PHYS 460
LECTURE 3

THIS COURSE WILL LARGELY BE CONCERNED WITH THE BEHAVIOUR OF ELECTRONS INSIDE A MATERIAL. AS ELECTRONS ARE QUANTUM MECHANICAL OBJECTS, THEIR BEHAVIOUR IS ENTIRELY DETERMINED BY SOLVING THE SCHRODINGER EQUATION

$$\hat{H}\Psi = E\Psi$$

SO FAR, WE HAVE ONLY CONSIDERED "FREE" ELECTRONS, WHERE THE ONLY ENERGY IS KINETIC ENERGY (i.e $\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$). IN COMING WEEKS, WE ARE GOING TO CONSIDER HOW OUR RESULTS ARE MODIFIED BY THE PRESENCE OF A PERIODIC POTENTIAL (FROM AN ARRAY OF POSITIVE NUCLEI) AND FROM ELECTRON-ELECTRON INTERACTIONS.

IT IS WORTH STOPPING FOR A MOMENT, HOWEVER, AND FIRST CONSIDERING HOW SOLIDS ARE ACTUALLY FORMED. HOW DO WE GO FROM OUR PICTURE OF ELECTRONS IN INDIVIDUAL ATOMS (WHICH WE UNDERSTAND WELL), TO CHEMICAL BONDS IN A SOLID LATTICE? WHAT IS PROVIDING THAT ENERGY?

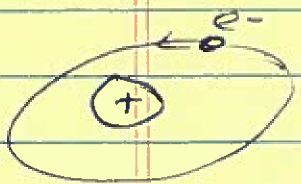
THIS WILL ALLOW US TO SORT SOLIDS INTO 4 (NOT DISTINCT) CATEGORIES

(I) COVALENT SOLIDS
(II) IONIC SOLIDS
(III) MOLECULAR SOLIDS
(IV) METALS

AND SOMETIMES (V) HYDROGEN BONDED SOLIDS

CATEGORY (IV) (METALS) IS ACTUALLY THE HARDEST TO CONSIDER IN THIS REGARD, SO WE WILL START BY CONSIDERING INDIVIDUAL ATOMS AND HOW THEY COME TOGETHER TO FORM COVALENT BONDS.

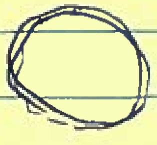
RECALL (THIS SHOULD BE REVIEW) THAT THE SOLUTION TO THE SINGLE ELECTRON SCHRODINGER EQUATION FOR A SINGLE ATOM INVOLVED ORBITALS WITH THE FOLLOWING QUANTUM NUMBERS



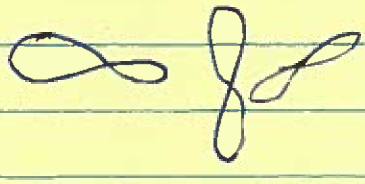
$n = 1, 2, \ldots$	PRINCIPLE
$l = 0, 1, \ldots, n-1$	ANGULAR MOMENTUM
$l_z = -l, -l+1, \ldots, l$	Z-COMPONENT OF $\vec{L}$
$s_z = -\frac{1}{2}$ OR $\frac{1}{2}$	SPIN

EACH OF THE l_z ORBITALS HAD A DISTINCT SHAPE IN REAL SPACE

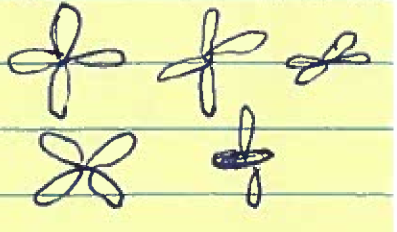
$l=0$ (S-ORBITAL)



$l=1$ (p-ORBITAL)



