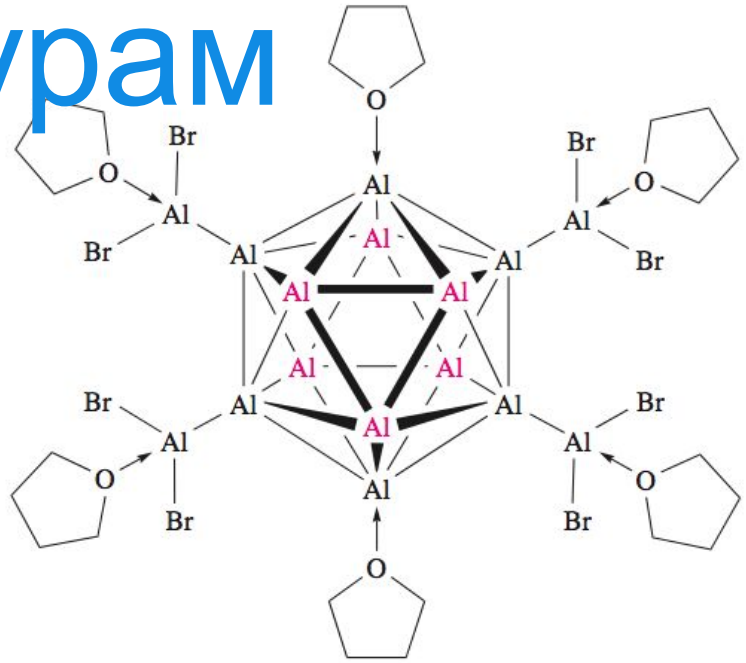
От простых правил к сложным структурам



Лекцию подготовил: Шлапаков Никита,
студент 6 курса Химического факультета МГУ.

Вороново,
2019

Где начинается химия?..

$NaOH$

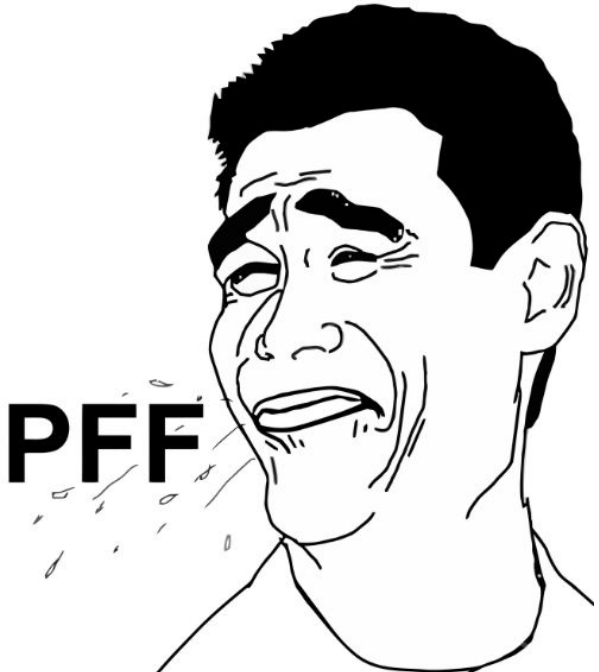
$MgSO_4$

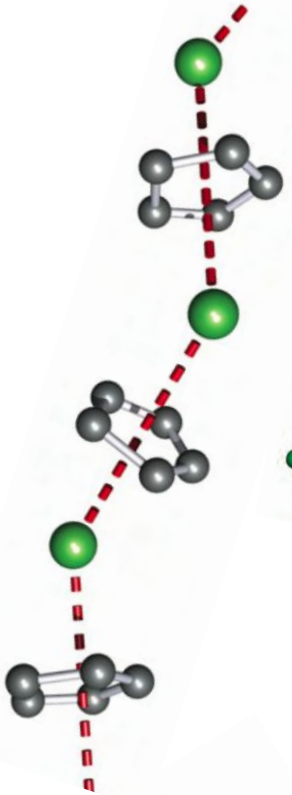
O_2

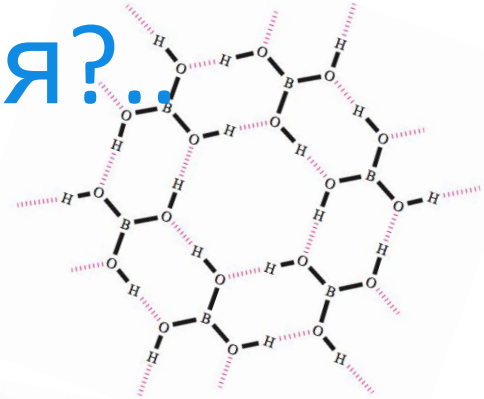
H_2SO_4

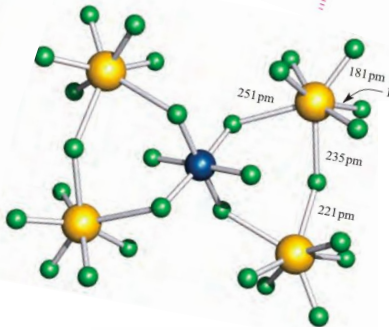
$Al(OH)_3$

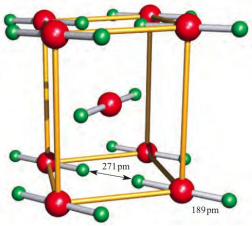
KCl

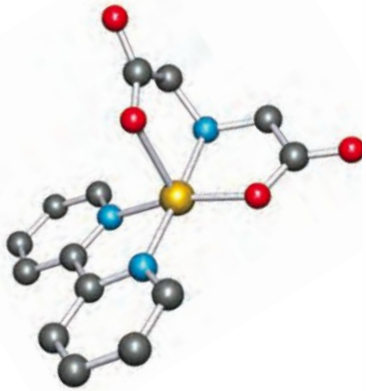






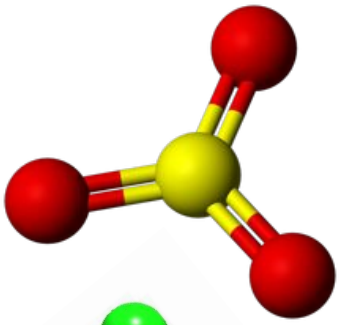


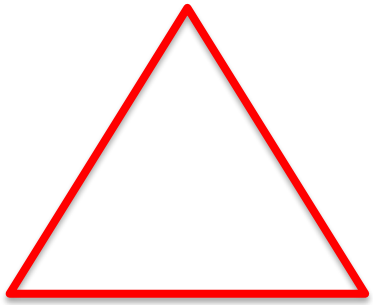


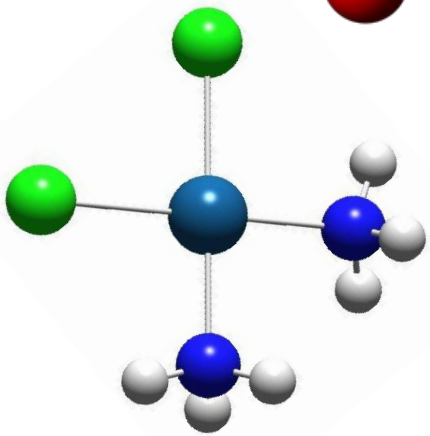


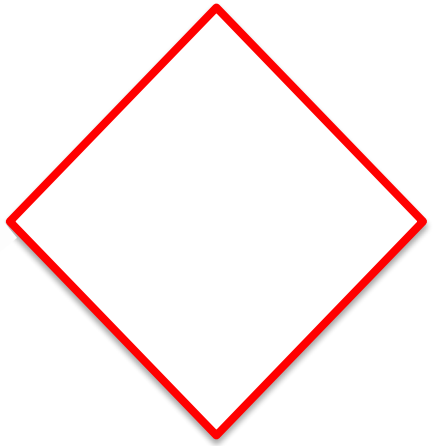
Что нам потребуется?

