

Diatomic - Diatomic Electronic Spectra $\left\{ \begin{array}{l} \frac{Ze^2}{4\pi\epsilon_0 r} \rightarrow SI \\ \text{in cgs} \rightarrow \frac{Ze^2}{r} \end{array} \right.$

Simplest diatomic is H_2^+ - Sturme 4.3
Levine 13.4

only 1e⁻ simplifies problem, Hel at some const R_{AB}

(cgs)

$$H_{el} = \frac{-\hbar^2}{2me} \nabla_{\mathbf{r}}^2 - \frac{e^2}{r_{EA}} - \frac{e^2}{r_{EB}} + \frac{e^2}{R_{AB}}$$

const \rightarrow part of eigenvalue

$$(r = \text{elect pos.}) \quad r_A = |r_{\mathbf{r}} - R_A| \quad r_B = |r - R_B|$$

Can be solved exactly using confocal elliptical coord but this is unique soln not worth working on

Handout - does some things from point of view of variation principle \rightarrow see eq 1

Approx let LCAO \rightarrow MO ϕ_A, ϕ_B atomic state on A, B

$$\psi = c_A \phi_A + c_B \phi_B$$

due to sym if $\phi_A = \phi_B$ then $|c_B| = |c_A|$

$$\psi_{\pm} = c (\phi_A \pm \phi_B)$$

$$c_{\pm} = (2 \pm 2S_{AB})^{-1/2} \quad \text{where } S_{AB} = \langle A | B \rangle$$

so if use 2AO's \rightarrow 2MO's

Now if solve $\langle \psi_{\pm} | H_{el} | \psi_{\pm} \rangle = E_{\pm}(R)$

$R = \infty$ - clearly get $E_A = E_B = E_{\pm} = E_{1s}$ if $\phi_A = \phi_B$

$$R = R \quad - \quad E_{\pm}(R) = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} \quad \begin{array}{l} H_{AA} = \langle \phi_A | H_{el} | \phi_A \rangle \\ H_{BB} = \langle \phi_B | H_{el} | \phi_B \rangle \end{array}$$

Note

$$H_{el} = H_A - \frac{e^2}{r_B} = H_B - \frac{e^2}{r_A} \quad \left\{ \begin{array}{l} \text{equivalent} \\ \text{expression} \end{array} \right.$$

$$\begin{aligned} \text{Now } H_{AA} &= \langle \phi_A | H_A | \phi_A \rangle - \langle \phi_A | \frac{e^2}{r_B} | \phi_A \rangle + \frac{e^2}{r_{AB}} \langle \phi_A | \phi_A \rangle \\ &= E_{1s} + J + \frac{e^2}{r_{AB}} \quad \text{J - coulomb} \end{aligned}$$

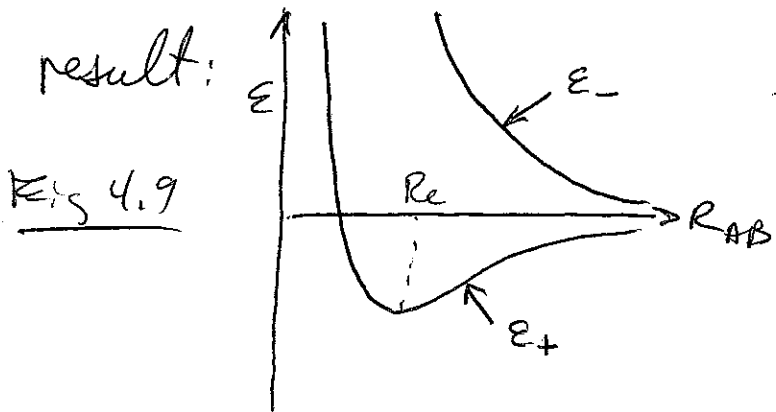
$$\begin{aligned} H_{AB} &= \langle \phi_B | H_A | \phi_A \rangle - \langle \phi_B | \frac{e^2}{r_B} | \phi_A \rangle + \frac{e^2}{r_{AB}} \langle \phi_B | \phi_A \rangle \\ &= E_{1s} S_{AB} + K + \frac{e^2}{r_{AB}} S_{AB} \quad \begin{array}{l} K\text{-exchange} \\ S_{AB} = \text{overlap} \end{array} \end{aligned}$$

J, K perfectly analogous to J, K for the atomic problem

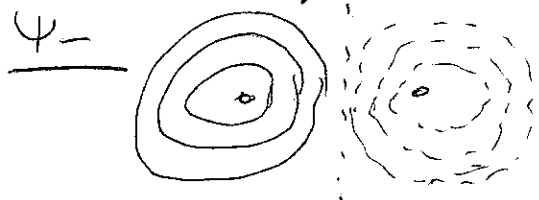
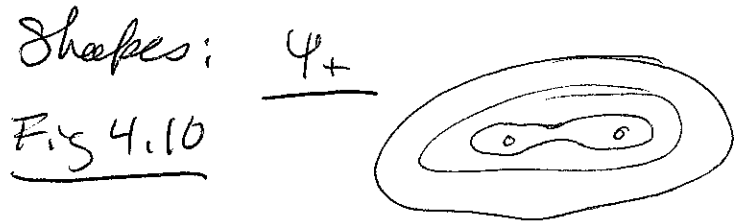
- J - coulomb attract elect on A to B
- K - quantum result exchange elect A ↔ B

energies: $E_{\pm} = E_{1s} + \frac{e^2}{r_{AB}} + \frac{J \pm K}{1 \pm S_{AB}}$

since J, K → 0 as r_{AB} → ∞
 E_± → E_{1s} as r_{AB} → ∞



so see result that
 E₊ → has a bound state
 i.e. r_{AB} = r_e where molecule stable
 E₋ → repulsive potential always dissociate.

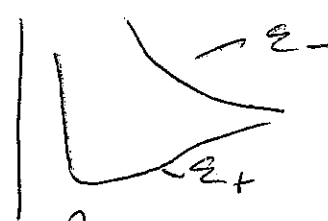


2/16/92

Levine
13.5-8
read
here
(bored)

EXAM?

Feb 24 drop date
Feb 28 prof TALK // V-3a



$$\psi_{\pm} = c(\phi_A \pm \phi_B)$$



Now these simple orbitals can be characterized by an angular momentum

$$[H, L^2] \neq 0$$

- no total L but

$$[H, L_z] = 0$$

→ Hamiltonian still has a term in $\frac{d^2}{dz^2}$

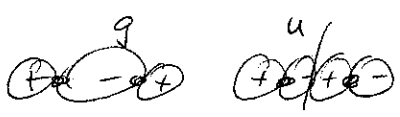
H₂ ϕ_{1s} AO's → each $m_l = 0$ → $M_L = 0$

Differentiate by sym for mirror reflection \perp to bond on for inversion $x, y, z \rightarrow -x, -y, -z$

g - even u - odd

Any 3 orbitals summed lead to σ

but also if combine p_0 orbitals / note axis - z is bond



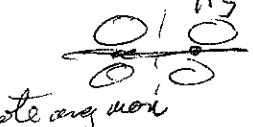
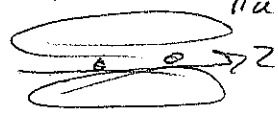
$\sigma \rightarrow m_l = 0$

and g, u depending on node plane

→ for σ orbitals →

g - sym → increase elect density between the nuclei - attractive force ⇒ bond promote

