = 1.53 - 6.09 + U^{exclusion}(r_{\min})$$

$$\rightarrow U^{exclusion}(r_{\min}) = 0.30 \text{ eV}$$

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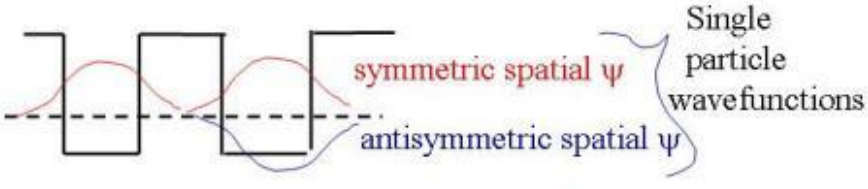
5. Covalent bond I

Covalent bond I

H_2 N_2 CO Symmetry of 2 e^- wavefunctions shared by 2 atoms

First: 1 dimensional model - 2 identical wells - 1 electron



As the 2 wells get closer together have $|\psi_S|^2>0$ at center, but $|\psi_A|^2=0$ at center. The ψ_S will have lower E than the ψ_A (node).

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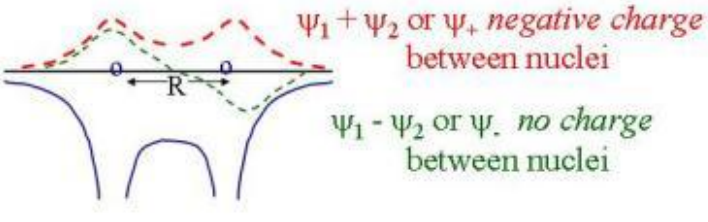
6. Covalent bond II

Covalent bond II

- H_2^+ first. If the 2 wells have + charge they are repelled. So symmetric wave function provides extra attraction. For 2 H nuclei (protons) there is a repulsive energy.



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7. Covalent bond III

Covalent bond III

Nuclei repulsion $U_{protons}(R) = +\frac{k_{EM}e^2}{R}$

For R fixed e^- sees $-\frac{k_{EM}e^2}{r_1} - \frac{k_{EM}e^2}{r_2}$

When $R >> a_0$ $E_{electron} = -\frac{13.6}{n^2}$ eV

When $R \to 0$ for ψ_+ $E_+ \to -\frac{13.6}{n^2}(Z=2)^2$ eV $= -\frac{54.4}{n^2}$ eV

But for ψ_- must get vanishing at $r = 0$ when $R \to 0$

So $\psi_-(r) \propto r$ or $\psi_- \sim$ 2p state

Then $E_- \to -\frac{13.6(2)^2}{(2)^2} = -13.6$ eV

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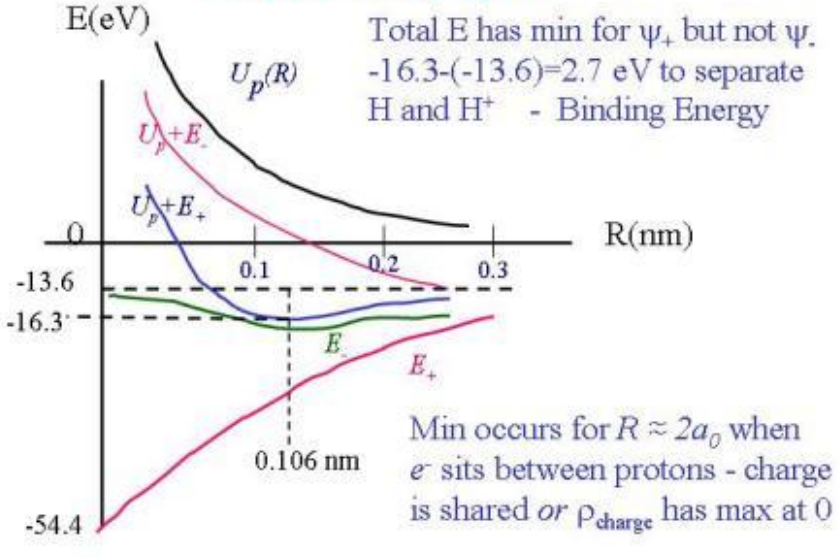
8. Covalent bond IV

Covalent bond IV



Total E has min for ψ_+ but not ψ_-
-16.3-(-13.6)=2.7 eV to separate H and H^+ - Binding Energy

Min occurs for $R \approx 2a_0$ when e^- sits between protons - charge is shared *or* ρ_{charge} has max at 0

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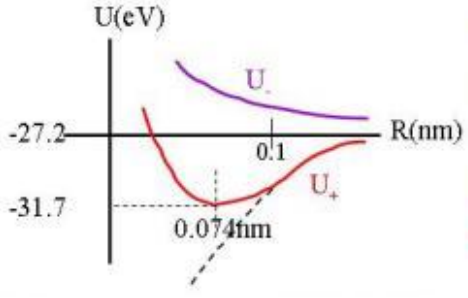
9. Covalent bond V