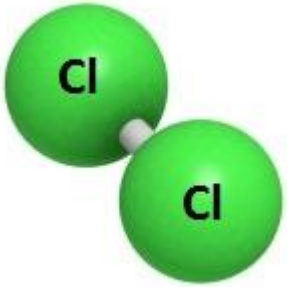
Геометрия в химии

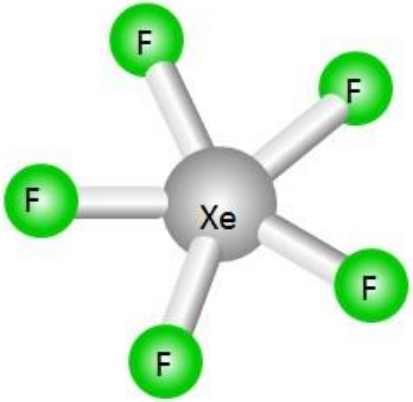


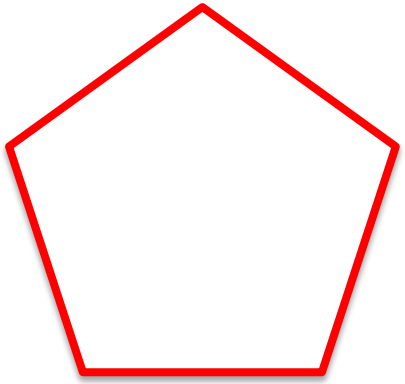




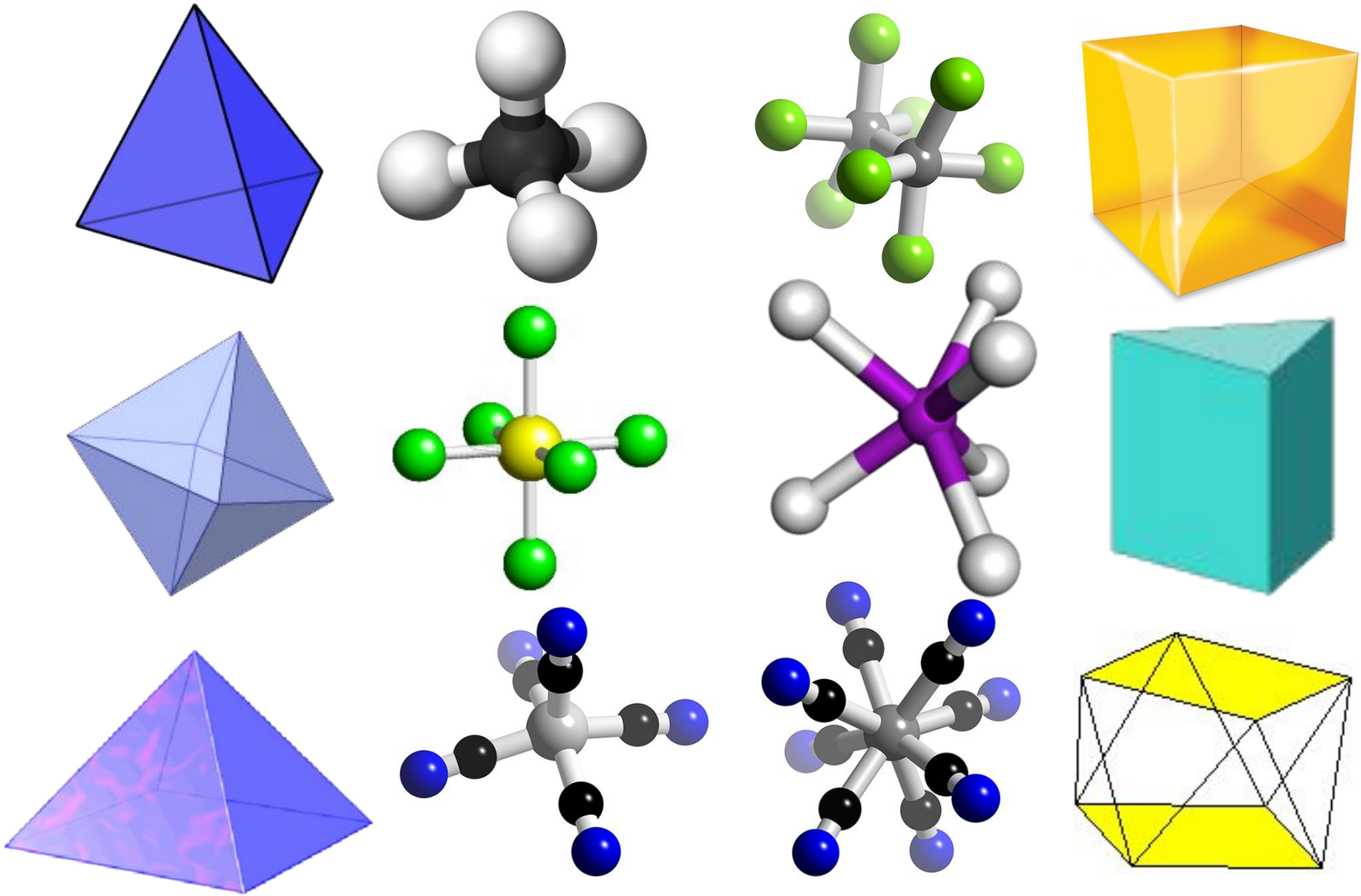




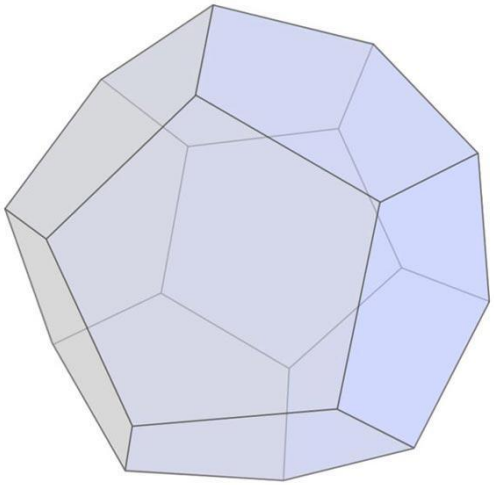


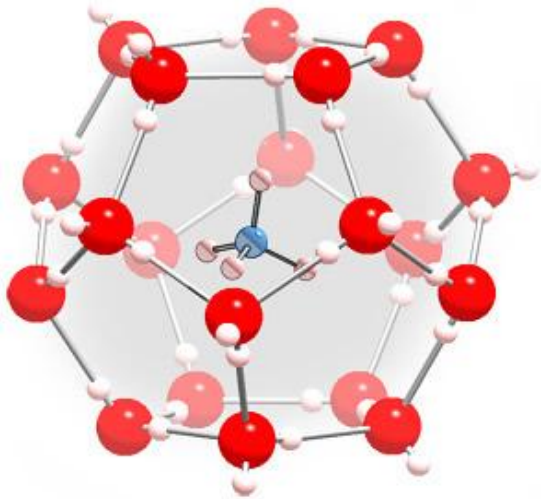


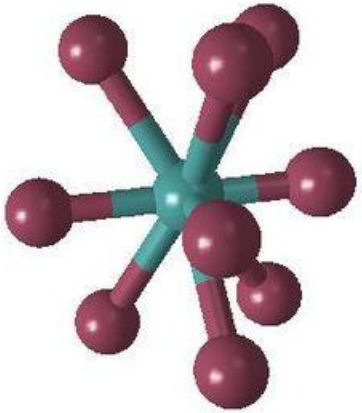
Геометрия в химии

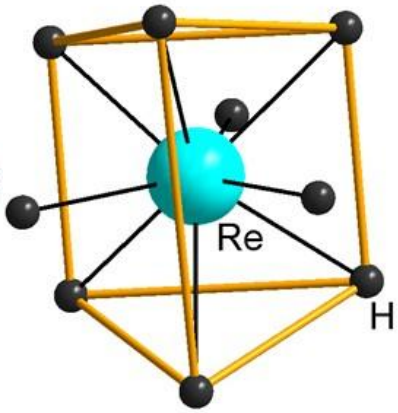


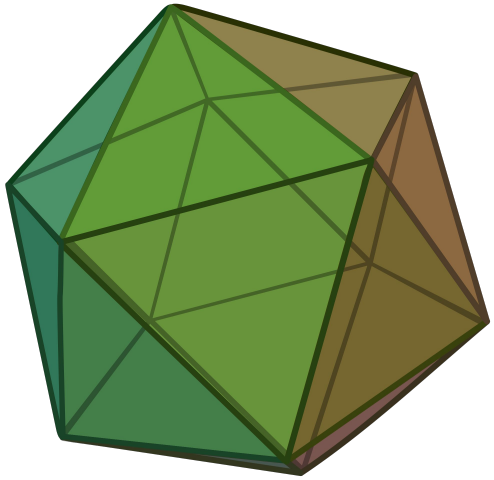
Геометрия в химии

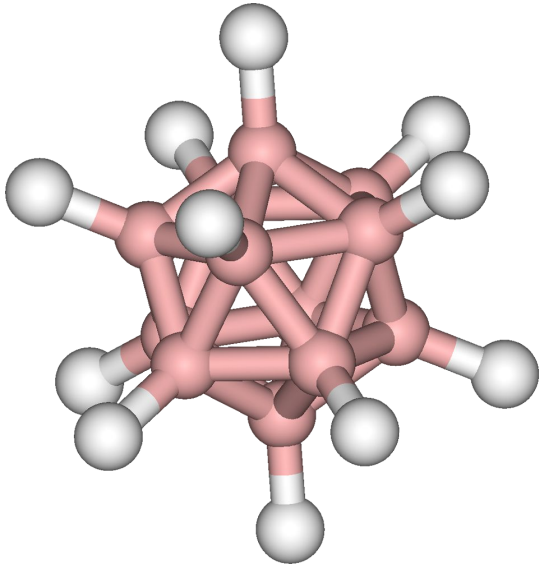


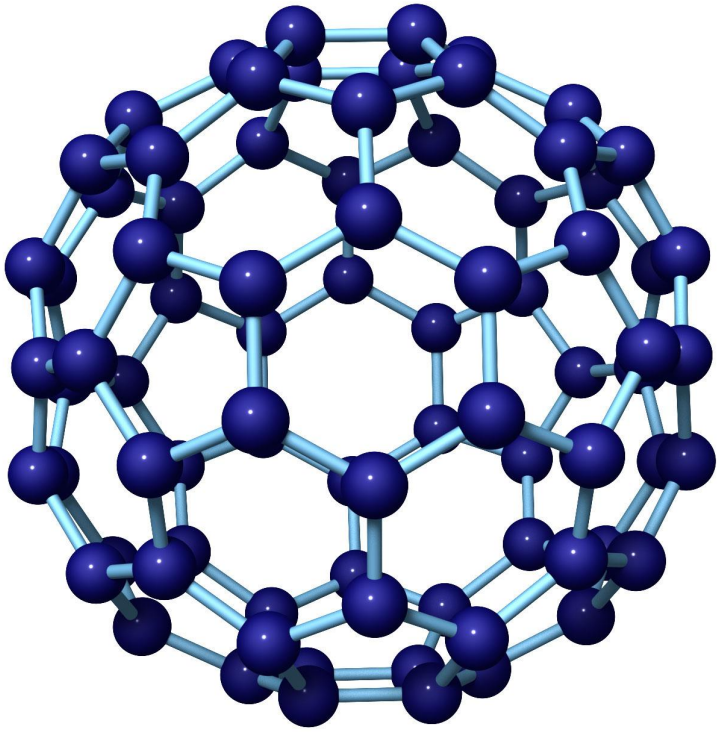












Метод валентных связей

1e 2e 3e 4e 5e 6e 7e 8e

Периоды	Ряды	I а	I б	II а	II б	III а	III б	IV а	IV б	V а	V б	VI а	VI б	VII а	VII б	VIII б			VIII а
1	1	H 1 водород 1,008																	He 2 гелий 4,003
2	2	Li 3 литий 6,941		Be 4 бериллий 9,0122		B 5 бор 10,811		C 6 углерод 12,011		N 7 азот 14,007		O 8 кислород 15,999		F 9 фтор 18,998					Ne 10 неон 20,179
3	3	Na 11 натрий 22,99		Mg 12 магний 24,312		Al 13 алюминий 26,092		Si 14 кремний 28,086		P 15 фосфор 30,974		S 16 сера 32,064		Cl 17 хлор 35,453					Ar 18 аргон 39,948
4	4	K 19 калий 39,102		Ca 20 кальций 40,08		21 Sc скандий 44,956		22 Ti титан 47,956		23 V ванадий 50,941		24 Cr хром 51,996		25 Mn марганец 54,938		26 Fe железо 55,849	27 Co кобальт 58,933	28 Ni никель 58,7	
	5	29 Cu медь 63,546		30 Zn цинк 65,37		Ga 31 галлий 69,72		Ge 32 германий 72,59		As 33 мышьяк 74,922		Se 34 селен 78,96		Br 35 бром 79,904					Kr 36 криптон 83,8
5	6	Rb 37 рубидий 85,468		Sr 38 стронций 87,62		39 Y иттрий 88,906		40 Zr цирконий 91,22		41 Nb ниобий 92,906		42 Mo молибден 95,94		43 Tc технеций [99]		44 Ru рутений 101,07	45 Rh родий 102,905	46 Pd палладий 106,4	
	7	47 Ag серебро 107,868		48 Cd кадмий 112,41		In 49 индий 114,82		Sn 50 олово 118,69		Sb 51 сурьма 121,75		Te 52 теллур 127,6		I 53 иод 126,905					Xe 54 ксенон 131,3
6	8	Cs 55 цезий 132,905		Ba 56 барий 137,34		57–71 лантаноиды		72 Hf гафний 178,49		73 Ta тантал 180,948		74 W вольфрам 183,85		75 Re рений 186,207		76 Os осмий 190,2	77 Ir иридий 192,22	78 Pt платина 195,09	
	9	79 Au золото 196,967		80 Hg ртуть 200,59		Tl 81 таллий 204,37		Pb 82 свинец 207,19		Bi 83 висмут 208,98		Po 84 полоний [210]		At 85 астат [210]					Rn 86 радон [222]
7	10	Fr 87 франций [223]		Ra 88 радий [226]		89–103 актиноиды		104 Rf резерфордий [261]		105 Db дубний [262]		106 Sg сиборгий [263]		107 Bh борий [262]		108 Hn ханий [265]	109 Mt мейтнерий	110	

Лантаноиды

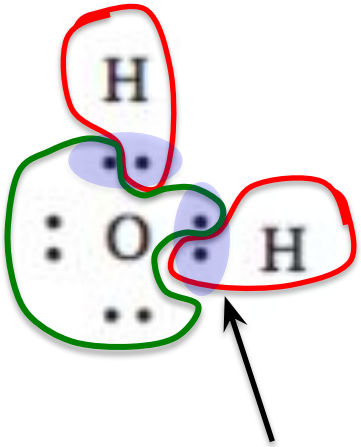
57 La лантан 138,906	58 Ce церий 140,12	59 Pr празеодим 140,908	60 Nd неодим 144,24	61 Pm прометий [145]	62 Sm самарий 150,4	63 Eu европий 151,96	64 Gd гадолиний 157,25	65 Tb тербий 158,926	66 Dy диспрозий 162,5	67 Ho гольмий 164,93	68 Er эрбий 167,26	69 Tm тулий 168,934	70 Yb иттербий 173,04	71 Lu лютеций 174,97

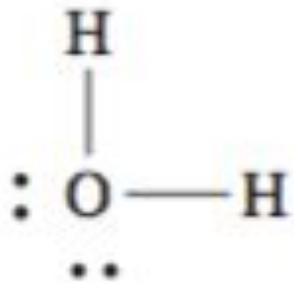
Актиноиды

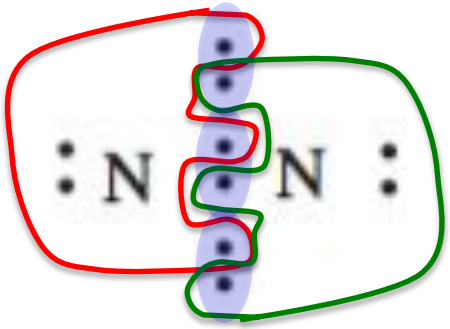
89 Ac актиний [227]	90 Th торий 232,038	91 Pa протактиний [231]	92 U уран 238,29	93 Np нептуний [237]	94 Pu плутоний [244]	95 Am америций [243]	96 Cm кюрий [247]	97 Bk берклий [247]	98 Cf калифорний [251]	99 Es эйнштейний [254]	100 Fm фермий [257]	101 Md менделевий [258]	102 No нобелий [259]	103 Lr лоуренсий

distant-lessons.ru

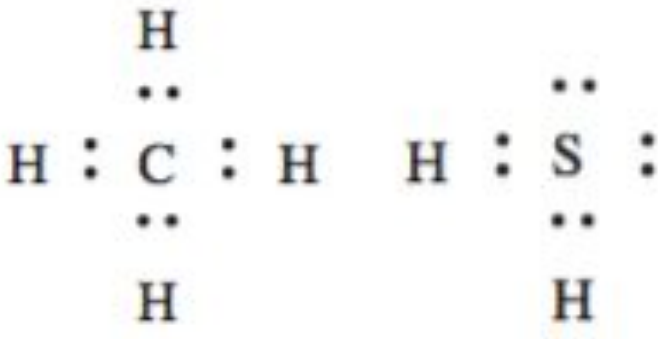
Правило октета. Структуры Льюиса.