If combine $p_{\pm 1}^A + p_{\pm 1}^B \rightarrow m_l = \pm 1 \rightarrow \pi$ - orbital



here π_u - inc. e density between → bonding

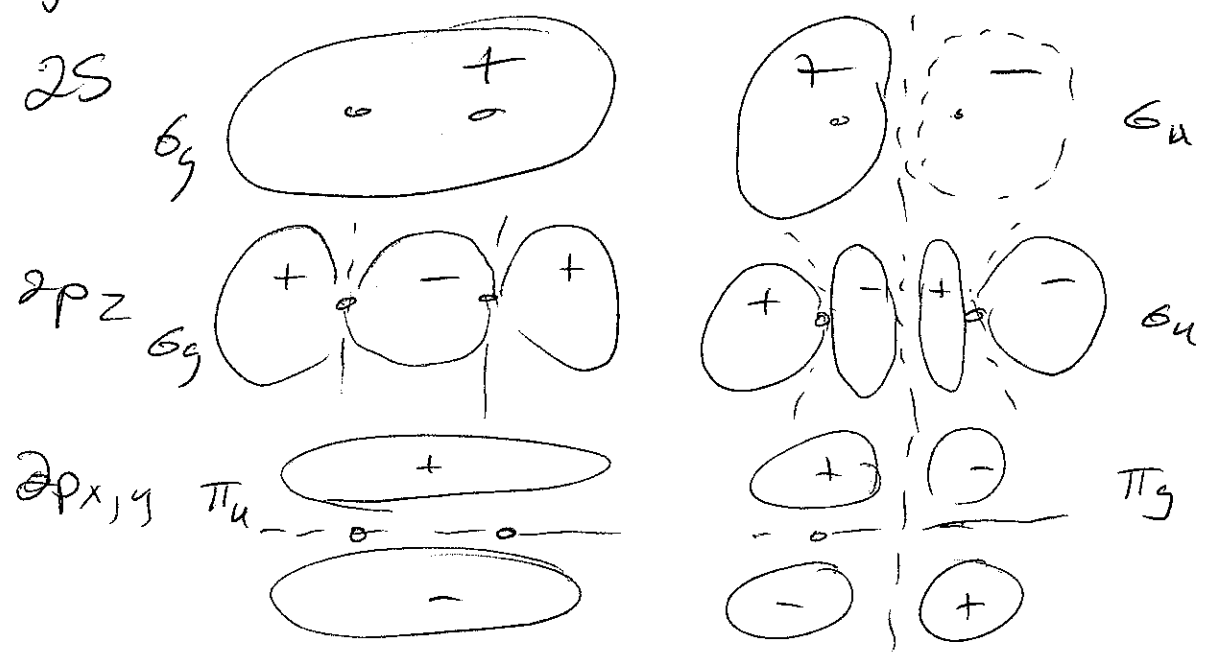
and note any node

In general see that nodal pattern ~ Energy
 Solutions to H_2^+ form a basis for
 building up soln to multi elect molec.

Perfect Analogous to Atoms \rightarrow
 Atom H-atom soln basis for multi elect
 Molec H_2^+ ion soln " " "

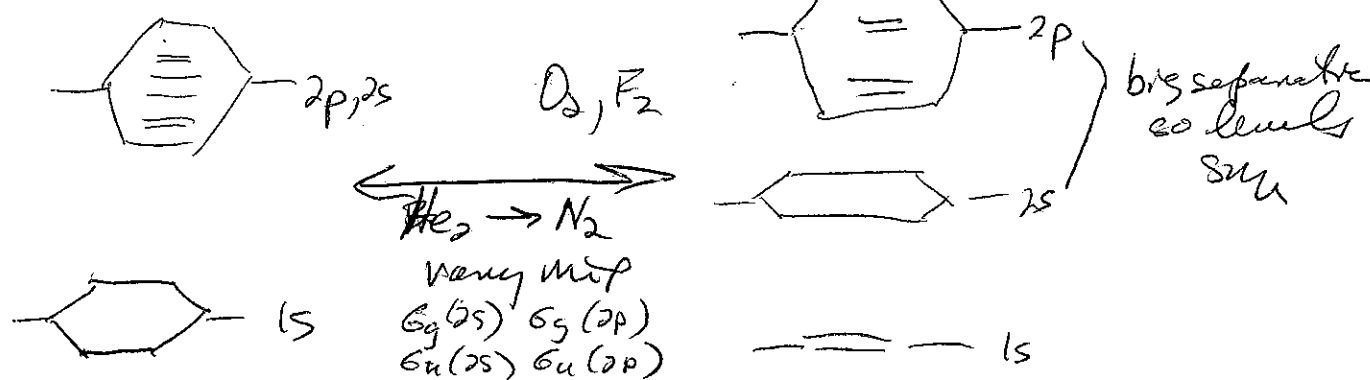
In general could solve exact but easier

Character σ - cylindrical sym
 π - along/below axis
 g - sym, u - asym
 (invert)

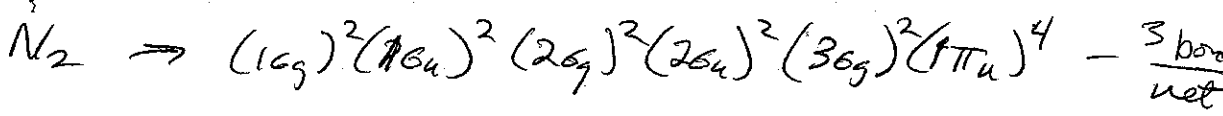
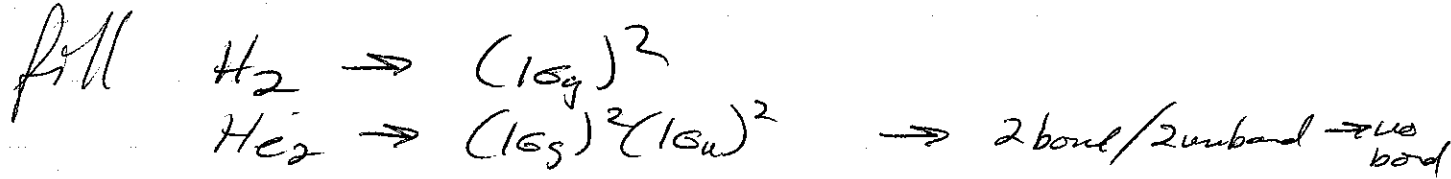


These have relative energies that vary

See Handout
 H_2^+



filling just like atoms again — 2e⁻ per orbital σ, 4e per π (double deg)



See Handout

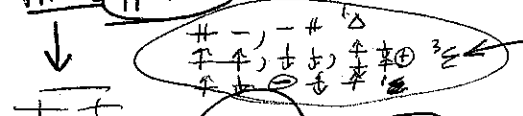
MULTIELECTRON

These can all be characterized by a molecular term symbol

total axial ang mom: Λ = M_L
 M_L = 0 → Λ = Σ[±]
 ± sym/asym
 M_L = ±1 → Π
 = ±2 → Δ
 = ±3 → Φ
 2S + 1 = 2

filled: 1 Σ_g⁺ ← M_L = 0 = Σ_{me}
 un filled: 1e → σ_{g,u} → Σ_{g,u}
 2e → σ_{g,u} → Σ

Sturwe pp 133



anti sym
 $\sigma_u (\pi_x(1)\pi_x(2) - \pi_x(2)\pi_x(1))_{ad} \rightarrow (-)$
 9 · 9 = 9
 9 · 4 = 4

Thick — Π → Π² = 1 Σ_g⁺ + 3 Σ_g⁻
 Hund's rule: max spin lowest

parity w/ spin

lent

N₂ Π⁴ → filled → 1 Σ_g⁺

Δ_g
 3 Σ_g⁻
 odd, ββ, αβ + βα
 ± sym spin w/ anti sym orbit → tot anti sym

How work: orbitals are eigen set L_z

i.e. diatomic, [H, L_z] = 0

σ → m_l = 0 Σ ⇒ Λ = 0

π → m_l = ±1 Π ⇒ Λ = ±1

L_z (Λ m_l) = Λ ħ () Δ ⇒ Λ = ±2

Λ total ang. mom.

