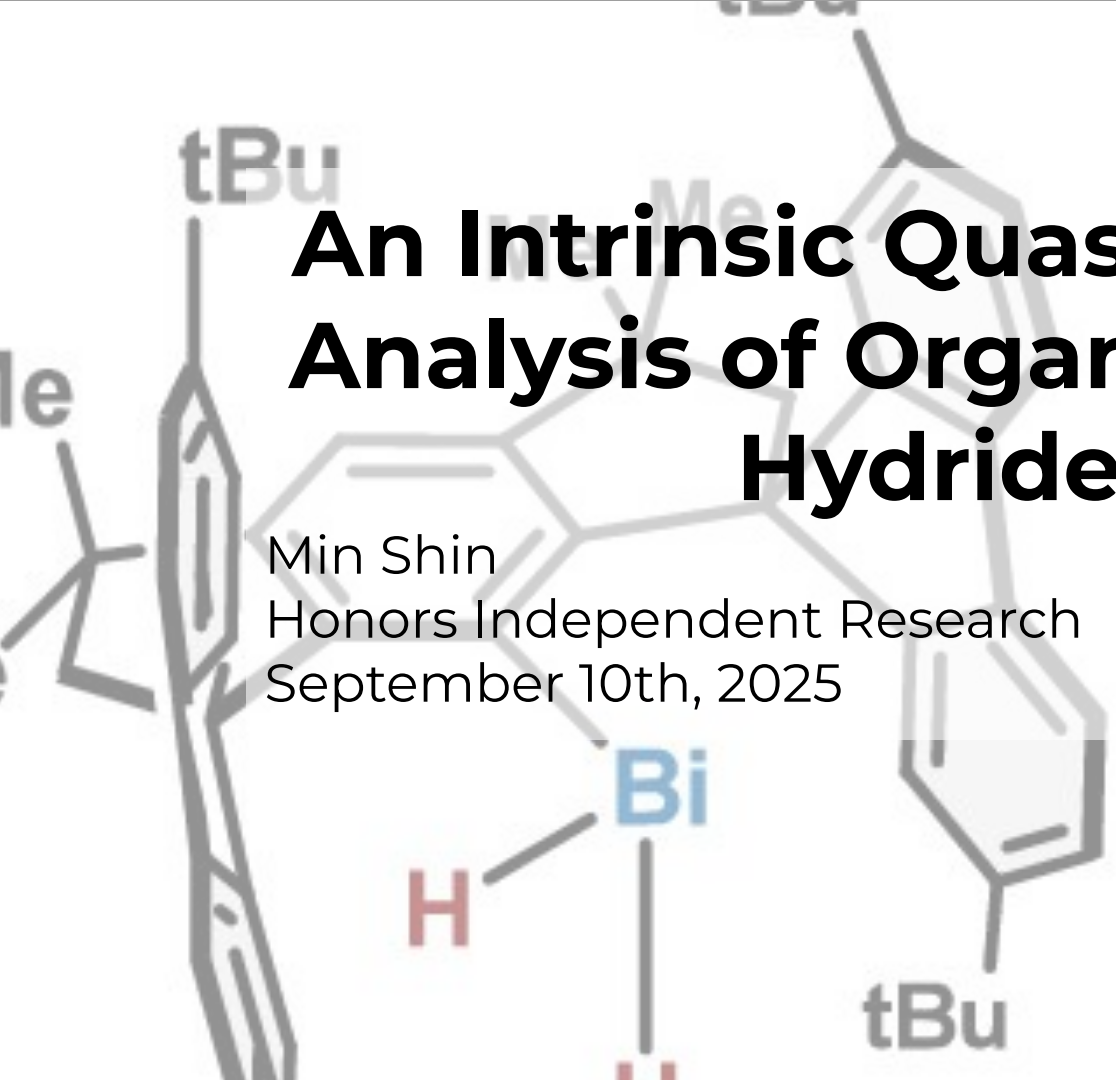
An Intrinsic Quasi-Bonding Analysis of Organobismuth Hydrides