Covalent bond V

- 2 electrons for H_2 - when separation $R \rightarrow \infty$ have 2x(-13.6 eV)=-27.2 eV for two H atoms
- Both in $\psi_- \rightarrow$ *anti-bonding* (symmetric spins)
- Both in $\psi_+ \rightarrow$ *bonding* (antisymmetric spins)



Molecular B.E.
31.7-27.2=4.5eV

Covalent bond
Saturated bond

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10. Covalent vs. Ionic Bond

Covalent vs. Ionic Bond

Pure ionic bond has Electric dipole moment

$+e \bullet\!\!-\!\!-r_0 \rightarrow \bullet\!-e$ $p_{ionic}=er_0$ where r_0 is the equilibrium separation

$Na^+ Cl^-$ $r_0 = 2.36 \times 10^{-10}$m

so expected $p_{ionic}=3.78 \times 10^{-29}$ Coul·m

but measured $p_{ionic}=3.00 \times 10^{-29}$ Coul·m

Hence less than pure 100% ionic

$p_{measured} / p_{ideal} = 0.79$ or 79% ionic binding

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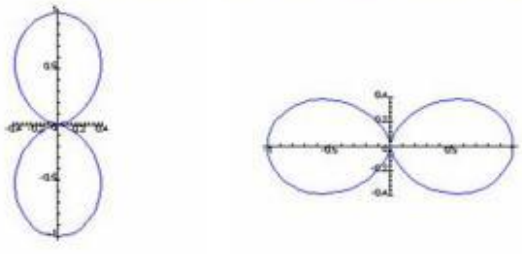
11. Covalent p-states

Covalent p-states

N_2 , O_2 , F_2 all involve 2p state electrons - form pp covalent bonds

Recall $l=1$, $m_l=+1,0,-1$ For $m_l=0$ had dumbell shape along z-axis -called p_z state. Linear combination of $m_l=+1$ and -1 will be along x-axis, p_x , and y-axis, p_y .



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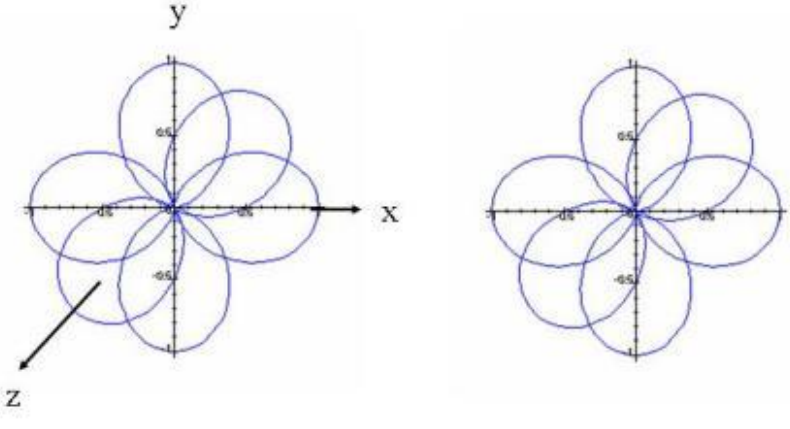
12. Directed p-states

Directed p-states



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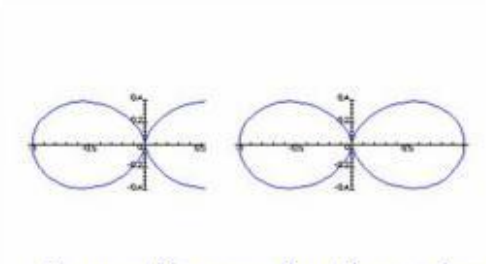
13. px -- px bonding

p_x -- p_x bonding



Symmetric wave function → bonding
Anti-symmetric wave function → anti-bonding

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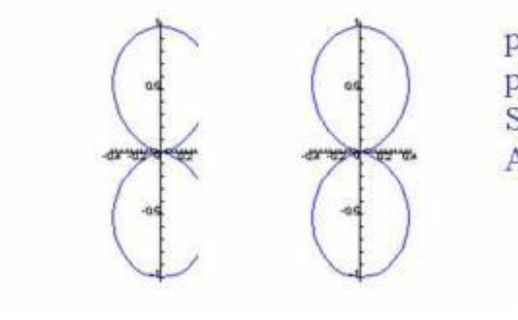
14. Other p - p bonding

Other p - p bonding



p_y with p_y or
p_z with p_z
Symmetric → less bonding
Anti-Symmetric → less anti-bonding