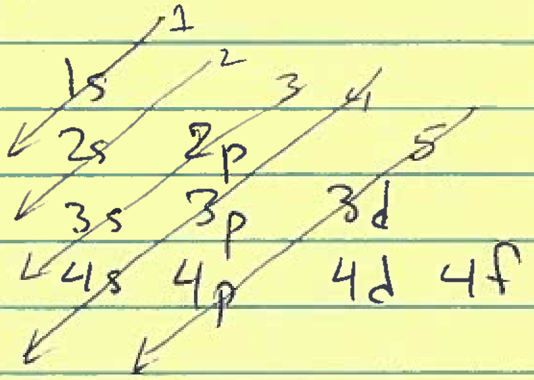
$l=2$ (d-ORBITAL)



FOR MULTI-ELECTRON ATOMS, WE APPROXIMATE THE MANY BODY SOLUTION BY POPULATING SINGLE ELECTRON LEVELS, WHILE OBEYIN PAULI EXCLUSION.

THIS IDEA NATURALLY EXPLAINS THE PERIODIC TABLE IF WE POPULATE STATES ACCORDING TO MADELUNG'S RULE (LOWEST $n+l$ TO LARGEST).

IN EFFECT, THIS MEANS SHELLS SHOULD BE FILLED ACCORDING TO:-



e.g. FOR Pr^{59} CONFIGURATION IS

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^3$$

MANY TRENDS ARE ALSO NATURALLY EXPLAINED, IF YOU CONSIDER THE FACT THE POSITIVE NUCLEAR CHARGE IS PARTIALLY "SCREENED" BY ELECTRONS WITH LOWER ORBITING RADIUS THAN THE PARTICULAR ELECTRON CONSIDERATION

LEFT ⟶ RIGHT

⟵ ATOMIC RADIUS

IONIZATION ENERGY ⟶

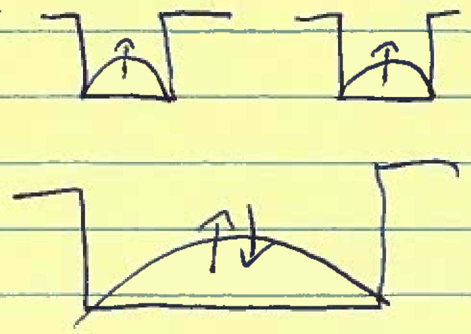
ELECTRON AFFINITY ⟶

ALSO EXPLAINS WHY ELEMENTS WITH FILLED SHELLS ARE "INERT"

CASE I : COVALENT BONDING

SO THIS IS THE PICTURE ONE EXPECTS WHEN ATOMS ARE APART. WHAT HAPPENS WHEN YOU BRING THEM TOGETHER? WELL, FOR SOME CASES, IT IS ENERGETICALLY FAVORABLE FOR ATOMS TO SHARE ELECTRONS. EVEN WITHOUT CONSIDERING SPECIFICS, SIMON MAKES THIS POINT WELL BY CONSIDERING A 1D PARTICLE-IN-A-BOX POTENTIAL

APART:



$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\Rightarrow \quad \psi = A\sin\left(\frac{n\pi}{L}\right),\ n\in\mathbb{Z}$$

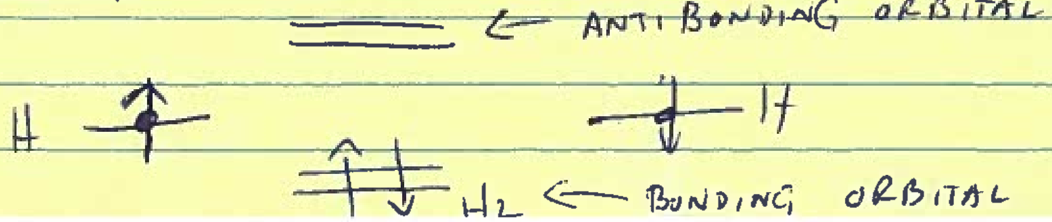
$$E_n = \frac{\hbar^2 n^2\pi^2}{2mL^2}$$