Min Shin

Honors Independent Research

September 10th, 2025

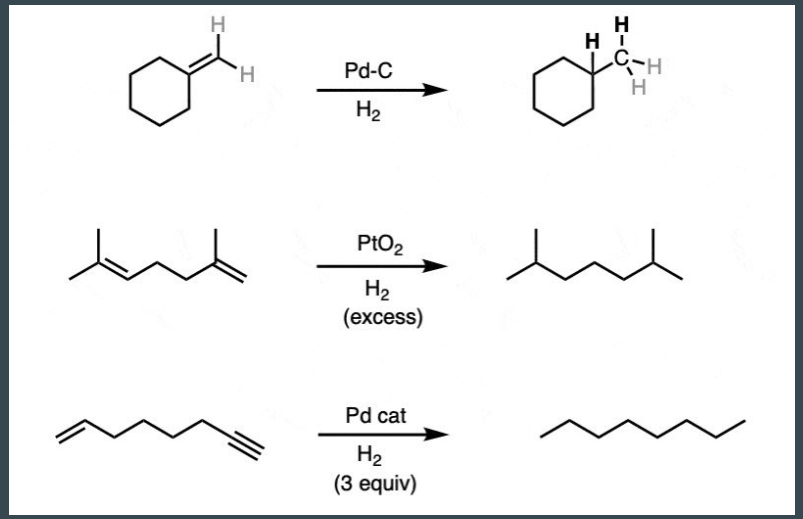


PERIODIC TABLE OF THE ELEMENTS

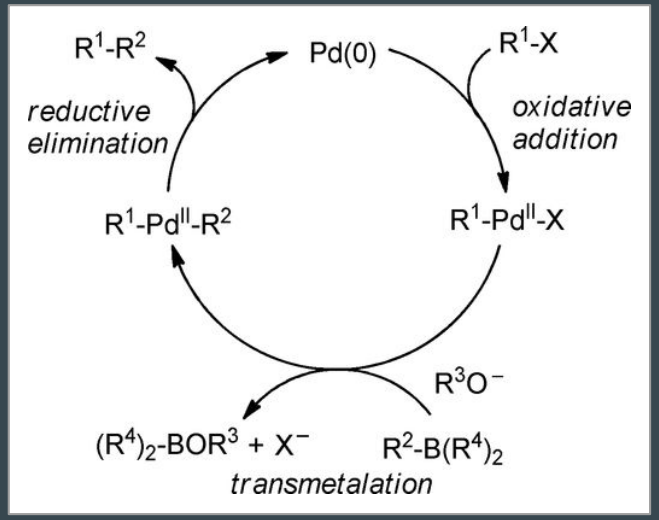
1 1A																	18 8A
1 **H** 1.008	2 **2A**											13 **3A**	14 **4A**	15 **5A**	16 **6A**	17 **7A**	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	3 **3B**	4 **4B**	5 **5B**	6 **6B**	7 **7B**	8 **8B**	9 **8B**	10 **8B**	11 **1B**	12 **2B**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Transition metals catalyze different reactions pathways such as hydrogenation, cross-coupling, etc.



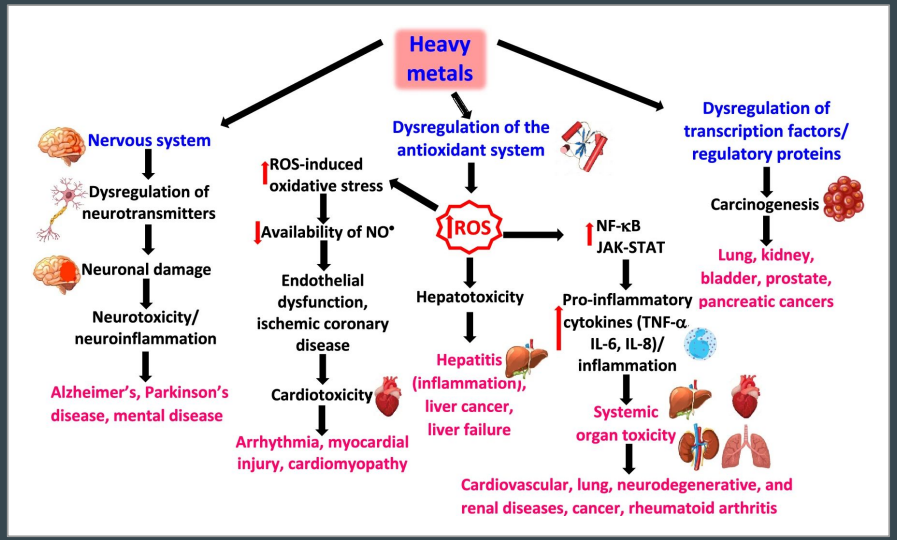
Hydrogenation



Cross-Coupling

(Jana et al., 2011)