Atom can have np_x^2, np_y^2, np_z^2 each filled or partially

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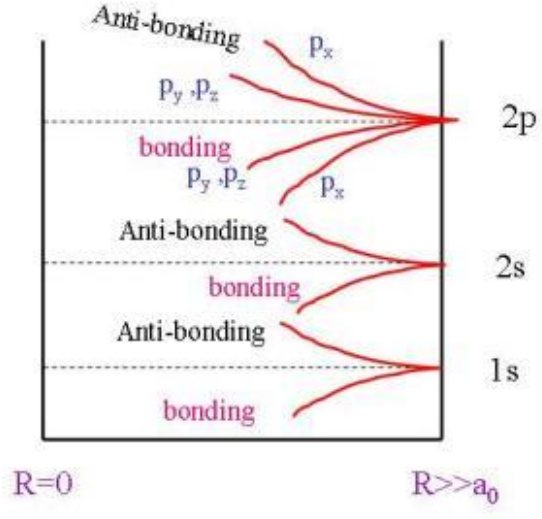
15. Energy of p-p covalent bonds

Energy of p-p covalent bonds



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16. Particular homopolar molecules

Particular homopolar molecules

- N_2 : $2p_x^1\ 2p_y^1\ 2p_z^1$ combines with same
  $\rightarrow$ 3 bonding covalent pairs
  E(dissociation)=9.8 eV Separation=0.11nm
- O_2 :$2p_x^1\ 2p_y^2\ 2p_z^1$x2$\rightarrow$ 3 bonding+1anti-bonding
  E(dissociation)=5.1 eV Separation=0.12nm
- F_2 : $2p_x^1\ 2p_y^2\ 2p_z^2$x2$\rightarrow$ 3 bonding+2anti-bonding
  E(dissociation)=1.6 eV

Note that $2p_y^2$ with $2p_y^2 \rightarrow$ 1 sym pair + 1 anti pair

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17. Other bonds

Other bonds

- Van der Waals - e-dipole with e-dipole
  - In atoms-atoms, molecules-molecules, gases
- H-bond in polyatomic molecules -e.g. proteins
  - H is shared between Oxygens and Carbons
- Metallic bond - lattice of A^+ 's in "gas" of electrons

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18. Polyatomic molecules

Polyatomic molecules

- H_2O $_8O$: $1s^2 2s^2 2p^4 \rightarrow$ 2 empty p-states

form covalent bonds when

(a) minimizes E

(b) maximizes overlap of wavefunctions for each atom - i.e.orbitals fit together best so e^-s are shared in symmetric states providing attraction

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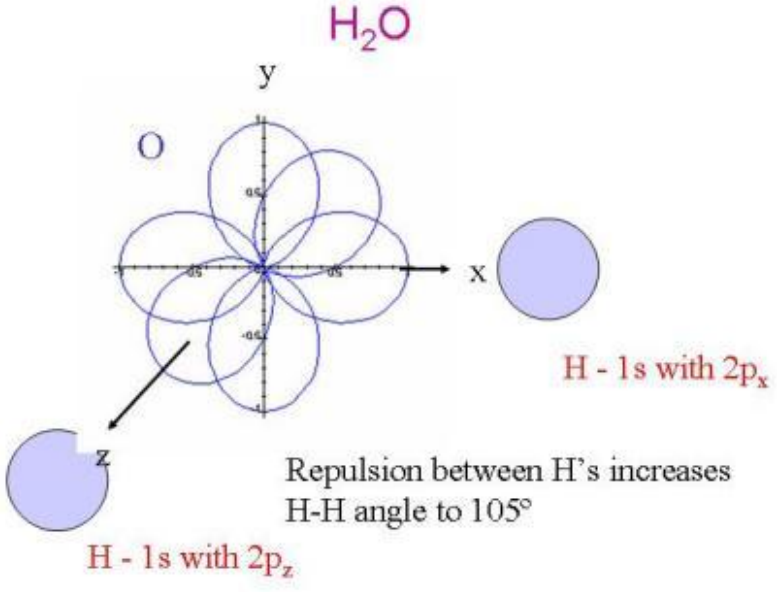
19. H2O



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20. Ammonia and Organic molecules

Ammonia and Organic molecules

- NH_3 $_7N$: $1s^2 2s^2 2p^3$ valence of 3
  - 3 "sp directed" bonds with H angles > 90°
- $_6C$: $1s^2 2s^2 2p^2$ but valence of 4
  - Forms bonds from excited $1s^2 2s^1 2p^3$
  - or $2s2p_x2p_y2p_z \rightarrow$ 4 hybrid equivalent orbitals
  - Tetrahedral structure
    - CH_4 methane
    - $CH_3 — CH_3$ with p-p covalent bonding ethane
    - C_2H_4 ethylene C_2H_2 acetylene different combinations of hybrids and p-p or s-p bonding

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