WHICH HAS LOWEST ENERGY $E_1 = \frac{\hbar^2\pi^2}{2mL^2}$

BUT IF WE DOUBLE THE SIZE OF THE BOX BY BRINGING TWO ATOMS TOGETHER

$$E_1' = \frac{\hbar\pi^2}{2m(2L)^2} = \frac{\hbar^2\pi^2}{8mL^2} < 2E_1$$

THAT IS, BOTH ELECTRONS CAN OCCUPY LOWEST ORBITAL BY HAVING OPPOSITE SPIN, THUS LOWERING OVERALL ENERGY



NOTE THAT THIS PROCESS ALSO ANTI-ALIGNS THE SPINS. THIS "EXCHANGE" INTERACTION WILL BE IMPORTANT FOR CONSIDERATION OF MAGNETISM LATER ON IN THE COURSE.

NOW, LET'S SEE IF WE CAN GO BEYOND THE CARTOON P-IN-A-B PICTURE TO SOMETHING MORE REALISTIC.

CONSIDER THE HAMILTONIAN FOR AN ELECTRON IN THE PRESENCE OF TWO POSITIVELY CHARGED NUCLEI. LET THE NUCLEI BE FIXED FOR NOW (BORN-OPPENHEIMER APPROX). THEN

$$\hat{H} = K + V_1 + V_2$$

WHERE $K = \frac{p^2}{2m}$ IS K.E.

$$V_i = \frac{e^2}{4\pi\varepsilon_0 |\vec{r} - \vec{R}_i|}$$

IS POTENTIAL DUE TO ATOM i

LET US DEFINE STATES $|1\rangle, |2\rangle$ SUCH THAT

$$(K + V_1)|1\rangle = E_0 |1\rangle$$

AND $(K + V_2)|2\rangle = E_0 |2\rangle$

THESE ARE JUST OUR ATOMIC ORBITALS.

NOTE THAT I HAVE SWITCHED TO STANDARD bra-ket NOTATION

NOW FINDING THE GENERAL SOLUTION TO $\hat{H}$ IS UGLY, AND NOT ENLIGHTENING IN A LECTURE SETTING. INSTEAD, LET'S TRY A VARIATIONAL SOLUTION USING THE "TIGHT BINDING" APPROXIMATION:

$$|\psi\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle \quad , \quad \phi_1, \phi_2 \in \mathbb{C}$$

THE FORM OF THE SOLUTION IS CALLED A "LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)", AND BASICALLY SAYS THAT THE FINAL ELECTRON DISTRIBUTION IS NOT TOO DIFFERENT FROM THE SHAPE OF ORIGINAL ORBITALS, TO A FIRST APPROXIMATION

TO MAKE LIFE EASIER, WE WILL FOR NOW ALSO ASSUME ORTHONORMALITY

$$\langle i | j \rangle = \delta_{ij}$$

WHICH IS GOOD FOR ATOMS FAR APART, BAD WHEN THEY ARE CLOSE TOGETHER, BUT ULTIMATELY WITHOUT CONSEQUENCE. SO WE LEAVE IT FOR NOW.

TO SOLVE SCHR EQ, $H|\psi\rangle = E|\psi\rangle$, LET'S RECAST AS A MATRIX EQUATION. IF $|1\rangle, |2\rangle$ ARE ACTING AS A BASIS, THEN

$$|\psi\rangle = \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

AND $$\hat{\mathcal{H}} = \begin{pmatrix} \langle 1|\mathcal{H}|1\rangle & \langle 1|\mathcal{H}|2\rangle \\ \langle 2|\mathcal{H}|1\rangle & \langle 2|\mathcal{H}|2\rangle \end{pmatrix}$$

$$\equiv \begin{pmatrix} \mathcal{H}_{11} & \mathcal{H}_{12} \\ \mathcal{H}_{21} & \mathcal{H}_{22} \end{pmatrix}$$