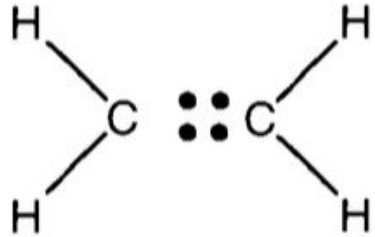


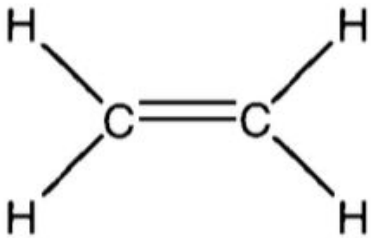


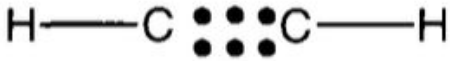


обобществлённые электроны – электроны «общего пользования», принадлежат обоим атомам

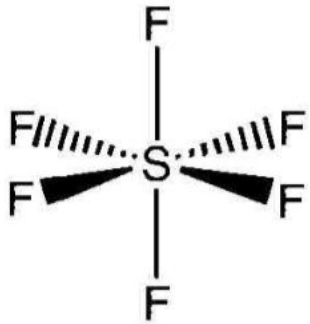


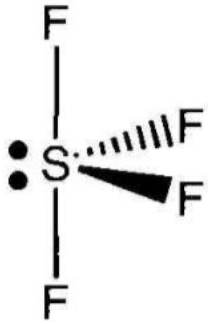


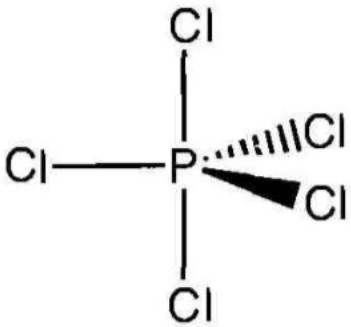


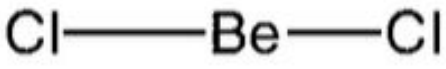


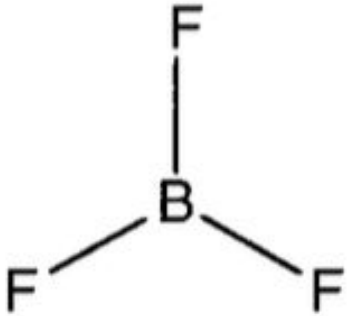
Неудачи «правила» октета

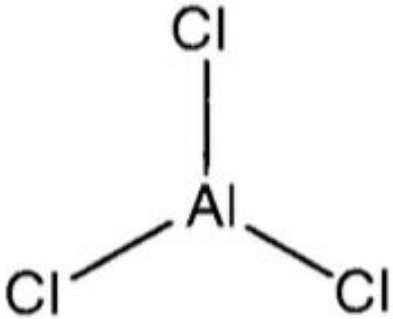


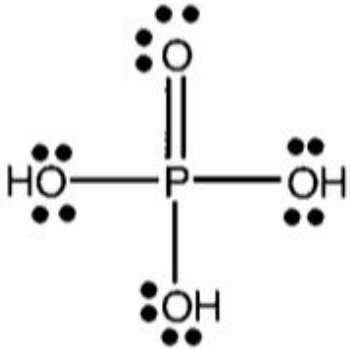


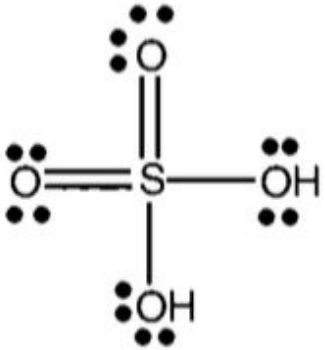


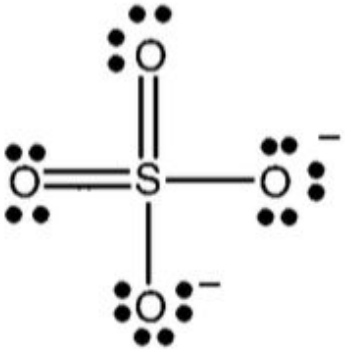


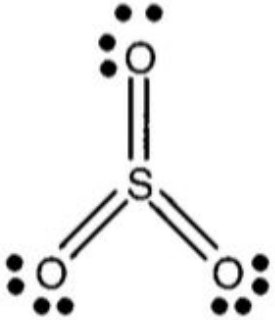






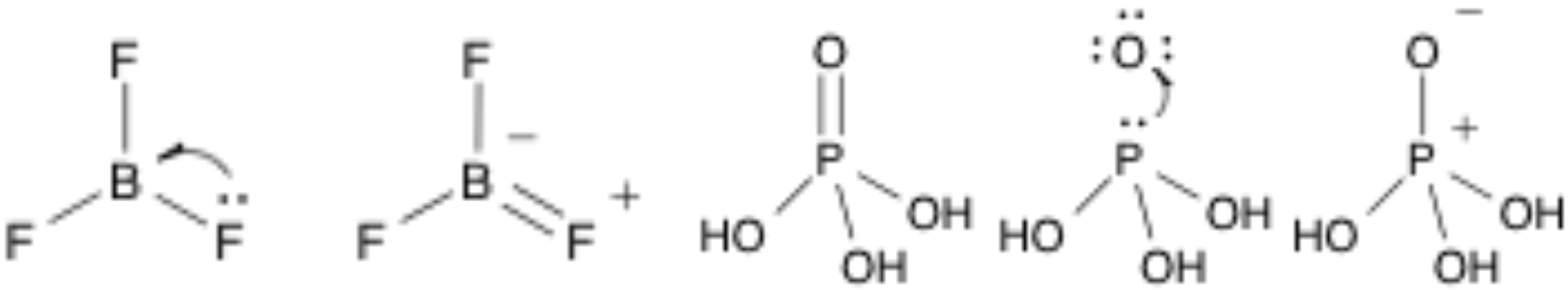




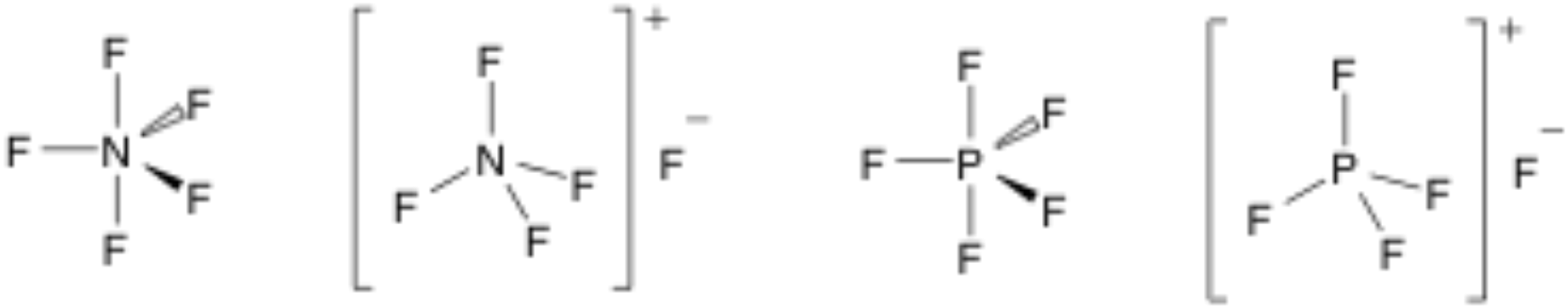


Необходимые меры

1) Донорно-акцепторные связи



2) Подключение свободных d-орбиталей в качестве «хранилища» электронов



Плохо! 10 e!
Нет 3d-вакансий!

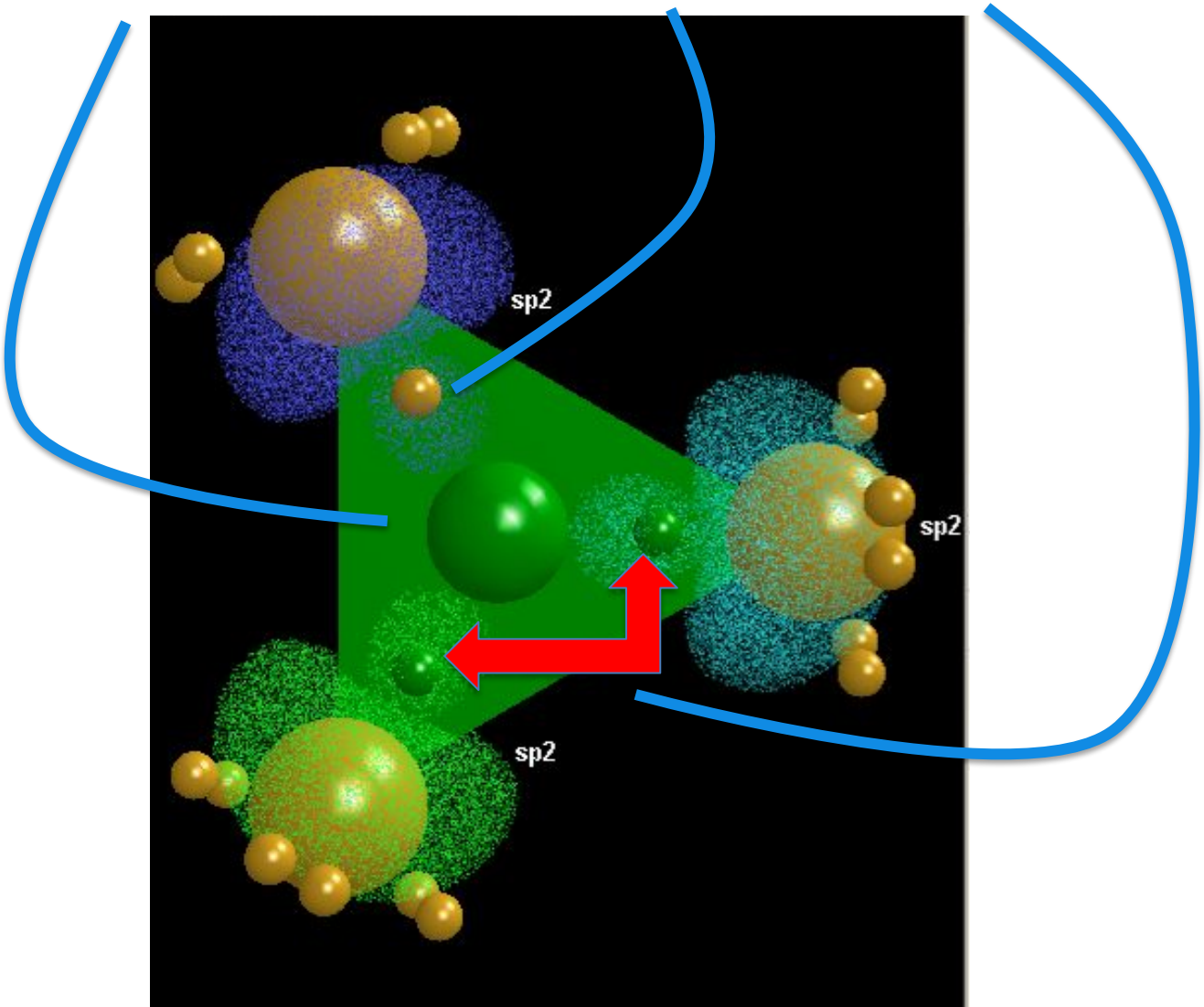
Хорошо! 8 e!
3d не нужны!

Хорошо! 10 e!
Есть 3d-вакансии!

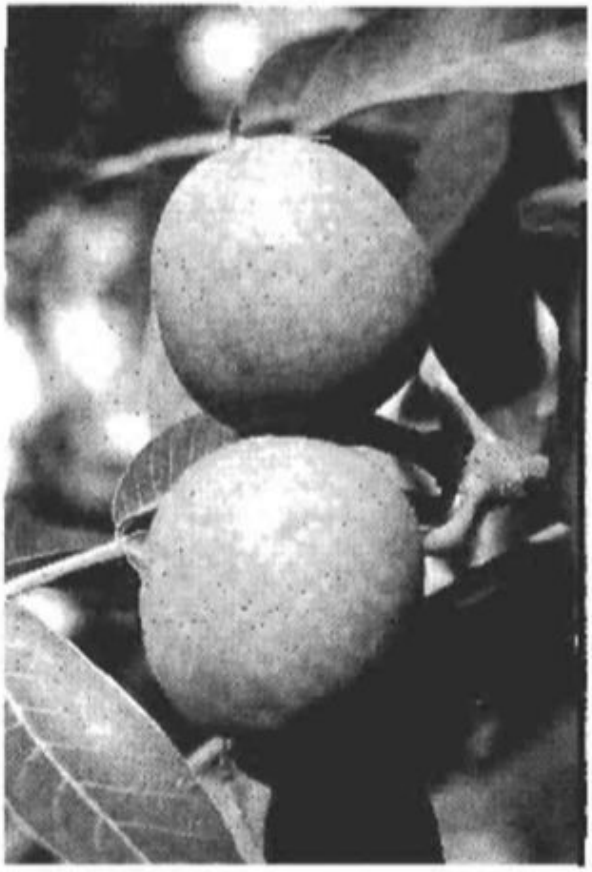
Плохо! Не согласуется
с экспериментом!