HF-SCF

→ extension: S_z = ±S, J_z = Λ + S ⇒ Ω = Λ + S, ..., |Λ - S|

Spin-Orbit coupling $-[H, J_z] = 0$ also works
 so have: $\Omega = \Lambda + S, \Lambda + S - 1, \dots, |\Lambda - S|$

$$J_z |\Omega\rangle = \pm \Omega \hbar |\Omega\rangle$$

- $^1\Sigma_{\pm}$ \rightarrow $^1\Sigma_0$
- $^3\Sigma_{\pm}$ \rightarrow $^3\Sigma_{\pm}$ (don't write if only one value)
- $^1\Pi$ \rightarrow $^1\Pi$
- $^3\Pi$ \rightarrow $^3\Pi_2, ^3\Pi_1, ^3\Pi_0$ etc
- $^3\Delta$ \rightarrow $^3\Delta_3, ^3\Delta_2, ^3\Delta_1$

Ordering \rightarrow Hund's rule still steps that
for given configuration -
 max spin should be lowest
 eg $O_2 \rightarrow \uparrow \uparrow (\pi_g)^2 \rightarrow ^1\Sigma^+ \ ^3\Sigma^- \ ^1\Delta$
 lowest \rightarrow $^3\Sigma^-$
 next up \rightarrow $^1\Delta$

Nomenclature \rightarrow normally let $X^{2S+1}\Lambda$
 represent ground state
 \rightarrow letters A, B, C ...
 represent states of same X as ground
 i.e. letters a, b, c ... other mult
 Many variations in literature

$^1\Pi_1$ & $^3\Sigma^-$ same
 + diatomic
 (Handout) N_2 just opposite
 Many variations in literature

Secular Equations - Chem. 347

Let MO: $\Psi_i = \sum_j a_{ij} \phi_j$

where ϕ_j - atomic orbitals

Ψ_i - delocalized 1-electron orbital

Energy of MO: $\langle \mathcal{H} \rangle = E_i = \langle \Psi_i | \mathcal{H} | \Psi_i \rangle / \langle \Psi_i | \Psi_i \rangle$

$$\sum_{j,k} \langle a_{ij} \phi_j | \mathcal{H} | a_{ik} \phi_k \rangle = E_i \sum_{j,k} \langle a_{ij} \phi_j | a_{ik} \phi_k \rangle$$

$$\sum_{j,k} a_{ij}^* a_{ik} \langle \phi_j | \mathcal{H} | \phi_k \rangle = E_i \sum_{j,k} a_{ij}^* a_{ik} \langle \phi_j | \phi_k \rangle$$

\mathcal{H}_{jk}
|||
S_{jk}

Goal to minimize energy by varying a_{ij} & a_{ik} , rearrange above equation and take $\frac{\partial E}{\partial a_{il}}$:

$$0 = \sum_j a_{ij}^* \mathcal{H}_{jl} + \sum_k a_{ik} \mathcal{H}_{lk} - E_i \left(\sum_j a_{ij}^* S_{jl} + \sum_k a_{ik} S_{lk} \right) + \frac{\partial E}{\partial a_{il}} \sum_{k,j} a_{ij}^* a_{ik} S_{jk}$$

note: - at minimum $\frac{\partial E}{\partial a_{il}} = 0$

- terms in \mathcal{H} + terms in S are identical

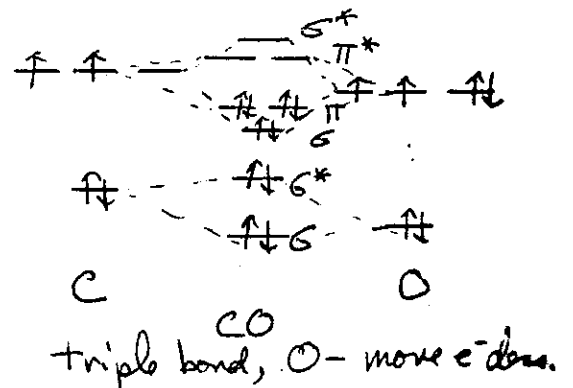
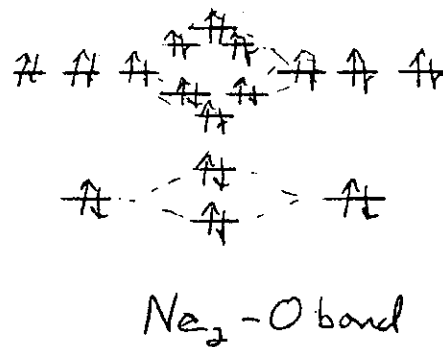
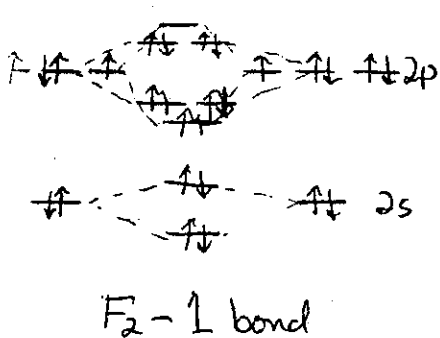
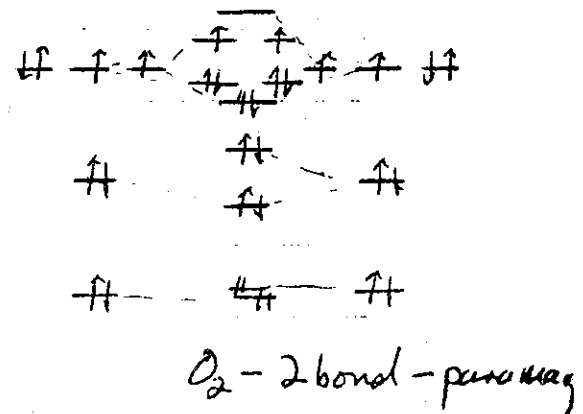
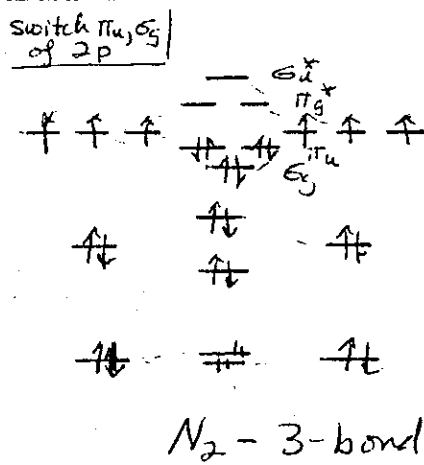
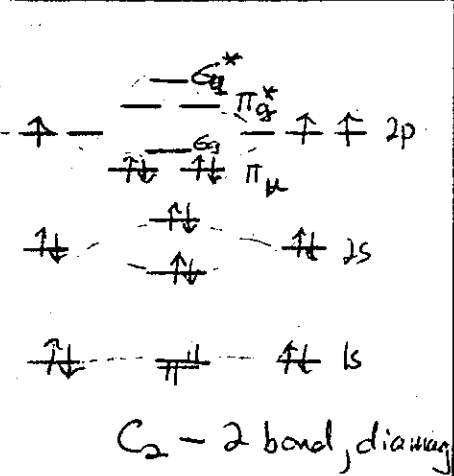
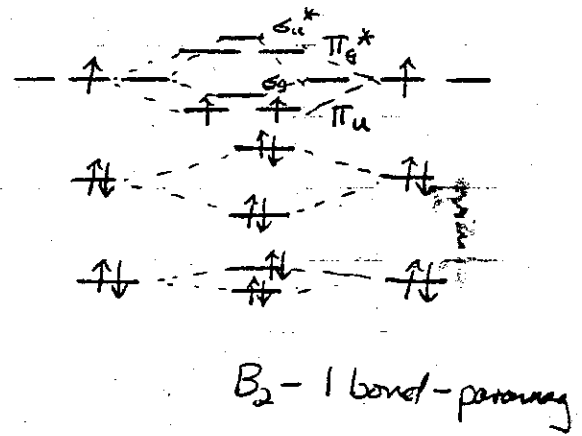
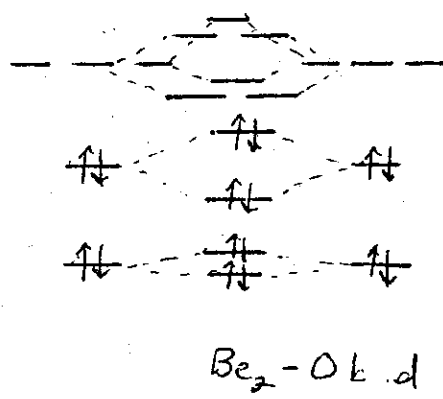
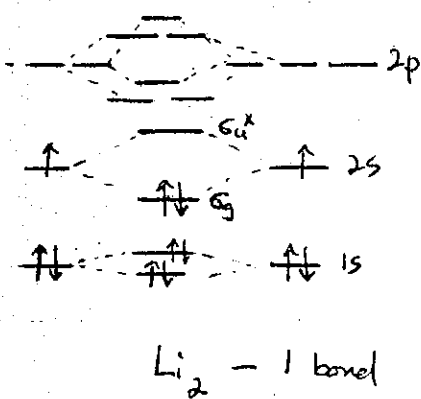
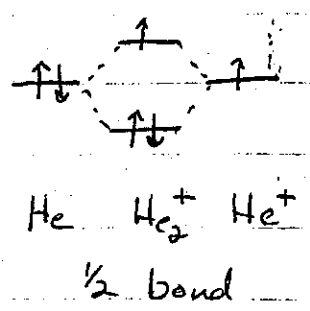
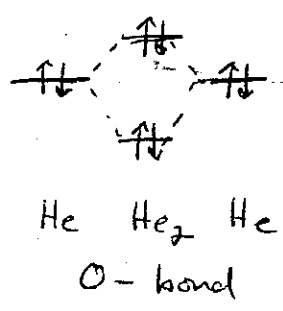
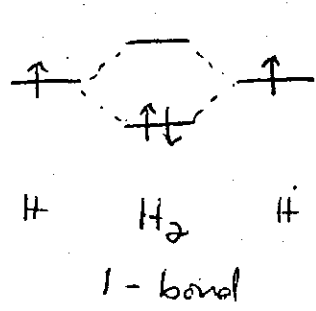
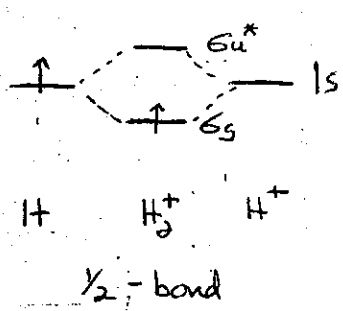
$$\therefore 0 = \sum_j a_{ij} (\mathcal{H}_{jl} - E_i S_{jl}) - \text{secular eqn.}$$