WE CAN WORK OUT THESE MATRIX ELEMENTS

$$\mathcal{H}_{11} = \langle 1| K + V_1 |1\rangle + \langle 1| V_2' |1\rangle = E_0 + V_{CROSS}$$

$$\mathcal{H}_{22} = \langle 2| K + V_2 |2\rangle + \langle 2| V_1 |2\rangle = E_0 + V_{CROSS}$$

$$\mathcal{H}_{12} = \langle 1| K + V_2 |2\rangle + \langle 1|V_1|2\rangle$$

$$= E_2 \langle 1|2\rangle + \langle 1|V_1|2\rangle = 0 - t$$

$$\mathcal{H}_{21} = 0 - t^*$$

WHERE WE DEFINE

$V_{CROSS} \equiv \langle 1|V_2|1\rangle$ AS THE ENERGY OF THE FIRST ELECTRON DUE TO THE SECOND ATOM

AND $t \equiv -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$

THE "HOPPING TERM" WHICH IS A MEASURE OF ORBITAL OVERLAP INTEGRAL

$$\rightarrow \begin{pmatrix} E_0 + V_{CROSS} & -t \\ -t^* & E_0 + V_{CROSS} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

WE SOLVE BUT DIAGONALIZING, BUT FIRST LET'S STOP AND CONSIDER LIMITS AND INTERPRETATION

- FIRST WE NOTE THAT, AS SEPARATION BETWEEN ① & ② → ∞, BOTH V_{cross} AND $t \rightarrow 0$. THE UNMIXED WAVEFUNCTION BECOMES DIAGONAL, AS EXPECTED, $\forall\, \phi_1, \phi_2$

- V_{cross} SIMPLY INCREASES ENERGY OF THIS ORIGINAL SOLUTION, AS IT ONLY COMES IN ON THE DIAGONAL

- t INTRODUCES OFF-DIAGONAL TERMS, WHICH ALLOWS SOME OF WAVEFUNCTION $|1\rangle$ TO EVOLVE INTO WAVEFUNCTION $|2\rangle$ ⇒ "HOPPING"

NOW DIAGONALIZE

$$\det\begin{pmatrix} E_0+V_{cross}-E & -t \\ -t^* & E_0+V_{cross}-E \end{pmatrix} = 0$$

$$\Rightarrow \quad (E_0+V_{cross}-E)^2 - |t|^2 = 0$$

$$E_0+V_{cross}-E = \pm |t|$$

$$\boxed{E_{\mp} = E_0+V_{cross} \mp |t|}$$

IT IS A SIMPLE MATTER TO GET WAVEFUNCTIONS. FOR EXAMPLE, IF $t > 0$ (HOPPING GIVES ENERGY GAIN), THEN SOLUTIONS ARE

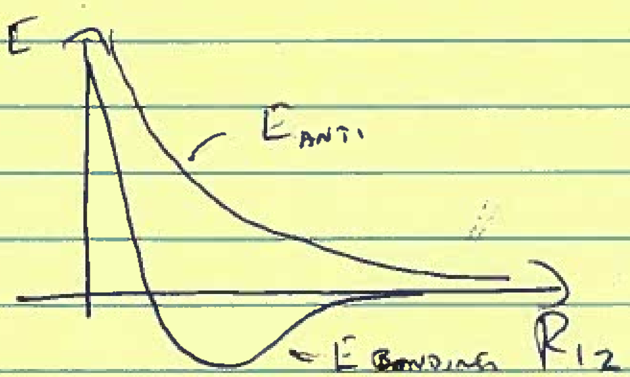
NOTE: EQUALLY EVERYWHERE, ESP. MIDDLE!

$$\rightarrow \quad |\psi_{\text{BONDING}}\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$$

AND $$|\psi_{\text{ANTIBONDING}}\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right)$$

WITH "BONDING" BEING LOWER ENERGY

THIS COVALENT BONDING WILL DRAW ATOMS TOGETHER UNTIL NUCLEI-NUCLEI REPULSION SAYS STOP



CASE II : IONIC BONDING

THE ABOVE PICTURE WAS FOR TWO IDENTICAL ATOMS WHICH HAD EQUAL "AFFINITIES" FOR ELECTRONS. WE KNOW HOWEVER THAT SOME ATOMS WANT ELECTRONS MORE DUE TO HIGHER NUMBERS OF PROTONS AND POORER SCREENING