Принцип VSEPR

(VSEPR) valence-shell *electron-pair* **repulsion**

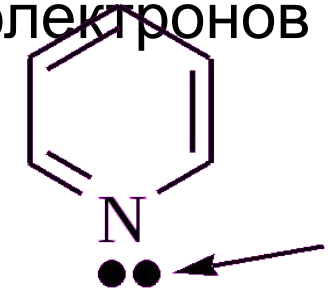


Принцип VSEPR



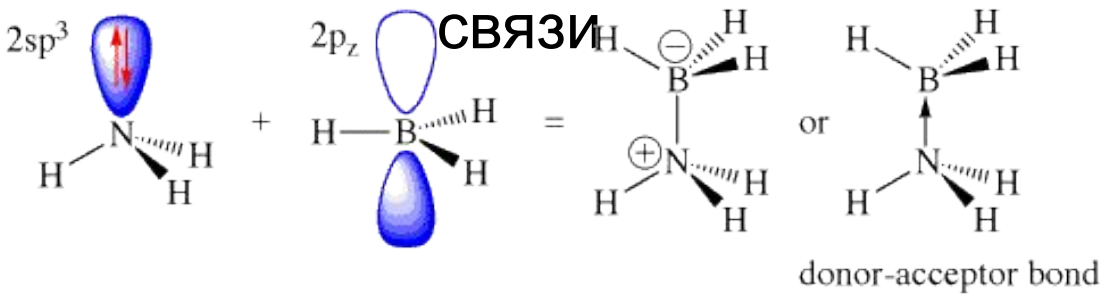
Виды электронных пар

Свободные (несвязанные) пары электронов



Связанные пары электронов

Донорно-акцепторные связи



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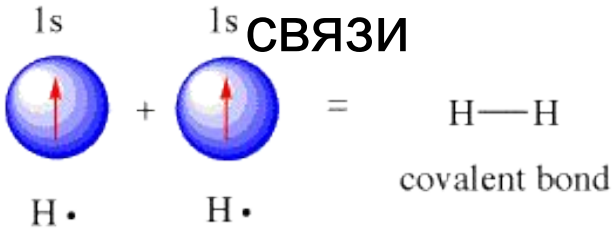
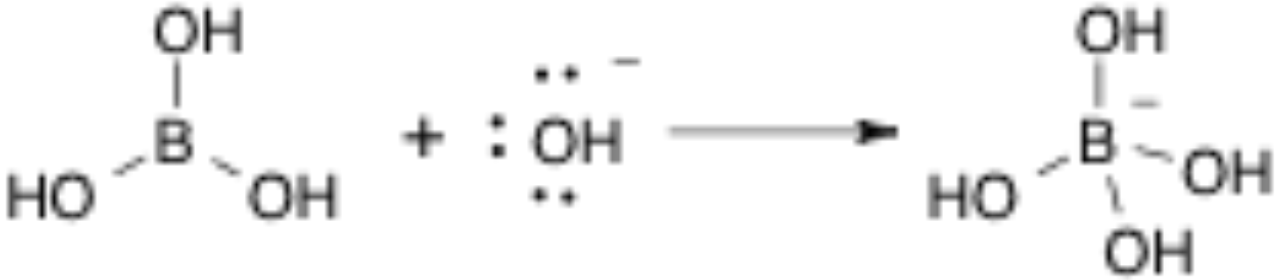


Виды электронных дыр

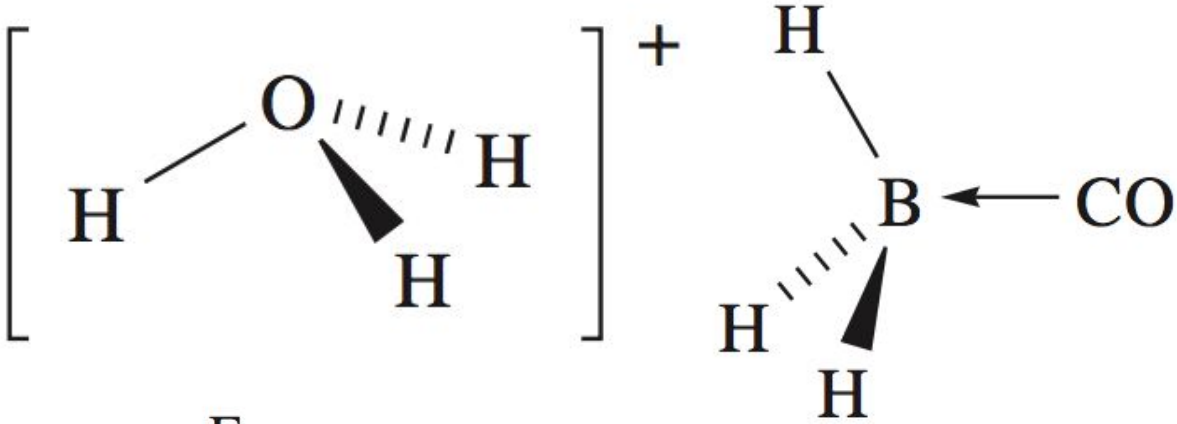
1) s-дыры

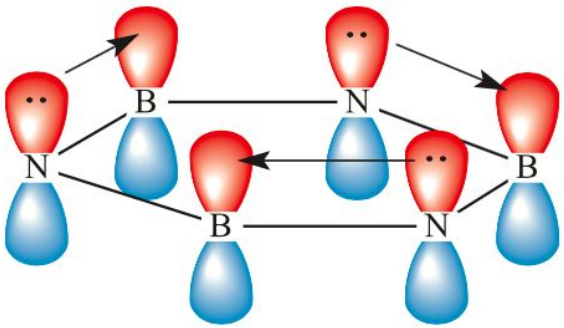
2) p-дыры

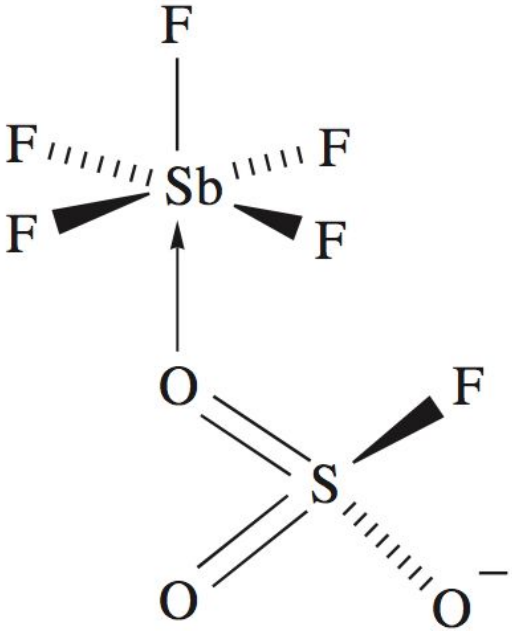


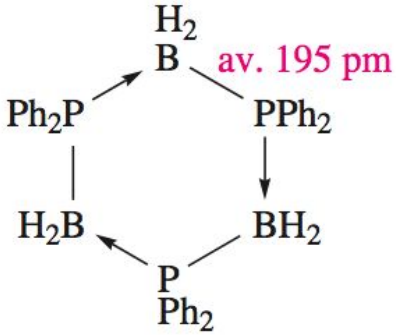
3) d-дыры

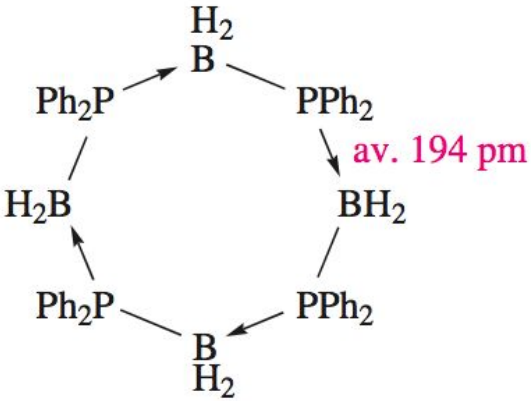
Донорно-акцепторная связь

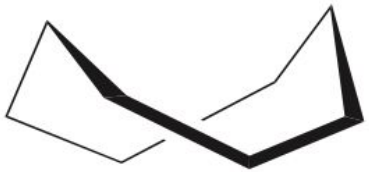












Принцип VSEPR (правила Гиллеспи)

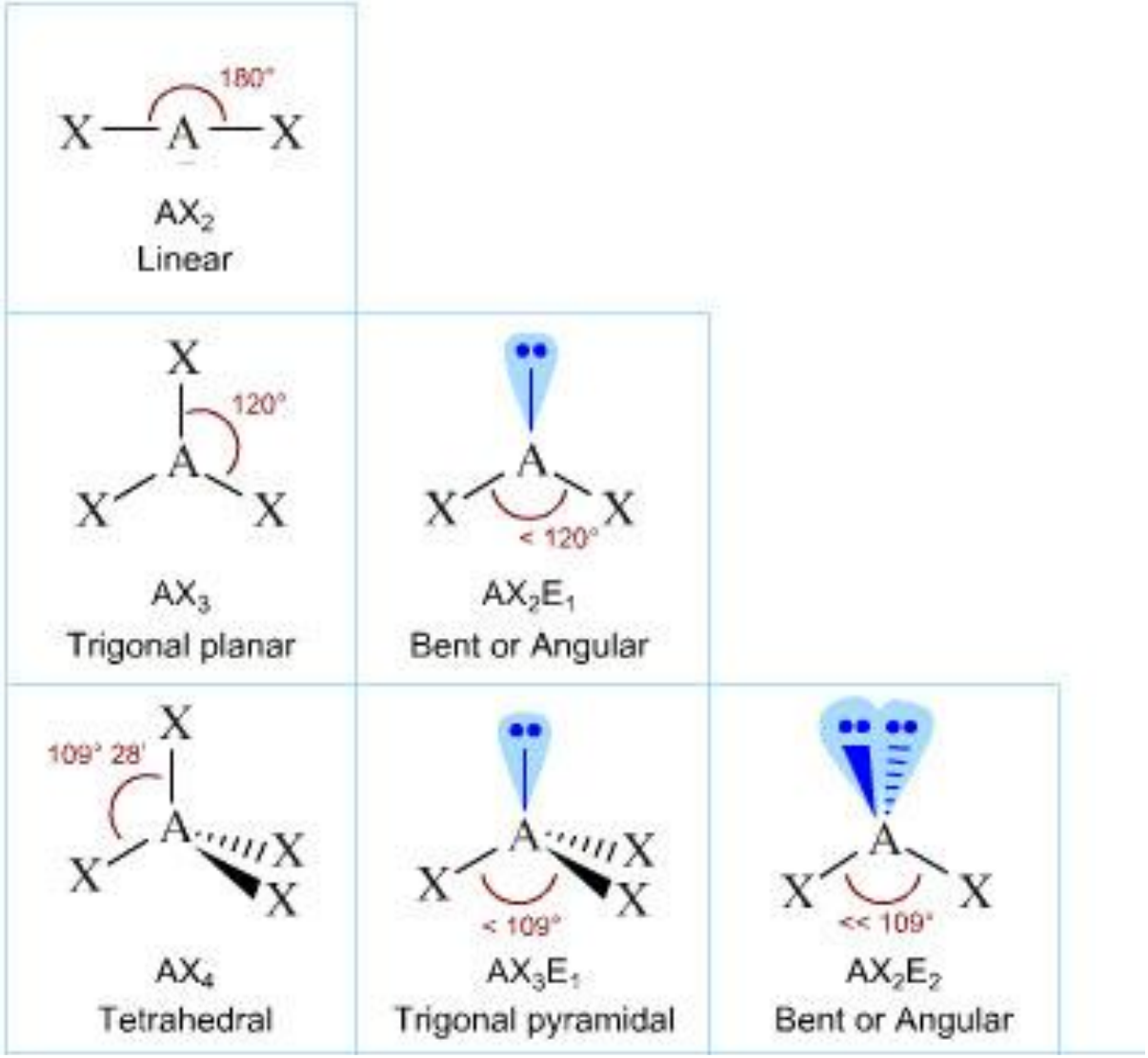
1. Пары электронов внешней оболочки центрального атома испытывают взаимное отталкивание;
2. Электронное отталкивание между парами ослабевает, если электронная плотность связи уменьшается. Следствия:
   - Отталкивание ослабевает при оттягивании электронной плотности от центрального атома за счёт электроотрицательности лигандов;
   - Отталкивание ослабевает при уменьшении порядка связи с лигандом;
3. Молекула стремится к такому расположению окружающих центральный атом лигандов, при котором отталкивание минимально.