a_{ij} 's and E_i 's unknown - solve secular det:

$$\begin{vmatrix} (\mathcal{H}_{11} - E S_{11}) & (\mathcal{H}_{12} - E S_{12}) & \dots \\ (\mathcal{H}_{21} - E S_{21}) & \dots & \dots \\ \vdots & & (\mathcal{H}_{nn} - E S_{nn}) \end{vmatrix} = 0$$

shorthand:
 $|\mathcal{H}_{ij} - E S_{ij}| = 0$

MO diagrams (LCAO approach)



Home nuclear Diatomics

Molecule	De (eV)	Re (Å)	"bond order"	Configuration (lowest energy)	Ground Term	Comment
H ₂ ⁺	2.78	1.06	1/2	(σ _g ^{1s}) ¹	2Σ _g ⁺	
H ₂	4.76	0.74	1	(σ _g ^{1s}) ²	1Σ _g ⁺	ground state
He ₂	—	—	0	(σ _g ^{1s}) ² (σ _u ^{1s}) ²	1Σ _g	unbound
Li ₂	1.1	2.67	1	(σ _g ^{1s}) ² (σ _u ^{1s}) ² (σ _g ^{2s}) ²	1Σ _g	weak ground state
Be ₂	—	—	0	[KK](σ _g ^{2s}) ² (σ _g ^{2s}) ²	1Σ _g	unbound
B ₂	2.9	1.6	1	KK(σ _g ^{2s}) ² (σ _u ^{2s}) ² (π _u) ² (KK(σ _g ^{2s}) ² (σ _u ^{2s}) ² (π _u) ² (σ _g ^{2p}) ¹)	3Σ _g	2 possible configs. paramagnetic ground state
C ₂	6.4	1.24	2	KK(σ _g ^{2s}) ² (σ _u ^{2s}) ² (π _u) ⁴	1Σ _g	
N ₂	10.1	1.12	3	KKσ _g ² σ _u ² π _u ⁴ (σ _g ^{2p}) ²	1Σ _g	strongest bond
O ₂	5.2	1.21	2	KKσ _g ² σ _u ² π _u ⁴ σ _g ² (π _g [*]) ²	3Σ _g	paramagnetic relative stability of σ _g ^{2p} + π _u ^{2p} cfg.
F ₂	1.6	1.42	1	KKσ _g ² σ _u ² σ _g ² π _u ⁴ (π _g [*]) ⁴ (σ _u [*]) ⁰	1Σ _g	
Ne ₂	—	—	0	KKσ _g ² σ _u ² σ _g ² π _u ⁴ π _g ⁴ σ _u ²	1Σ _g	unbound

- Note:
- "bond order" reflected in D_e, R_e trends
 - He₂, Be₂, Ne₂ all possible as excited states (bound) — eg. He₂^{*} — (σ_g)²(σ_u^{*})¹(σ_g^{2s})¹ — 1/2
 - More than half-filled less well bound yet shorter bond than less than half-filled for some bond order
 - Open shells have more than one possible terms (π_u²) → ¹Δ_g, ³Σ_g, ¹Σ_g