THIS "TILTS" OUR HAMILTONIAN IN FAVOR OF ATOM WITH HIGHER AFFINITY

$$\begin{pmatrix} E_A + V_{CROSS,1} & t^* \\ -t^* & E_B + V_{CROSS,2} \end{pmatrix}, \quad E_B < E_A$$

AND SOLUTION WILL HAVE A WAVEFUNCTION THAT IS MORE LOCATED AT SECOND ATOM

$$|\psi_{BONDING}\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle$$

$$\phi_2 > \phi_1$$

IN THIS SCENARIO, IF THE DIFFERENCE IS LARGE, THE CONVERSATION SHIFTS TO "IONIC BONDING", FROM COULOMB INTERACTION BETWEEN +VE CATION ! -VE ANION

(NOTE, THAT DESPITE BEGINNING DISCUSSION WITH COVALENT BONDS, THE PHYSICS IS QUITE DIFFERENT. THE ABOVE CALCULATION DIDN'T EVEN MENTION THE POSITIVE NUCLEI!)

Or rather, it didn't take into account that the opposite electron will effectively modify the total positive charge

IN A SENSE, IONIC BONDING IS SIMPLER AND MAY BE MORE FAMILIAR. IF WE DEFINE

$E_{A\to A^+}$ = IONIZATION ENERGY = ENERGY REQUIRED TO REMOVE AN ELECTRON

AND $E_{B\to B^-}$ = ELECTRON AFFINITY = ENERGY GAINED BY TAKING ON AN ELECTRON

AND $E_{COHESION}$ = ENERGY GAINED BY TAKING TO OPPOSITELY CHARGED IONS AND PUTTING THEM TOGETHER

THEN IF

$$\Delta E_{A+B \to AB} = E_{A \to A^+} - E_{B \to B^-} - E_{COHESION}$$

$$< 0$$

YOU FORM AN IONIC BOND!

FROM LOOKING AT PERIODIC TABLE, COMMON IONIC SOLIDS FORM FROM I - VII, II - VI

III - V SOMEWHERE IN BETWEEN

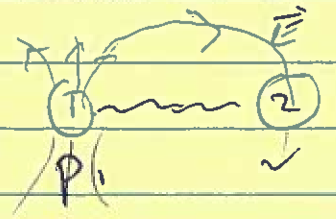
CASE III : MOLECULAR BONDS

WHAT IF YOU ARE CONSIDERING IDENTICAL ATOMS AND THERE IS NO ENERGY BENEFIT FROM FORMING BONDING ORBITAL? WHAT ABOUT SOLID ARGON? HOW DOES THAT BOND?

IN "FULL SHELL" ATOMS LIKE Ar, AND OTHER SITUATIONS WITHOUT AVAILABLE MODES, THE ELECTRON DENSITY IS ALMOST PERFECTLY SPHERICALLY SYMMETRIC AND UNCHARGED.

IN THIS CASE, THERE IS NO COULOMB FORCE. ON AVERAGE, THERE IS ALSO NO DIPOLE (OR ANY DEVIATION FROM SPHERICAL SYMMETRY). HOWEVER, ONE CAN IMAGINE THAT INSTANTANEOUSLY, THERE CAN BE A QUANTUM FLUCTUATION SUCH THAT A DIPOLE IS FORMED.