Принцип VSEPR (до 8 электронов)

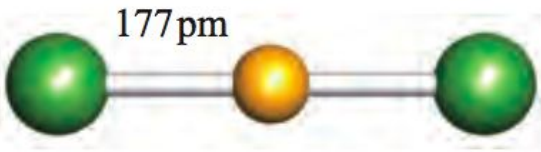
4 e

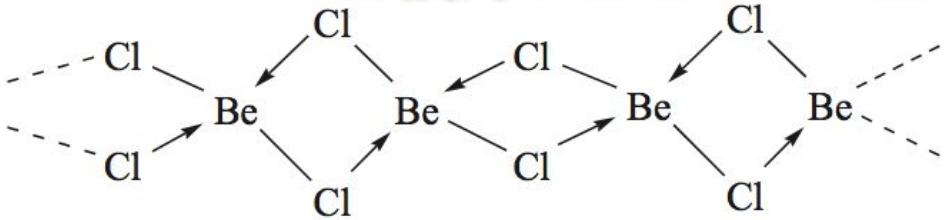
6 e

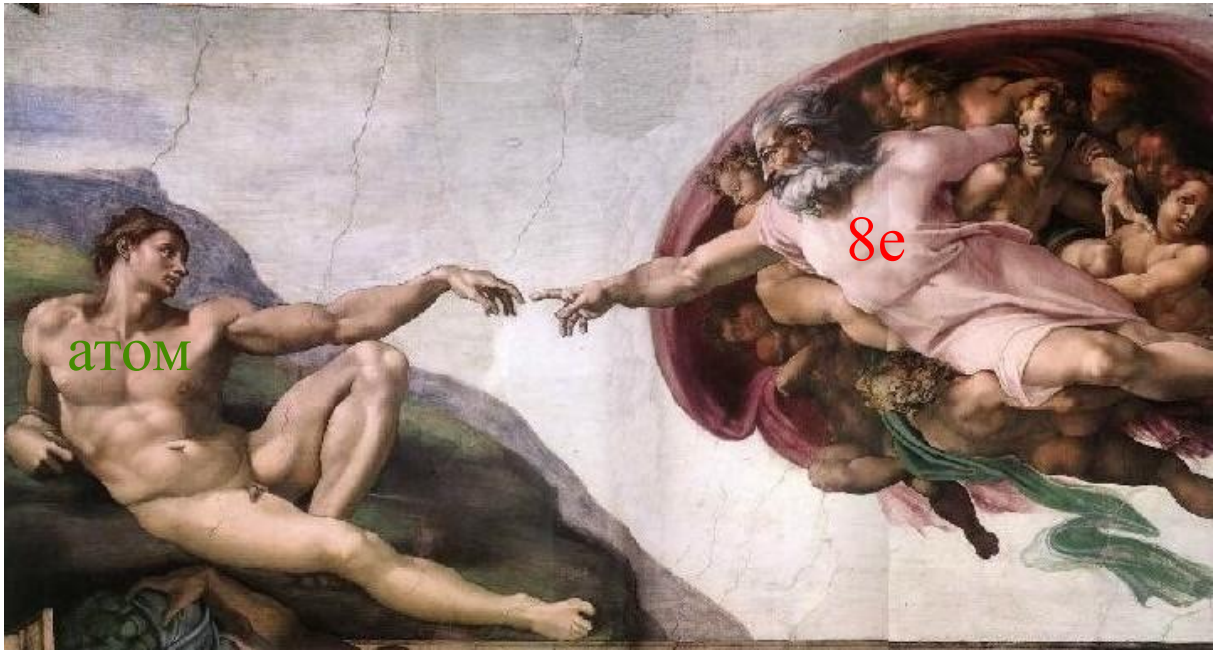
8 e



Примеры







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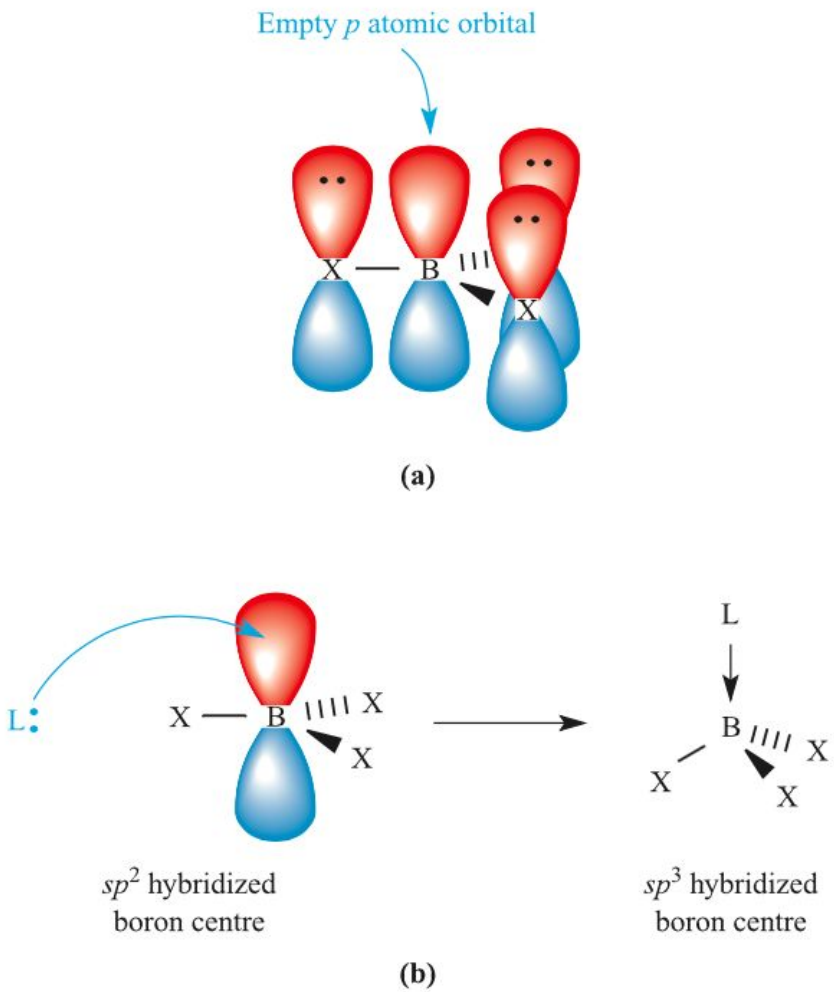
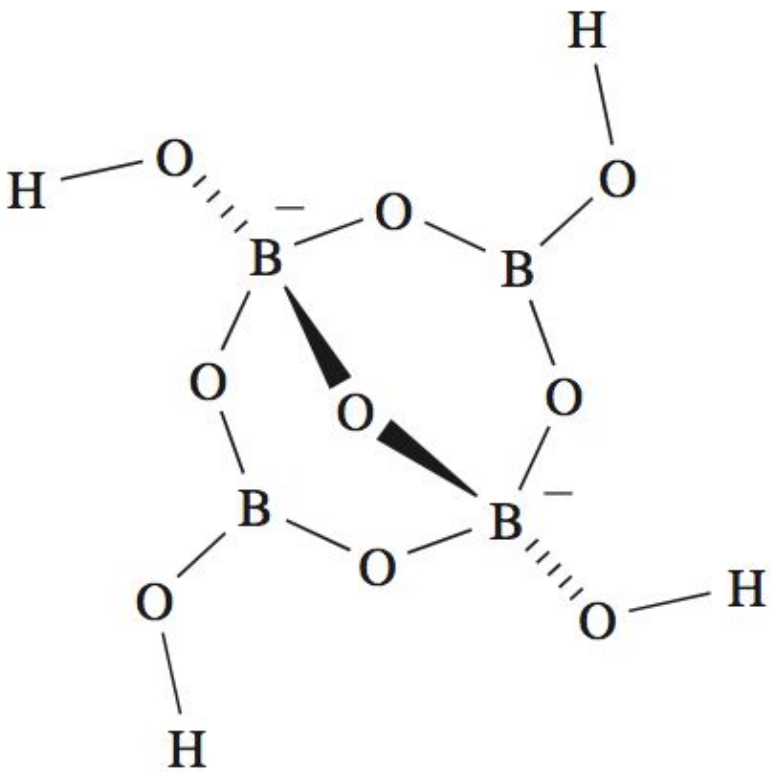
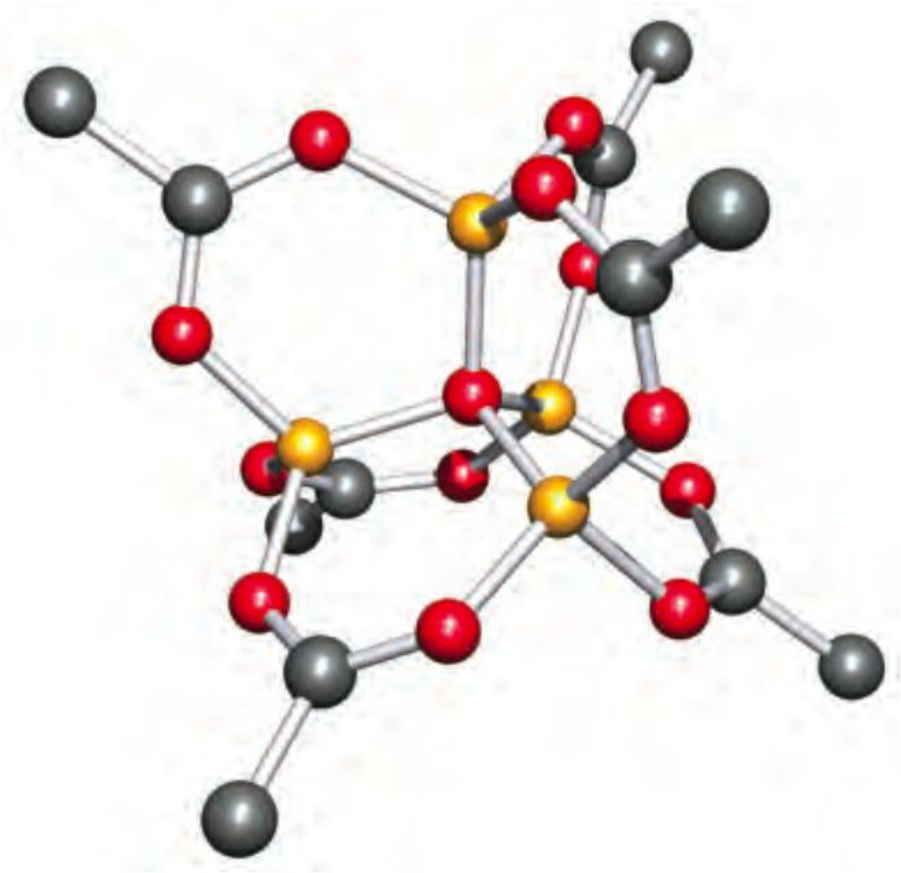




$[B_4O_5(OH)_4]^{2-}$

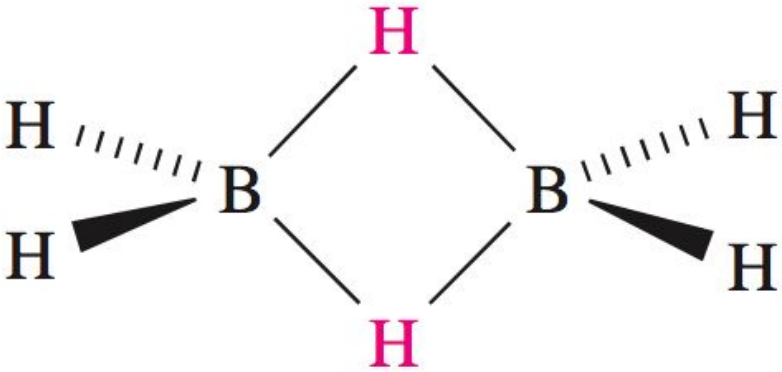
$$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons [B(OH)_4]^-(aq) + [H_3O]^+(aq)$$