T
o
i
a
l

$1\pi^*$

1π

3σ

$2\sigma^*$

2σ

$1\sigma^*$

1σ

$2s$

F_2

O_2

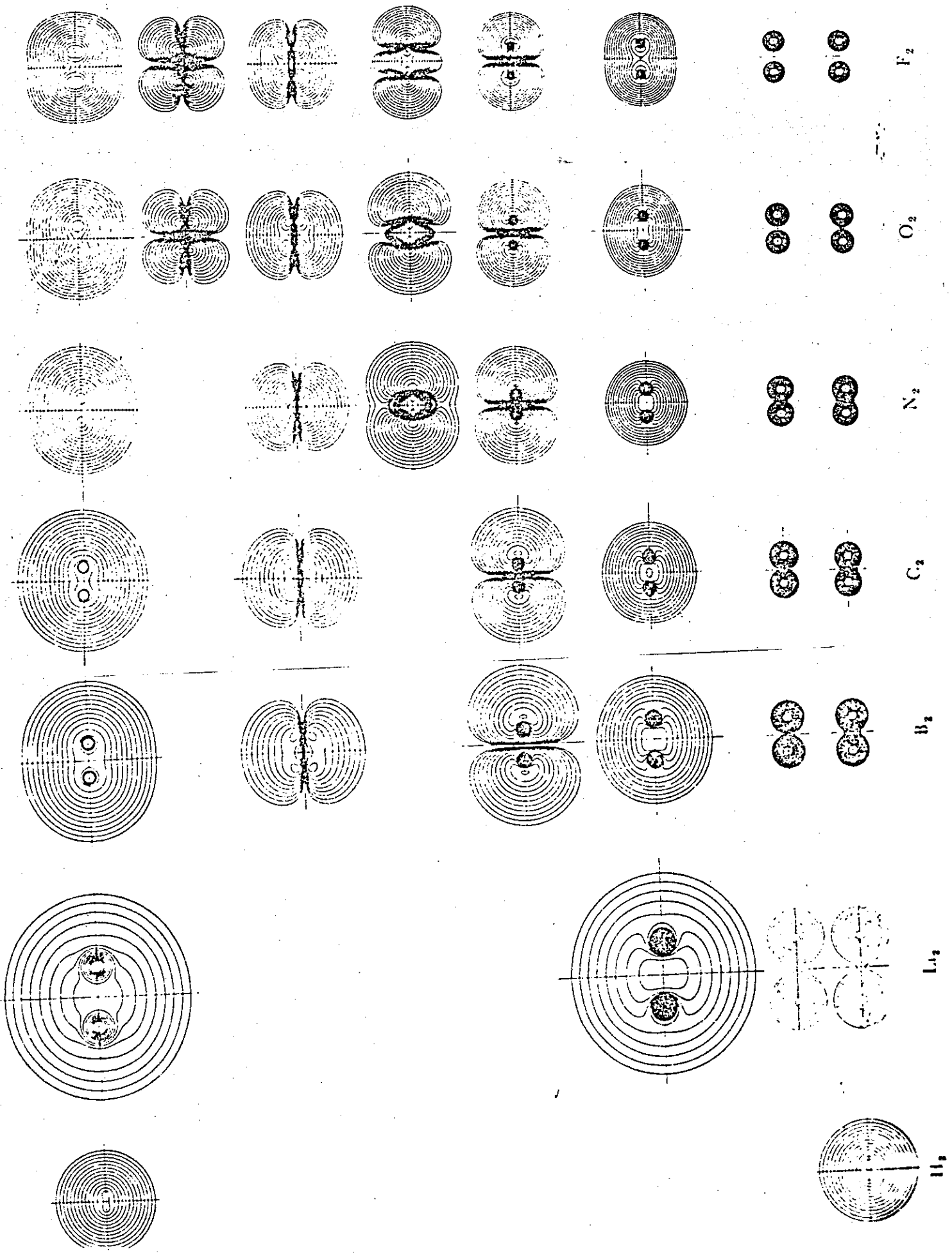
N_2

C_2

B_2

L_2

H_2



H₂ excited states

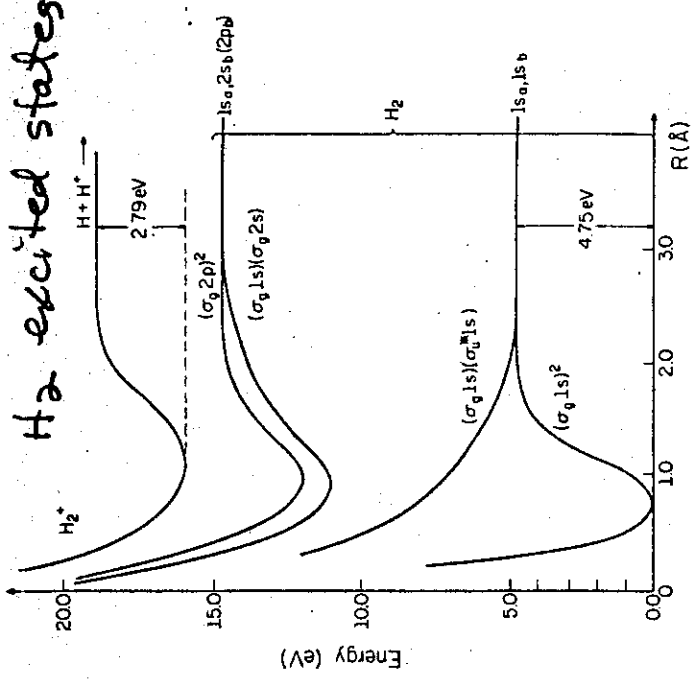
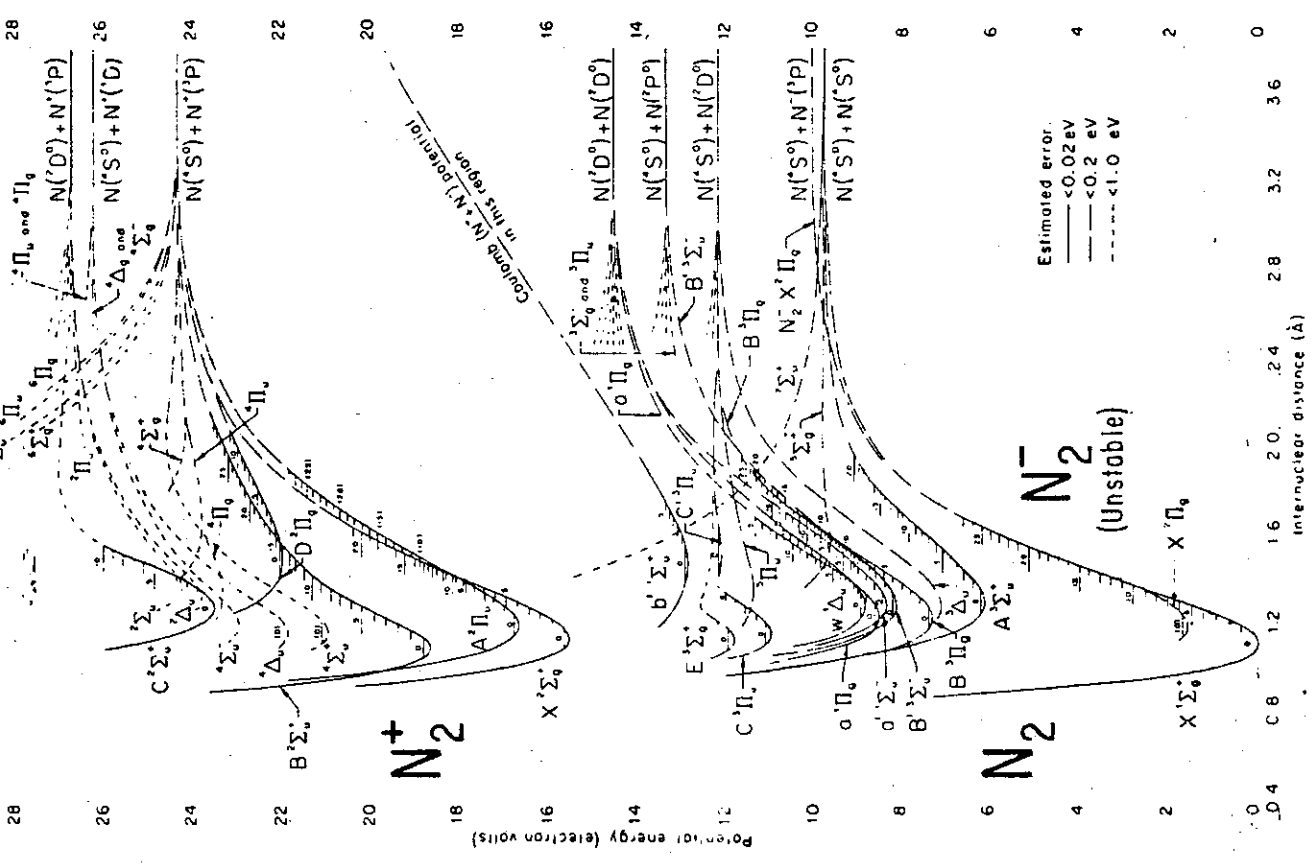


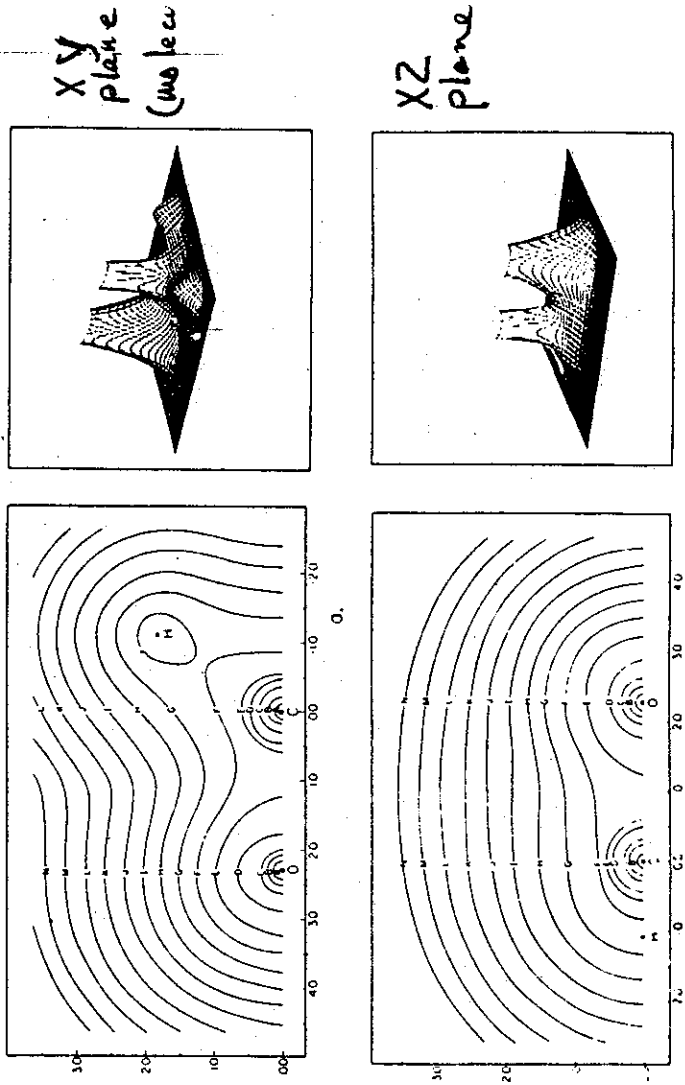
Figure 6-2 Energy level diagram showing some of the electronic states in H₂ and the lowest state of H₂ obtained by ionizing H₂. Only the singlet state manifold is shown.

