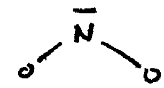
Answers

Selected Problems

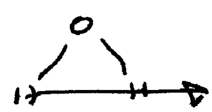
17. ⟨ $|\bar{O}=\bar{N}-\bar{O}|^{\ominus}$, $^{\ominus}|\bar{O}-\bar{N}=\bar{O}|$ ⟩



$|O=N=O|^{\oplus}$ linear

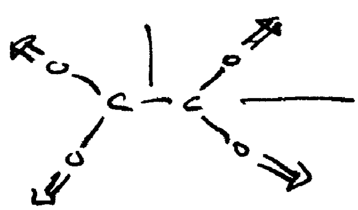
$\dot{N}O_2$ would be in between since we have no other model to estimate its properties.

22.2

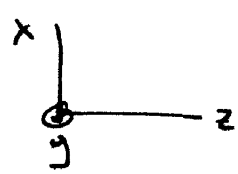


E	C_2	σ_{plane}	$\sigma_{\perp}$
1	−1	1	−1

25.3.



Four vectors representing stretch of each of the four C–O bonds. Four things.

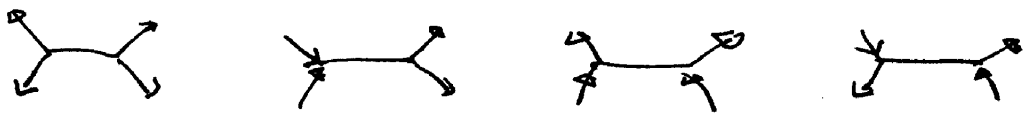


E	C_2^z	C_2^x	C_2^y	i	σ_{xy}	σ_{yz}	σ_{xz}
4	0	0	0	0	0	0	4

This is (from table)

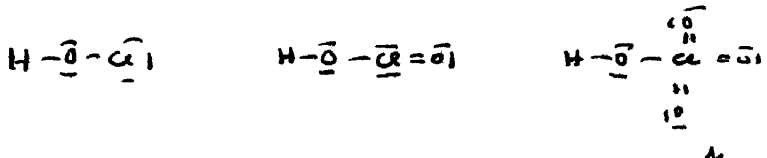
$a_g + b_{2g} + b_{1u} + b_{3u}$

the "pretty" pictures are



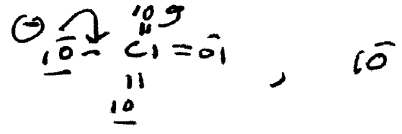
a_{1g} b_{1u} b_{3u} b_{2g}

32.5. Acidity HClO $HClO_2$ $HClO_3$



only O in all cases: this

more resonance in conjugated base than others.

∴ Strongest acid  , etc.

HOCl weakest acid. No resonance in conjugate base.

37.6. Generally must make a gas a product to increase volume a lot. Secondly, most of a gas ↑ at ↑T, so higher T is good, which occurs if reaction liberates heat; $\Delta H^\circ < 0$.

47.

$$MO(s) + M'CO_3(s) = M'O(s) + M(CO_3)(s)$$

M is small M' big

So if rule is correct, this reaction should be energetically downhill to the left.

47. (mmT'J)

~~ΔE = U_MO + ...~~

$$MO(s) = M^{2+}(s) + O^{2-}(s) \qquad U_{MO}$$

$$M'CO_3(s) = M'^{2+}(s) + CO_3^{2-}(g) \qquad U_{M'CO_3}$$

$$M^{2+}(s) + CO_3^{2-}(s) = MCO_3(s) \qquad -U_{MCO_3}$$

$$M'(s) + O^{2-}(s) = M'O(s) \qquad -U_{M'O}$$

$$\Delta E = U_{MO} + U_{M'CO_3} - U_{M'O} - U_{MCO_3}$$

$$= 256\left[\frac{(2)(2)(1-4)}{r_M + r_O} + \frac{(2)(2)(1-21)}{r_{M'} + r_{CO_3}} - \frac{(2)(2)(1-21)}{r_{M'} + r_O} - \frac{(2)(2)(1-21)}{r_M + r_{CO_3}}\right]$$

$$= (256)(8)\left[\frac{1}{r_M + r_O} + \frac{1}{r_{M'} + r_O} + \frac{1}{r_{M'} + r_{CO_3}} - \frac{1}{r_M + r_{CO_3}}\right]$$

$$= 256\,(8)\left[\frac{r_{M'} - r_M}{(r_M + r_O)(r_{M'} + r_O)} + \frac{r_M - r_{M'}}{(r_M + r_{CO_3})(r_{M'} + r_{CO_3})}\right]$$

$$= (256)(8)\,(r_{M'} - r_M)\left[\frac{1}{(O)(O)} - \frac{1}{(\quad)(CO_3)}\right]$$