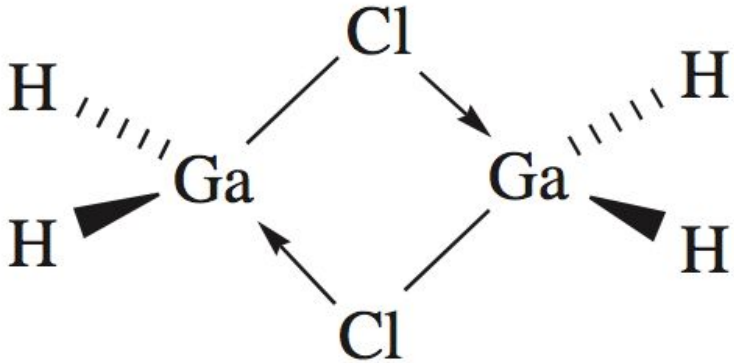
Примеры

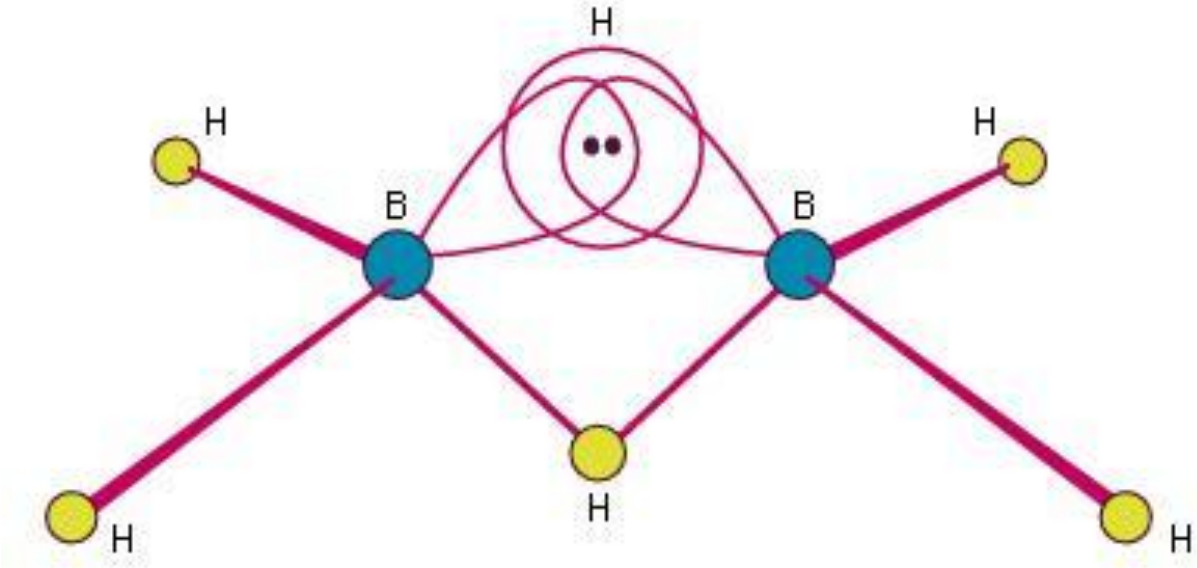


$[Be_4(\mu_4\text{-}O)(\mu\text{-}O_2CMe)_6]$

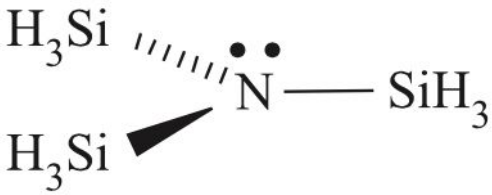
Примеры (хитрые)

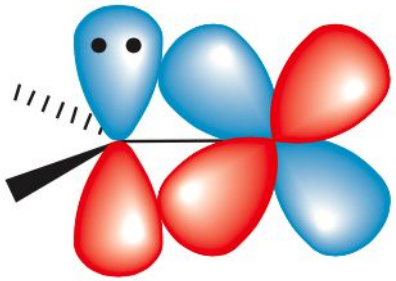




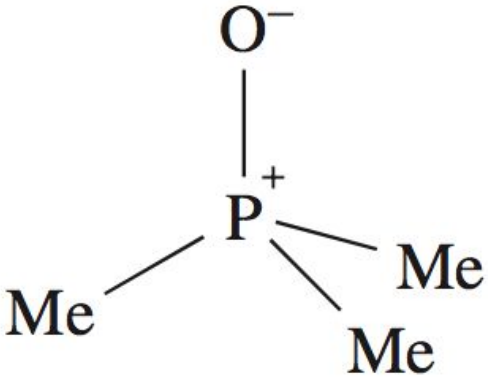


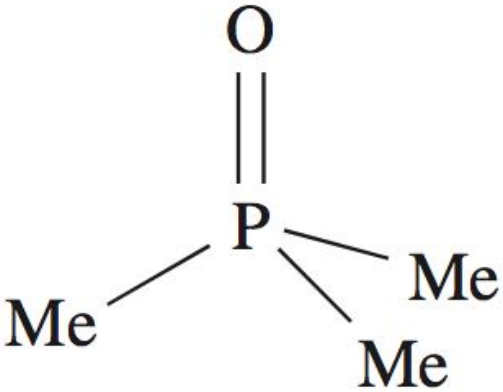
Примеры (хитрые)

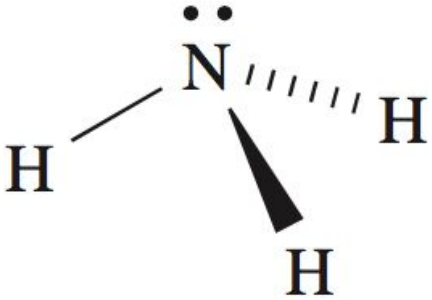


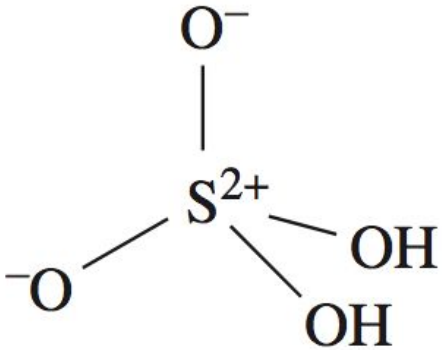


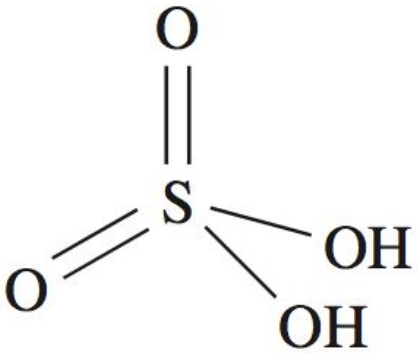
(*p*–*d*) π overlap



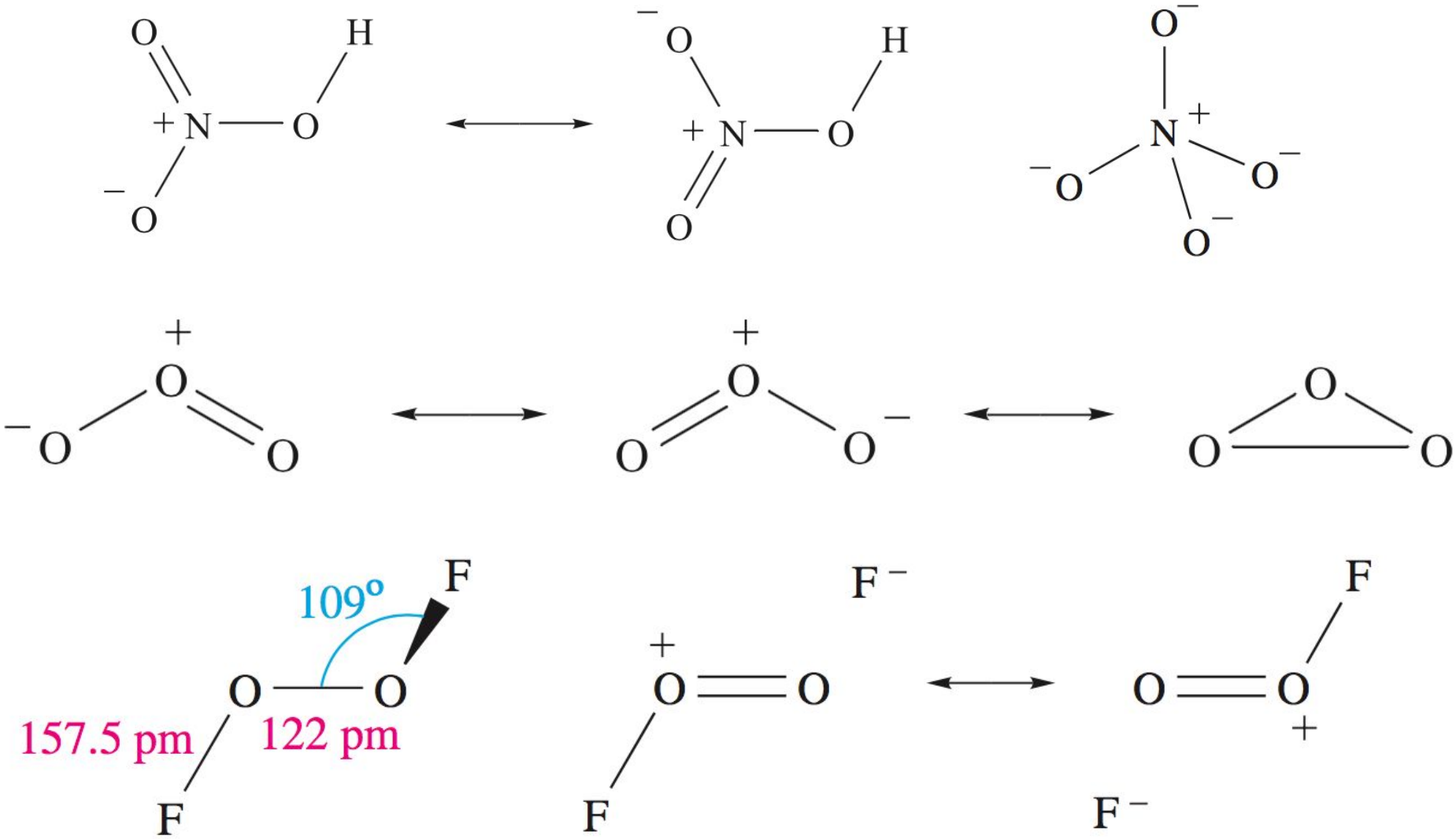




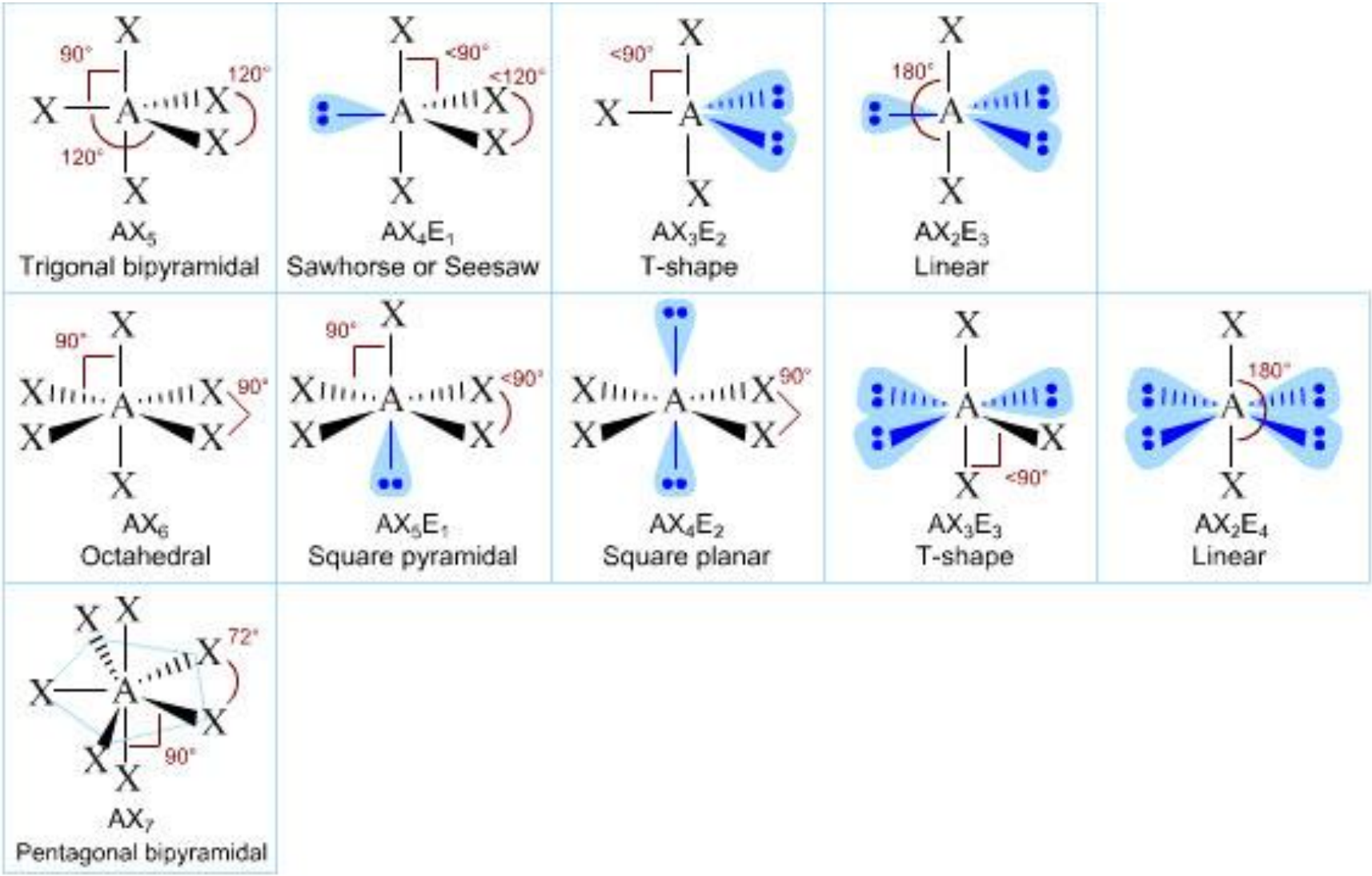




Примеры (хитрые)