N₂ excited states



Potential energy curve for N₂ (unstable) N₂ and N₂⁺

Figure 6-3 Potential energy level diagram for the N₂ + e⁻ system from I. R. Slonimski and J. J. Thomson, *Radiat. Environ. 8* (1968)



Formaldehyde e⁻ density

2/12/92

IV-6

Hartree Fock - LCAO/MO approach

$$H_{el} = \sum_{i=1}^n \left[\frac{-\hbar^2}{2m} \nabla_i^2 - \sum_{\alpha=1}^N \frac{Z_{\alpha} e^2}{|r_i - R_{\alpha}|} \right] + \sum_{i < j}^n \frac{e^2}{|r_i - r_j|}$$

$$= \sum_{i=1}^n H_i(r_i) + \sum_{i < j}^n \frac{e^2}{r_{ij}}$$

\uparrow one electron \rightarrow orbital ϵ_i ~~state~~
 \uparrow elect repulsion $\rightarrow J, K$

Basis - diatomics could use $F(r, \theta) e^{i\phi}$ but impractical since calc so large, geom vary

$$|\phi_i\rangle = \sum c_{ji} |\chi_j\rangle \quad \text{expand in AO's}$$

$|\chi_j\rangle$ - atomic orbitals

- STO - Slater Type Orb $\rightarrow e^{-Z_{eff} r}$
 can be used - pick Z_{eff} , opt c_{ji}
 but integrals messy

- Gaussians more typical - rep each AO by linear comb Gaussians

$$|G_{new}(i)\rangle = N r_i^n \exp(-\sigma r_i^2) Y_{lm}(\theta, \phi)$$

$\langle ij|ic\rangle + \langle ij|is\rangle$ more easily computed even though need to do more of them (analyt)

Still have correlation error (contrast to HF \rightarrow avg potent)

Read Levin 13.9 - 13.12 compare MO & VB

Levine 13.16 - Hartree Fock Roothaan

Hartree Fock energy - expectation value

$$E_{HF} = \langle \Phi | H_{el} + V_N | \Phi \rangle$$

$V_N \sim$ const - at some fix nucl posn

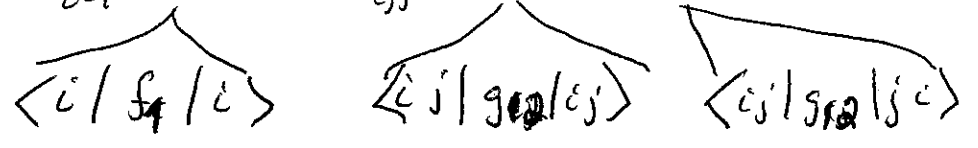
$H_{el} \sim \sum_{i=1}^N f_i + \sum_{i,j} g_{ij}$ one elect + 2 elect

$f_i = \frac{\hbar^2 \nabla_i^2}{2m} - \sum_a \frac{Z_a e^2}{r_{ia}}$ KE + atra all nuclei

$g_{ij} = \frac{e^2}{r_{ij}}$ electron repulsion terms

just like in atoms - sum over orbitals (2e/orbital)

$$E_{HF} = 2 \sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i,j} (2J_{ij} - K_{ij}) + V_N$$



To determine $|i\rangle$ & E_i solve

$$F(1) |i\rangle = E_i |i\rangle$$

$F \rightarrow$ Fock operator

$$F(1) = H_1^{core} + \sum_{j=1}^{N/2} (2J_j(1) - K_j(1))$$

coulomb: $J_j(1) = \int \int |j(2)| \frac{e^2}{r_{12}} |j(2)\rangle$

exch: $K_j(1) = \int \int |j(2)\rangle \frac{e^2}{r_{12}} |j(2)\rangle$

So the $F(1)$ is a one elect operator -

but depends on its eigenfcts $|j\rangle$

so solve iteratively

1-elect soln (mult left by $\langle e |$

$$E_i = \langle i | F | i \rangle = H_{ii}^{core} + \sum_{j=1}^{N/2} (2J_{ij} - K_{ij})$$

by comparison

$$E_{HF} = 2 \sum_{i=1}^{N/2} E_i - \sum_{i,j} (2J_{ij} - K_{ij}) + V_N$$

{ correct for double count 2-elect integrals

This soln assures we find the best $|i\rangle$
 one elect wave-fct commiserate
 with this avg. pot. picture —
 could be very difficult problem

Roothaan suggest expand $|i\rangle$ in basis $|s\rangle$

$$|i\rangle = \sum_{s=1}^b c_{si} |s\rangle$$

S-general but
 in our case usually
 AO's

subst into $F|i\rangle = \epsilon_i |i\rangle$

$$\sum_s c_{si} F|s\rangle = \epsilon_i \sum_s c_{si} |s\rangle$$

mult by $\langle r|$ and integrate:

Roothaan eqn:
$$\sum_{s=1}^b c_{si} (F_{rs} - \epsilon_i S_{rs}) = 0 \quad r = 1, 2, \dots, b$$

$$F_{rs} = \langle r|F|s\rangle, \quad S_{rs} = \langle r|s\rangle$$

Solve by: $\det(F_{rs} - \epsilon_i S_{rs}) = 0$

Again — must be iterative $\rightarrow F$ dep on j dep on c_{sj}

Procedure \rightarrow guess initial wavefunction
 — compute F + matrix el F_{rs}
 — compute $\epsilon_i |i\rangle$ by solving det \rightarrow SCF

Bases: Minimal — one fct each inner + valence shell AO
 Extended — none / typically much larger

More labor — polynomials

Electronic Spectra (Strune 4.4)

for excited state

$$E(v', j') = G'(v') + F_{v'}(j') + T_e$$

$$\Delta = T_c + [G'(v') - G''(v'')] + [F_{v'}(j') - F_{v''}(j'')]$$

when $G = \bar{D}_e \left(v + \frac{1}{2} \right) - \bar{D}_e^2 x_e \left(v + \frac{1}{2} \right)^2$
 $F = B_e j(j+1) + \alpha \left(v + \frac{1}{2} \right) j(j+1) + D_e j^2(j+1)^2$

Selection Rules

BO states: $|\psi'\rangle = |\phi_e'\rangle |v' j' m'\rangle$
 $|\psi''\rangle = |\phi_e''\rangle |v'' j'' m''\rangle$

Transition operator - cover both elect & Nucl coord

$$\mu = \mu_{el} + \mu_N = -\sum e \vec{r} + \sum Z e R_N$$

$$\langle \psi' | \mu | \psi'' \rangle = \langle \phi_e' | \phi_e'' \rangle \langle v' j' m' | \mu_N | v'' j'' m'' \rangle + \langle v' j' m' | \langle \phi_e' | \mu_{el} | \phi_e'' \rangle | v'' j'' m'' \rangle$$

1st term \rightarrow vib/rot spectra where $\phi_e' = \phi_e''$
 i.e. stay on one pot surf

2nd term \rightarrow let $M_{el} = \langle \phi_e' | \mu_{el} | \phi_e'' \rangle$ note set nucl coord

\rightarrow recall ϕ_e', ϕ_e'' are eigenfct L_z

(E1) in this sense $\mu_z \sim |0\rangle, \mu_{x,y} \sim |\pm 1\rangle$ any mem

(so) $\Delta L = 0, \pm 1, \Delta S = 0$ (small δ_{so})

also $g \leftrightarrow u, g \leftrightarrow g, u \leftrightarrow u$ $+ \leftrightarrow -$ for $E \leftrightarrow E$

Electronic Spectra of Diatomics $\langle \psi' | \mu | \psi'' \rangle \neq 0 = \langle v' S' M' | \mu_e | v'' S'' M'' \rangle$

$\Delta L = 0, \pm 1$ ~~not~~ $\Delta S = 0$ $\Delta M = 0, \pm 1$ $\Delta \Sigma = 0$
 but this needs to be folded in now with vib / not

expand

$$\mu_e(R) = \overline{\mu_e(R_e)} + \frac{\partial \mu_e}{\partial R} \bigg|_{R_e} (R - R_e) + \dots$$
no vectors

Consider the 1st term

$$\begin{aligned} \langle \psi' | \mu | \psi'' \rangle &= |\overline{\mu_e(R_e)}| \langle v' S' M' | \mu_e | v'' S'' M'' \rangle \\ &= |\overline{\mu_e(R_e)}| \underbrace{\langle v' | v'' \rangle}_{\substack{\text{overlap} \\ \text{integrated} \\ \text{2 vib sets}}} \underbrace{\langle S' M' | S'' M'' \rangle}_{\substack{\Delta S = 0, \pm 1 \\ \Delta M = 0, \pm 1}} \end{aligned}$$

{0 if de not Σ }

Note $\langle v' | v'' \rangle \neq \delta_{v'v''}$ because potential surfaces of ψ' & ψ'' not the same