↑ bigger ↓ demand

hence [ ] is positive

hence ΔE is positive

QED

62.1. $n=3$ $\ell = 2, 1, 0$

$m_\ell = 2, 1, 0, -1, -2$ $m_\ell = 1, 0, -1$ $m_\ell = 0$ 9 orbitals

(or 18 spin orbitals)

62.2. $n=4$, $\ell = 3$ $m_\ell = 3, 2, 1, 0, -1, -2, -3$ 7

62.3. $n=4$, $\ell \neq 4$ None

62.4 $n=4$ $\ell = 2$ 5

62.5 only the one

62.6. 2, one with $m_s = \frac{1}{2}$ & one with $m_s = -\frac{1}{2}$

62.7. only one.

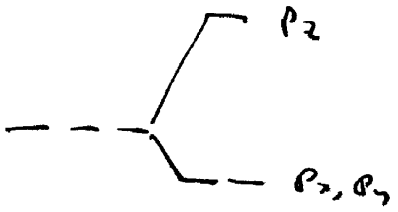
82.2. [Ar core] $3d^3$

87.1

$F-I-F \longrightarrow z$ p_z points at F^-, high E

p_x, p_y are $\perp$ to F^-, low E

& degenerate



98. λ_{max} for $Cr^{III}L_6$ = 550 nm

" " $Cr^{III}L'_6$ = 670 nm low E compared

So L' has smaller splitting energy which is due to

$t_{2g} \rightarrow e_g$ transition.

105.1.

$\uparrow\downarrow$ e_g

$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ t_{2g}

d^8 in octahedral field

2 unpaired

$S = 1$

$\uparrow$ $\uparrow$ e_g

$\uparrow$ $\uparrow$ $\uparrow$ t_{2g}

d^3 in octahedral field

only choice

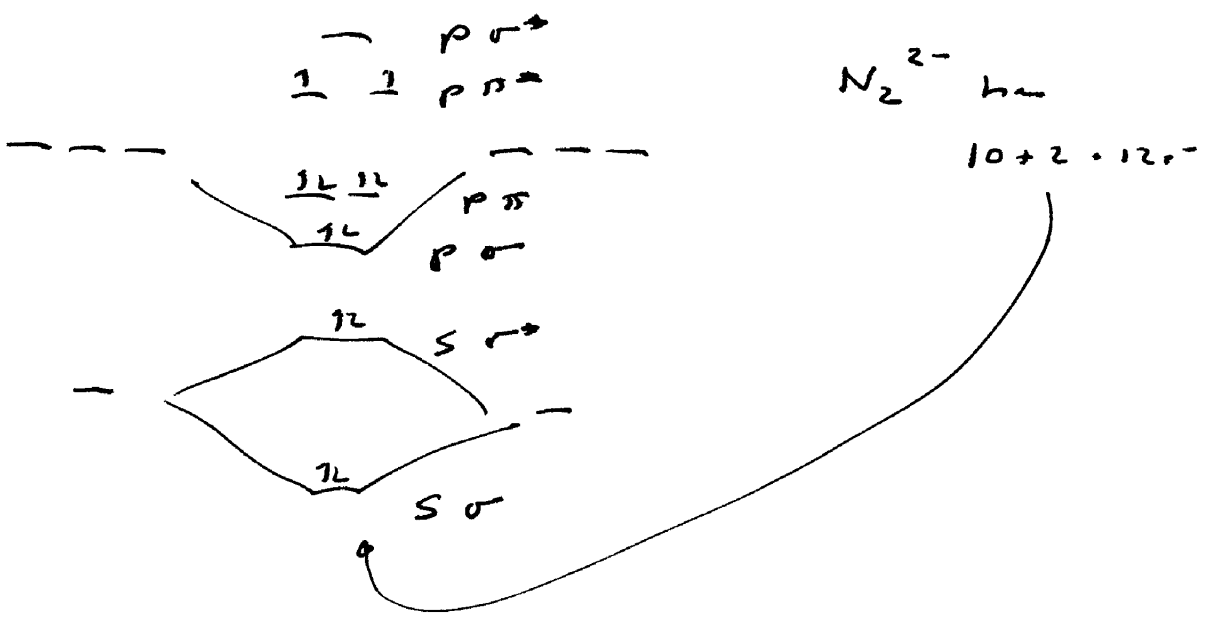
3 unpaired e⁻

$S = 3/2$

$2S+1 = 4$

112.1.

N N



So there is a σ bond, 2pσ & 2 "half" π bonds.

Total of 2 bonds.