Принцип VSEPR (расширенный)



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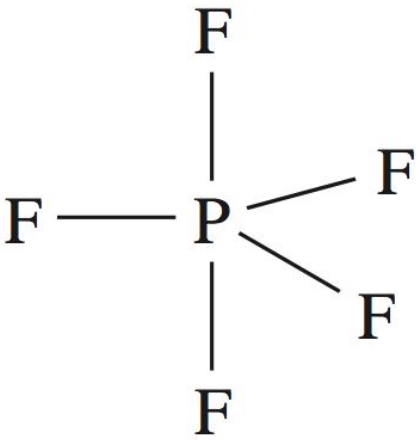

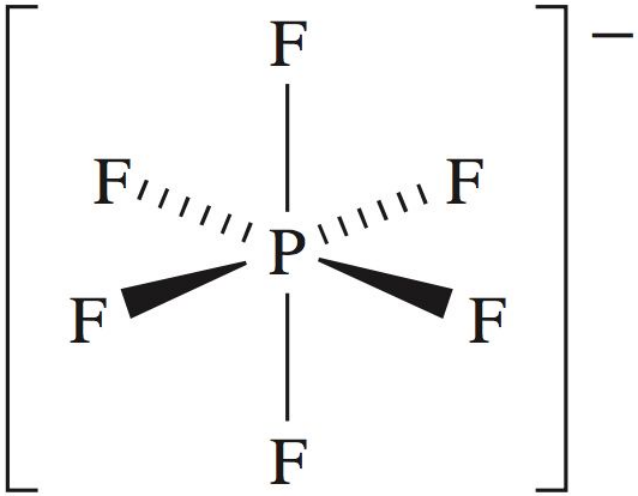

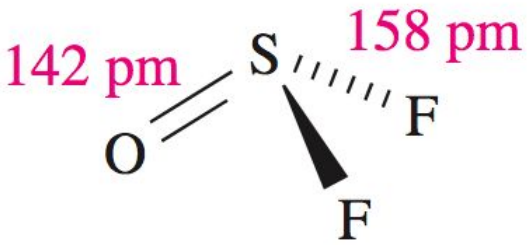

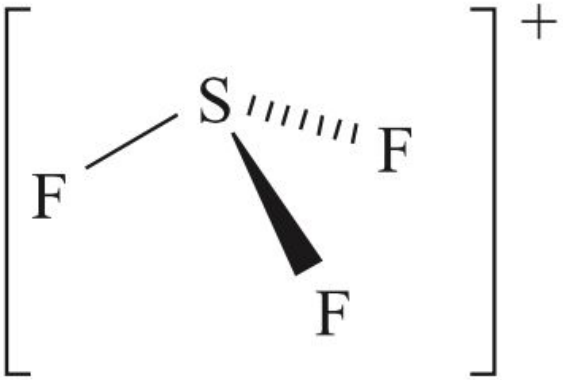

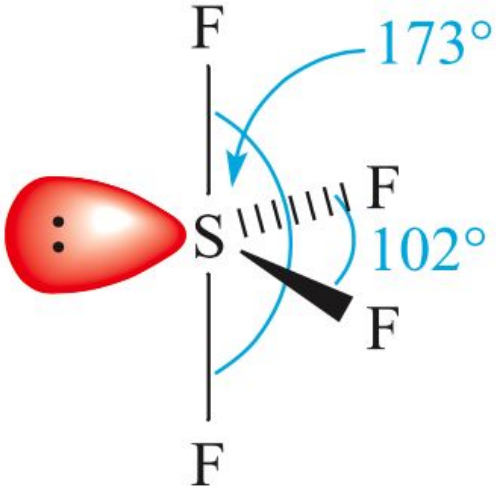

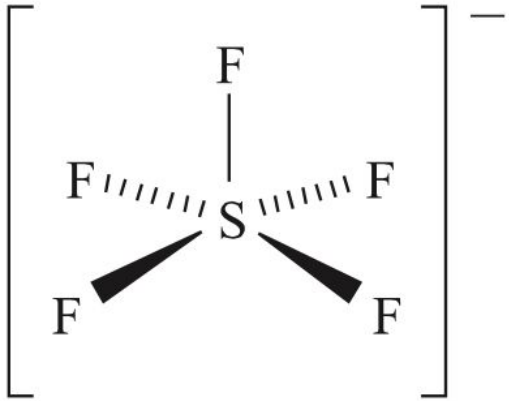

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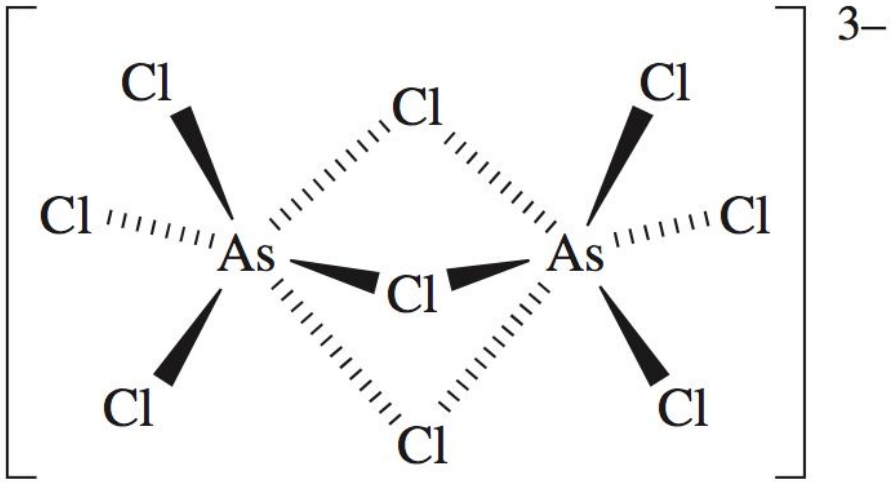
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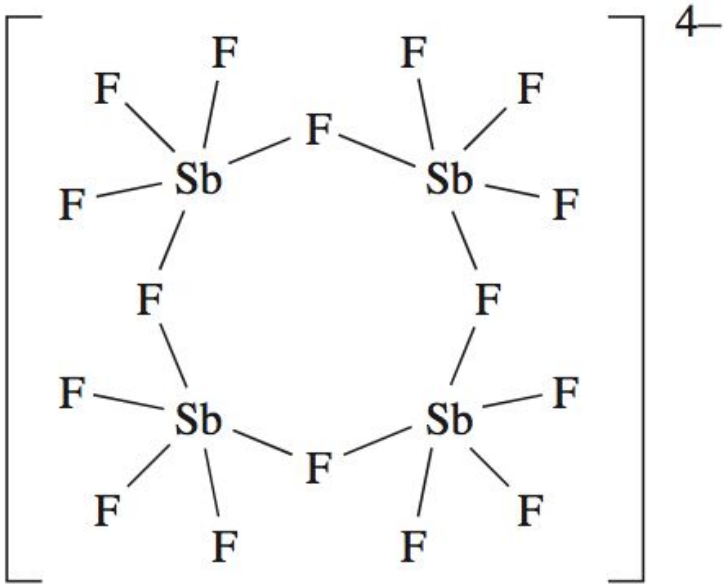
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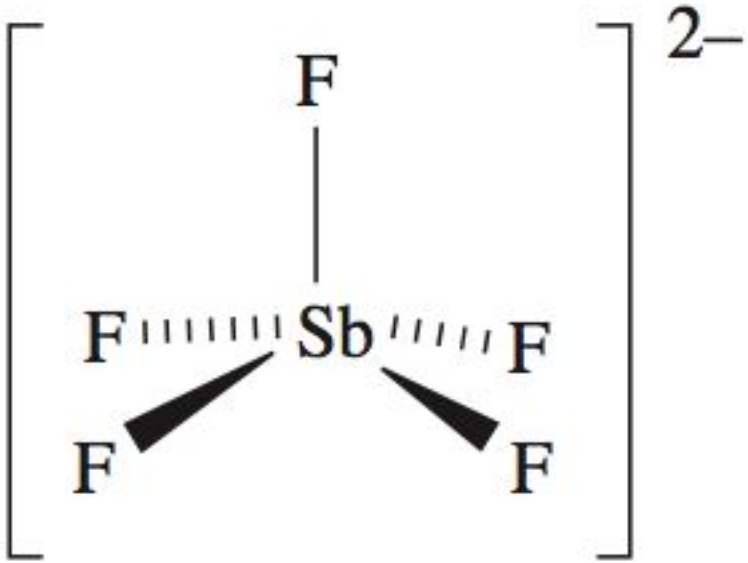
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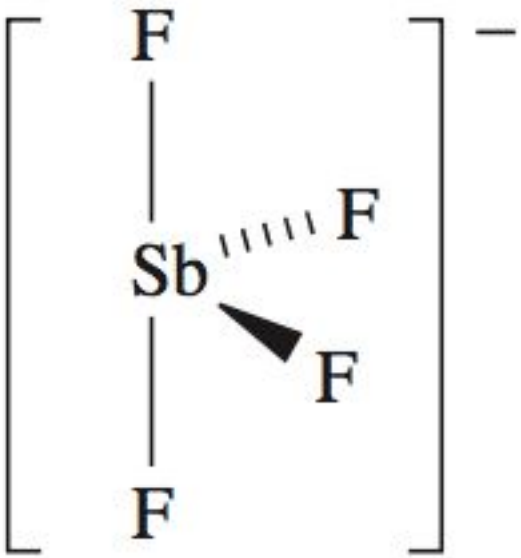
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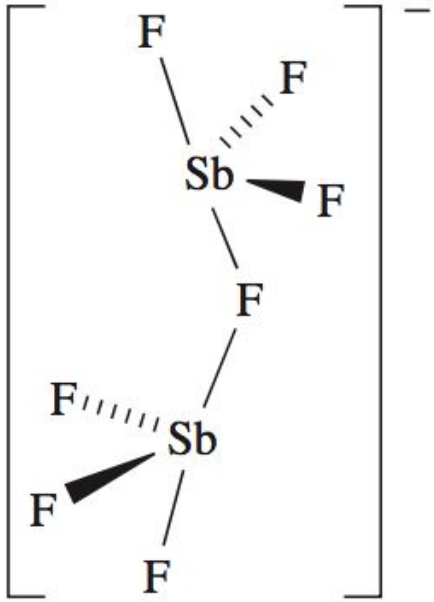
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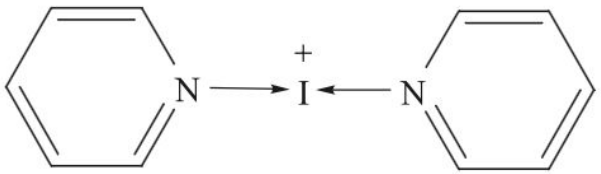
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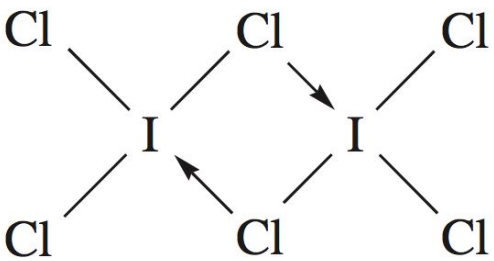
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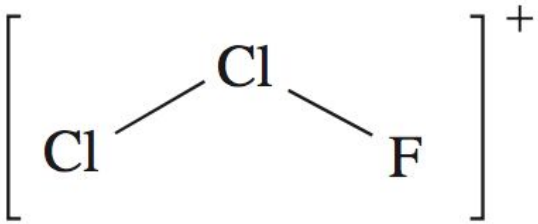
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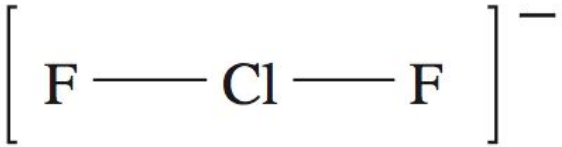