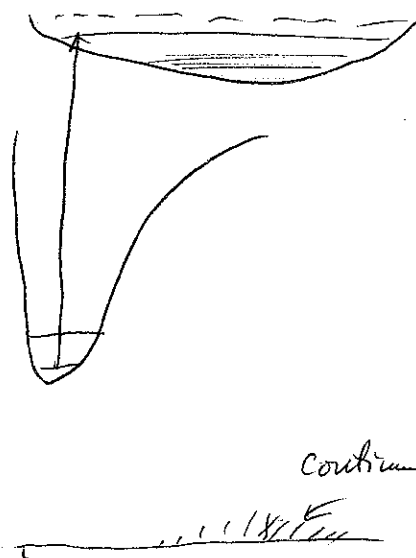
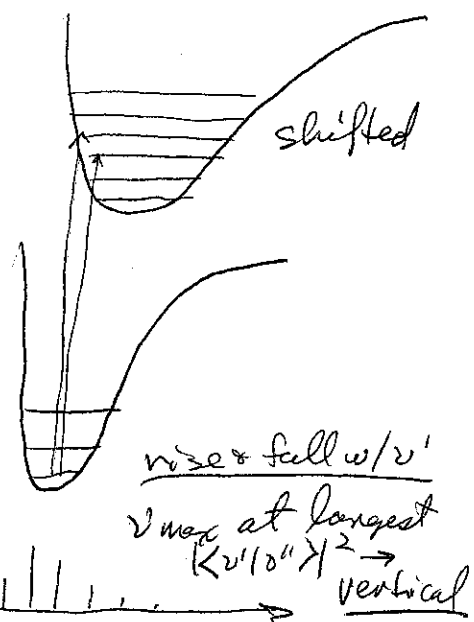
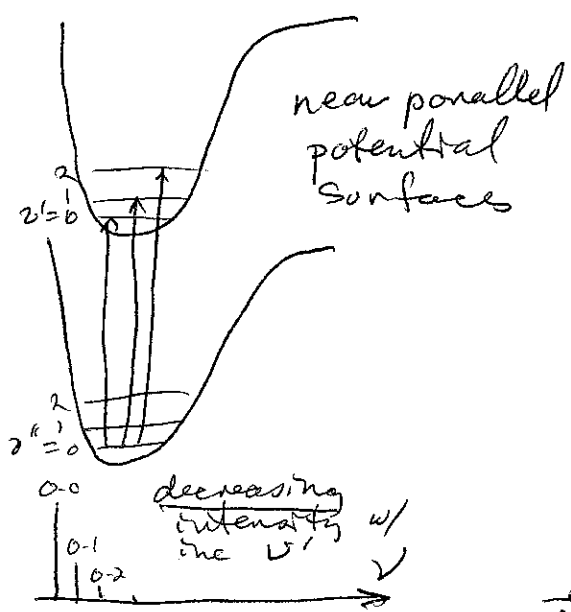
Probability of transition (sum over all S values)

$$P_{\psi' \rightarrow \psi''} \approx \overline{\mu_e(R_e)}^2 |\langle v' | v'' \rangle|^2$$

↑ Franck-Condon factor

Sum rule $\sum_v |\langle v' | v'' \rangle|^2 = 1$

FC_{max} $\rightarrow \langle v' | v'' \rangle$ max occurs for vertical transition - max overlap 2 vib sets



Strove ch 4.5

Above discussion works well for ${}^1\Sigma \rightarrow {}^1\Sigma$ trans if $S \neq 0$ or $\Lambda \neq 0$ then added ang. mom. — only total ang. mom. conserved so can mix w/ rot. ang. mom.

using Strove notation

Hund's case a: small s-o coupling, $\Lambda \neq 0$

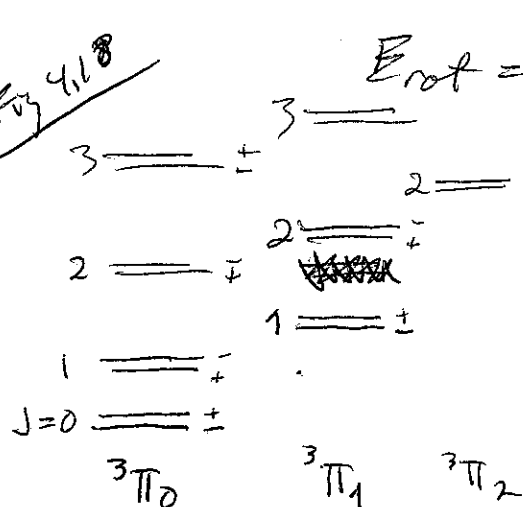
Total angular mom

$$J^2 = J_{\perp}^2 + J_z^2 = (L_{\perp} + S_{\perp})^2 + N^2 + 2N \cdot (L_{\perp} + S_{\perp}) + J_z^2$$

↑ not conserved
excil replica
↑ not Ang mom
↑ rot-elect coupling "vibronic"
↑ diatomic elect ang mom Ω

Backcalc $E_{rot} = \langle N^2 / 2I \rangle = B_0 N(N+1)$

Fig 4.18



$$E_{rot} = B_0 \left[\sqrt{J(J+1)} - \underbrace{\Omega^2}_{\text{expect value}} - \underbrace{\langle (L_{\perp} + S_{\perp})^2 \rangle}_{\text{expect}} - 2 \langle N \cdot (L_{\perp} + S_{\perp}) \rangle \right]$$

restricted $J \geq \Omega$ — total ang mom

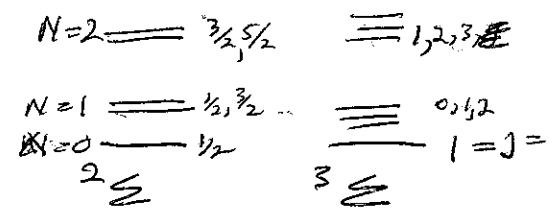
Correction to energy levels for coupling → split each J level into 2 levels Λ -doubling

Hund's case b: S uncoupled from internuclear axis Σ states and $\Lambda \neq 0$ for light atoms ($I_{so} \approx 0$)

$$\left[\begin{aligned} E_{rot} &= B_0 J(J+1) \\ J &= N+S, N+S-1, \dots, |N-S| \end{aligned} \right]$$

Fig 420

This leads to splitting of rotational levels by spin-para (weak) $2S+1$ - levels each $N \neq 0$

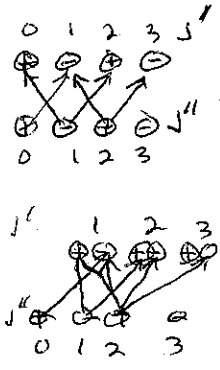


Hund's case c - large $\Omega_{so} \rightarrow L+S = J_{el}$ with fixed Ω

E_{rot} - same as case (a) except diff Ω components of $^{2S+1}\Sigma_{\pm}$ have different pot. surf.

Now this extra character of levels $\pm \Lambda$ doubling leads to an extension of selection rules

for $^1\Sigma^{\pm} \rightarrow \pm (-1)^J$ detm \pm of S level parity
 (-) flip signs
 but $^1\Pi$ has both $\pm 1 = \Omega$ values so each level is \pm except $J=0$ not exist ($J \geq \Omega$)



so $^1\Sigma^+ \rightarrow ^1\Sigma^+ \quad \Delta J = \pm 1$
 $^1\Sigma^+ \rightarrow ^1\Pi \quad \Delta J = 0, \pm 1 \quad J' \neq 0$
 so exhibit Q-branch $\Delta J = 0$ which has levels $v_2 + T_e$ but some displaced ($Be^+ - Be^+$)