IMAGINE TWO ATOMS SEPARATED BY DISTANCE, r, AND AN INSTANTANEOUS DIPOLE, p_1, IS FORMED ON ATOM ①



DIPOLE, NOT MOMENTUM

$$p_1 = ed$$

d = local distortion

THIS DIPOLE, IN $\hat{z}$ DIRECTION SAY, WILL CREATE AN ELECTRIC FIELD ALONG THE $\hat{z}$ AXIS OF

$$|\vec{E}_1| \propto \frac{p_1}{r^3}$$

NOW THE SECOND ATOM SEES A FIELD AND ADJUSTS ITS ELECTRON DENSITY ACCORDINGLY

$$p_2 = \underset{\text{POLARIZABILITY}}{\alpha} E_1 \sim \frac{\alpha p_1}{r^3}$$

NOW THERE ARE TWO DIPOLES, THEY HAVE AN INTERACTION ENERGY

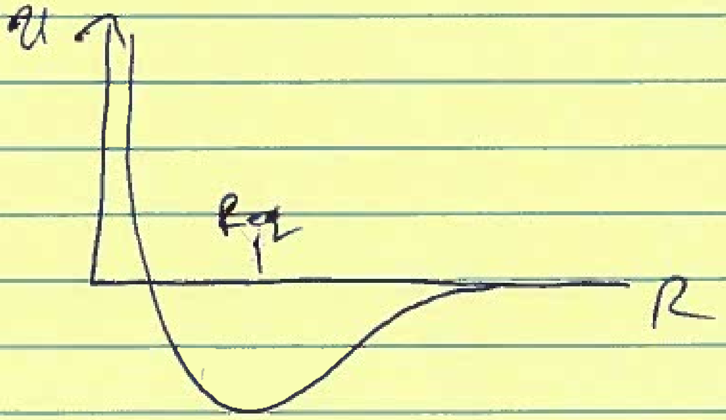
$$\mathcal{U}_{\text{DIPOLE}} = -\frac{p_2 p_1}{r^3} \sim -\frac{\alpha p_1^2}{r^6}$$

WHICH CREATES AN ATTRACTIVE FORCE

$$\boxed{F = -\frac{dU}{dr} = -\frac{\alpha p_1^2}{r^7}} \leftarrow \text{VAN DER WAALS FORCE}$$

LIKE THE COVALENT BONDING SCENARIO THOUGH, ATOMS CAN'T COME INFINITESMALLY CLOSE TOGETHER. IN THIS CASE, PAULI EXCLUSION SAVES THE DAY. A COMMON EMPIRICAL FORM FOR THE POTENTIAL IS KNOWN AS LENNARD-JONES POTENTIAL

$$U(R) = B\left[\left(\frac{A}{R}\right)^{12} - \left(\frac{A}{R}\right)^{6}\right]$$



BOND LENGTH AT MINIMUM

IMPORTANT NOTE - $\langle p_1 \rangle = \langle p_2 \rangle = 0$. THIS BONDING ONLY TAKES PLACE BECAUSE $\langle p_1^2 \rangle \neq 0$ THROUGH A SECOND ORDER QUANTUM EFFECT. THE PICTURE IS THAT THE TWO ATOMS ARE FLUCTUATING TOGETHER IN A CORRELATED WAY, AND GAINING ENERGY.

CASE (V) (?) : HYDROGEN BOND

- OFTEN SEPARATED BECAUSE OF ITS UNIQUE CHARACTER, BUT REALLY JUST A COVALENT - IONIC 1-2 PUNCH

  H GIVES UP ONLY ELECTRON TO FORM A COVALENT BOND WITH ONE ATOM, WHICH IN TURN CREATES A NET POSITIVE CHARGE AVAILABLE FOR IONIC BONDING

CASE (IV) : METALS

- HARDEST TO TREAT QUANTITATIVELY
- QUALITATIVELY CAN THINK OF AS EXTREME COVALENT BOND - WHERE ALL ATOMS ARE SHARING ALL ELECTRONS
- DIRECTIONLESS BONDING & WEAK

IN REALITY, THESE CLASSIFICATIONS ARE JUST GUIDELINES. ALL REAL MATERIALS EXPERIENCE ALL THESE EFFECTS. IN THE CASE ONE DOMINATES THOUGH, WE CAN USE DERIVED POTENTIAL ENERGIES TO MAKE ESTIMATES FOR COMPRESSIBILITY, SOUND PROPOGATION, THERMAL EXPANSION, MELTING TEMPERATURE, AMONG OTHER THINGS.