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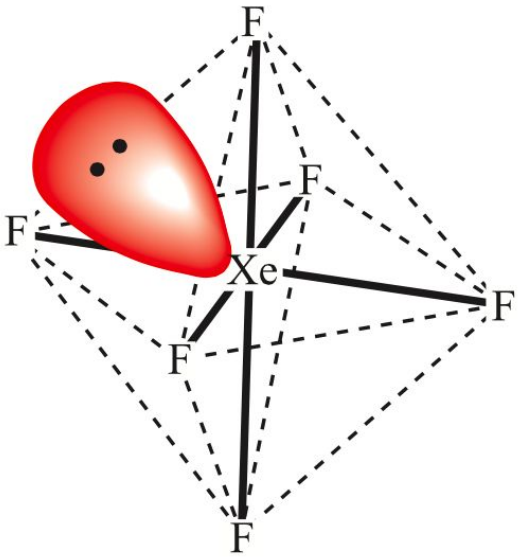
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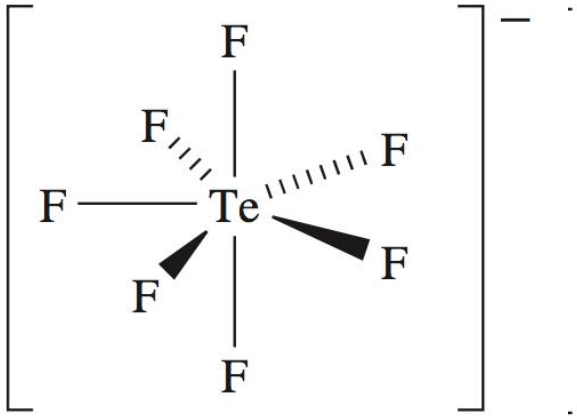
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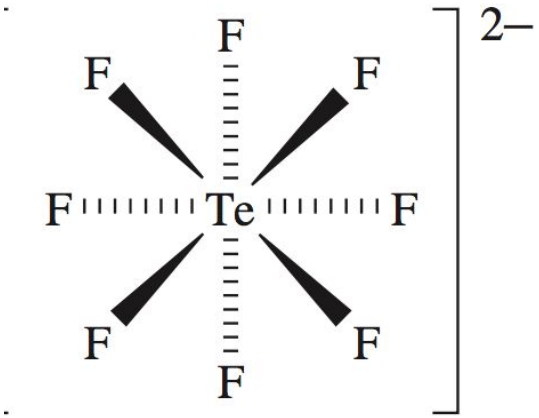
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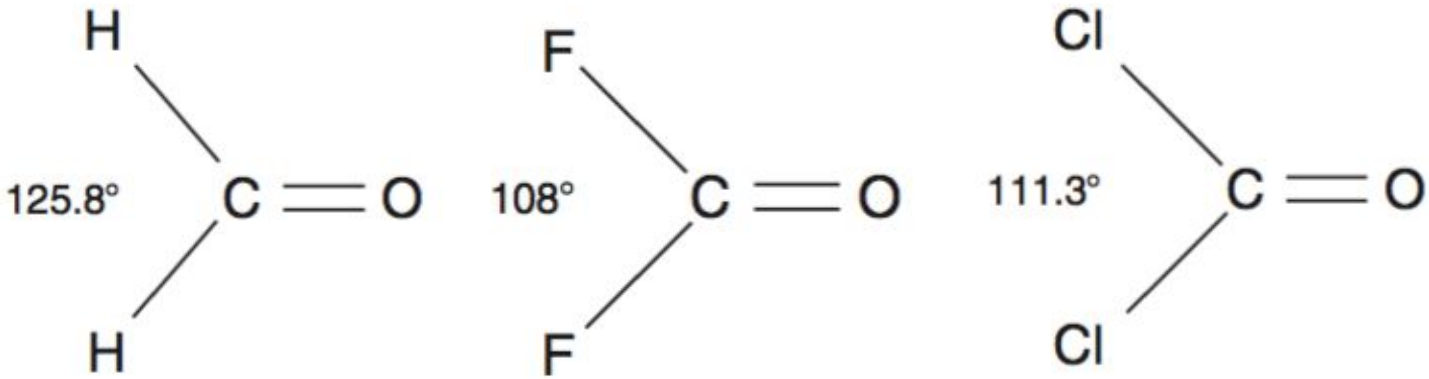
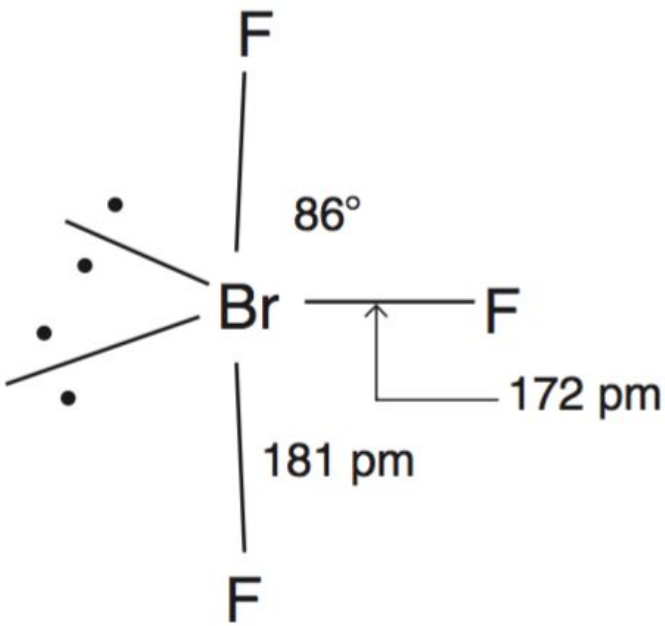
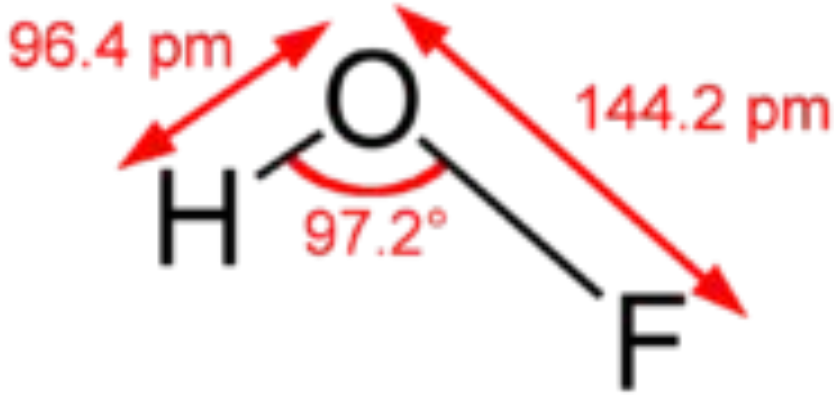
Ограничения использования VSEPR

1. Применим только для предсказания строения <u>p-элементов</u>
2. Наблюдаются отклонения от правила из-за наличия стереохимически <u>инертной s-пары у тяжёлых элементов</u> с большим количеством электронов
3. Не учитывает <u>отклонения от планарности</u> ввиду стерических эффектов
4. Не учитывает <u>специфические взаимодействия</u> между лигандами

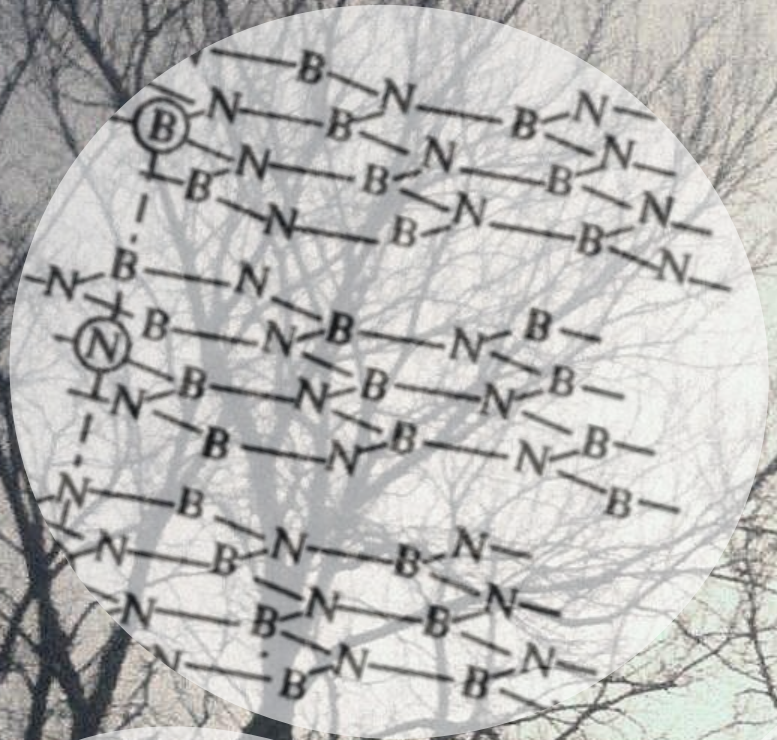
Искажения валентных углов







Конец



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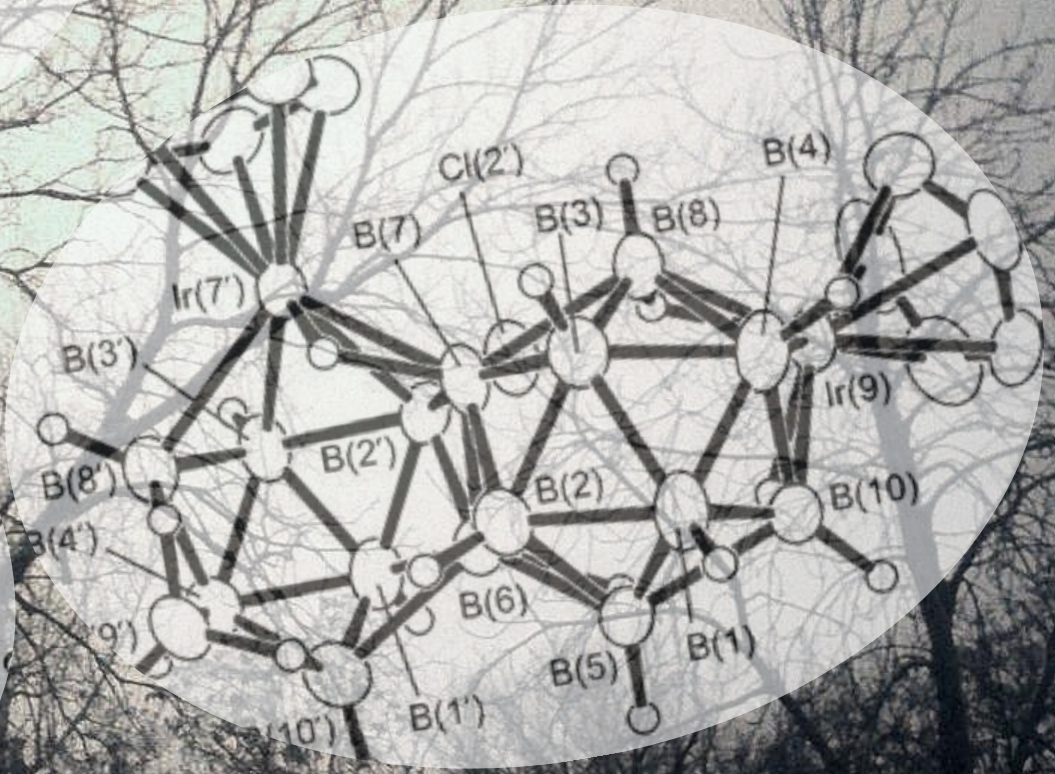
Sn
O
H
O–H
O–O
Sn–Sn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B(7)
B(3)
B(8)
Ir(7')
B(3')
Ir(9)
B(2')
B(8')
B(2)
B(10)
B(4')
B(6)
B(5)
B(1)
B(1')