§ 4.6

Sturwe pp 146-155 \rightarrow nuclear spin effects \Rightarrow intensity modulation can go on to develop more extensive selection rules to acct for nuclear spin and other aspects of molec wave fun \rightarrow result detail understanding of intensity pattern

detail disc
 No 2 $^1\Sigma \rightarrow ^1\Pi$

Discussed very fast on 2/14/92
 review(?) - 2/17/92

Rotational Splittings

$E_{rot}/hc = B J(J+1) - D J^2(J+1)^2$, note $B = B_0 + a(2J+1)$

for given trans $v'' \rightarrow v'$

$\bar{v}_0 = T_e + (v'' + \frac{1}{2})\nu'' - (v' + \frac{1}{2})\nu'$

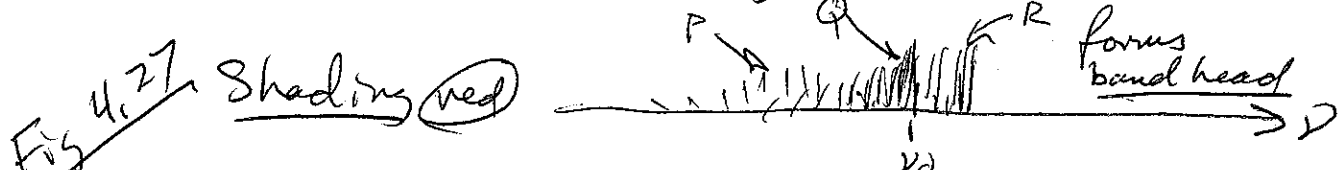
$J \rightarrow \begin{cases} J-1 \\ J \\ J+1 \end{cases}$

$$\begin{aligned} \bar{v}_P &= \bar{v}_0 - (B' + B'')J + (B' - B'')J^2 \\ \bar{v}_Q &= \bar{v}_0 + (B' - B'')J + (B' - B'')J^2 \\ \bar{v}_R &= \bar{v}_0 + 2B' + (3B' - B'')J + (B' - B'')J^2 \end{aligned}$$
 } ignore De eff
 all $a+x$ effect in B' & ν_e respect.

Note - assume - D_0 negligible
 - v + rot corrections in B', B''

Now (if) $B'' = B'$ i.e. I in both states same
 then regular space R+P branch
 separated lines $2B$
 and Q-branch \rightarrow single line

But if $B' < B''$, typical excited state less strongly bound, I are
 spacing of P-branch decreases w/ inc. J
 since both terms negative, J^2 dominates
 spacing of R-branch decrease w/ inc J
 $J^2(B' - B'')$ - neg overcome others at high J



Also can have $B' > B''$ shade to blue, P-band head
 posn $d\bar{v}_P/dJ = 0 = -(B' + B'') + 2(B' - B'')J \rightarrow J_P^* = (B' + B'') / 2(B' - B'')$

CuH

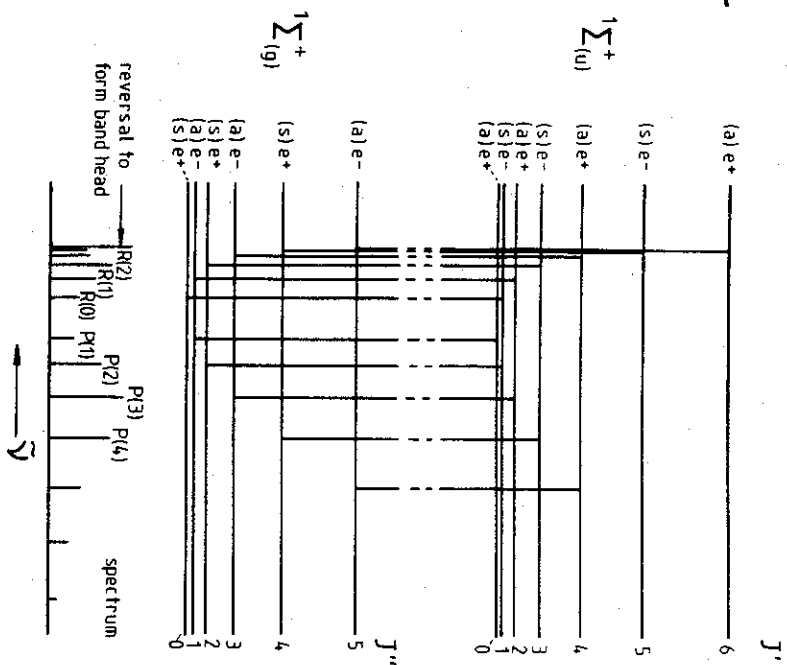
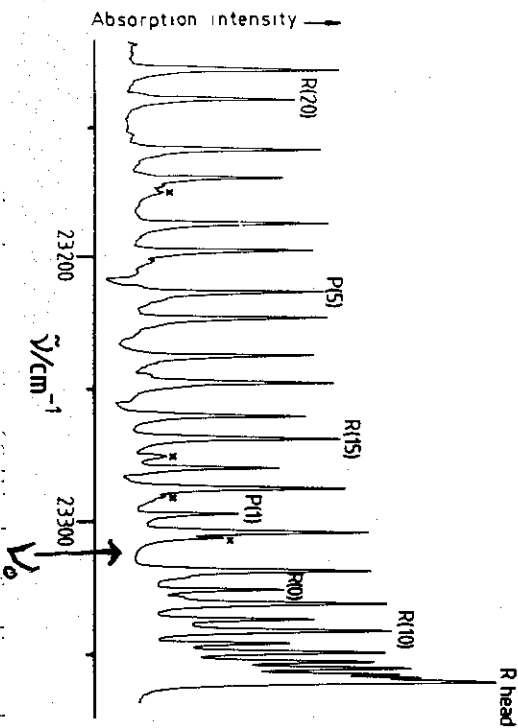


Figure 7.25 Rotational fine structure of a $1\Sigma^+ - 1\Sigma^+$ electronic or vibronic transition in a diatomic molecule for which $r_e' > r_e''$. The g and u subscripts and the s and a labels apply only to a homonuclear molecule; the +, -, e, and f labels can be ignored.



AlH

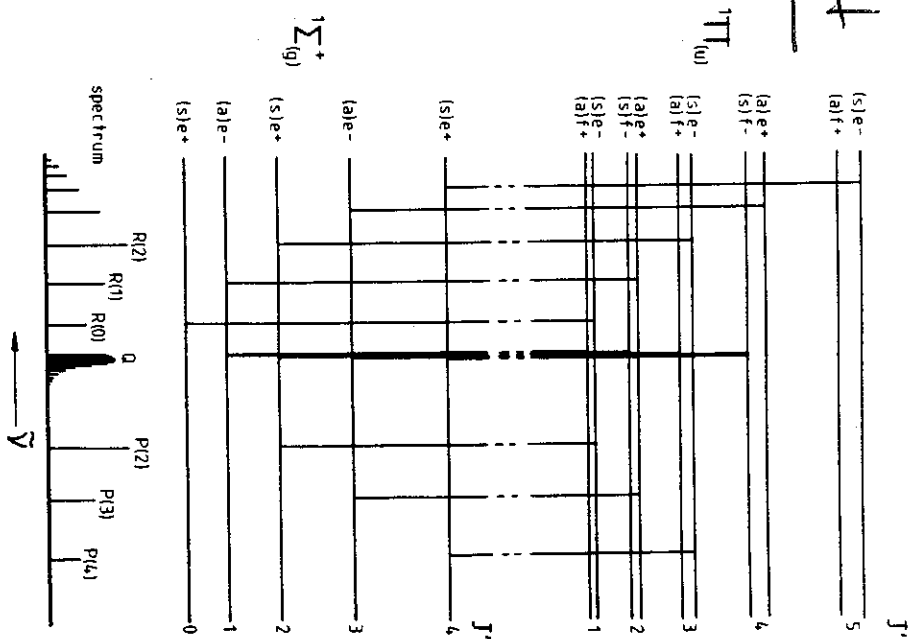


Figure 7.28 Rotational fine structure of a $1\Pi - 1\Sigma^+$ electronic or vibronic transition in a diatomic molecule for which $r_e' > r_e''$. The g and u subscripts and s and a labels apply only to a homonuclear molecule.

branches.

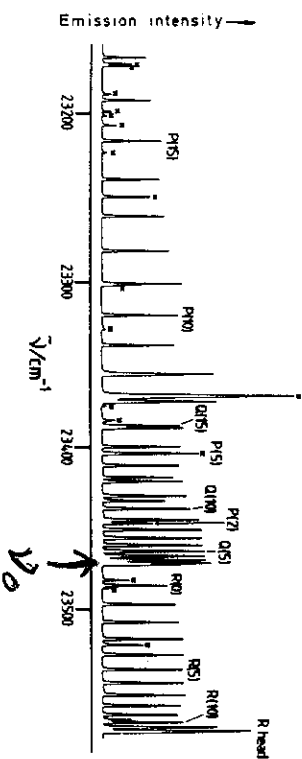


Figure 7.29 The $1\Pi - 1\Sigma^+$ electronic transition of AlH in emission. Lines marked with a cross are not due to AlH.