Transition Metals have inevitable downsides due to its affordability and toxicity



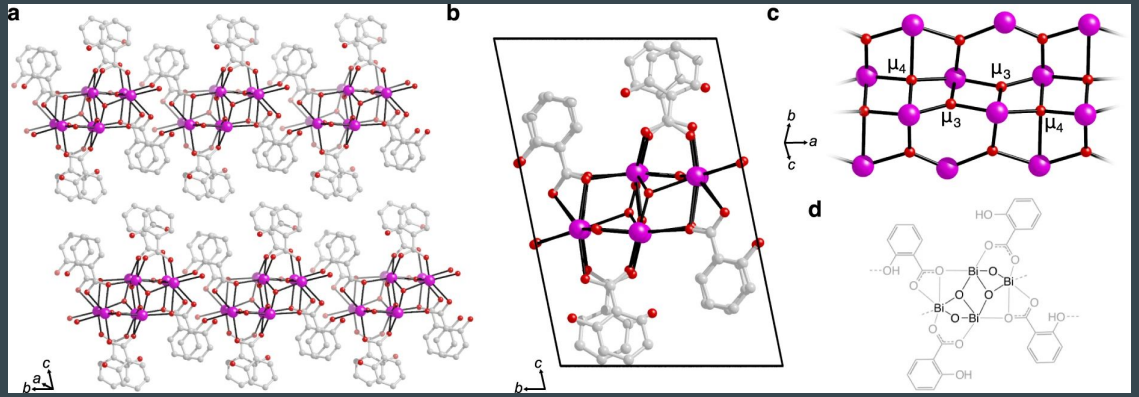
Potential Effects of Transition Metals on Human Health

(Jomova et al., 2024)

Platinum	Palladium	Rhodium
$44,551.26 per kg	$45,255.36 per kg	$217,020.87 per kg

Data collected on September 18th

Bismuth is Safer, Cheaper Metal

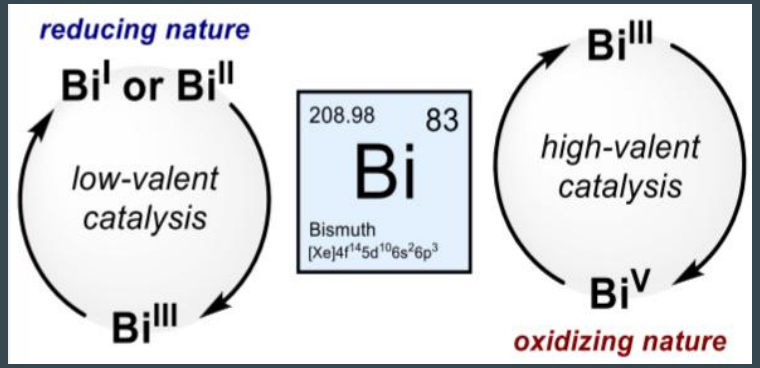


Structure of the active pharmaceutical ingredient bismuth subsalicylate
(Svensson Grape et al., 2022)

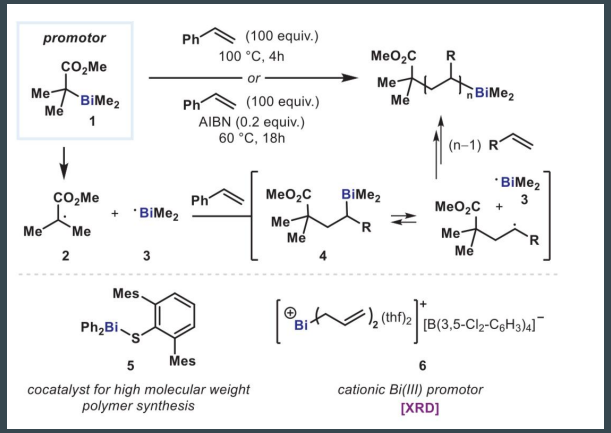
Platinum	Palladium	Rhodium	Bismuth
$44,551.26 per kg	$45,255.36 per kg	$217,020.87 per kg	$384.55 per kg

Data collected on September 18th

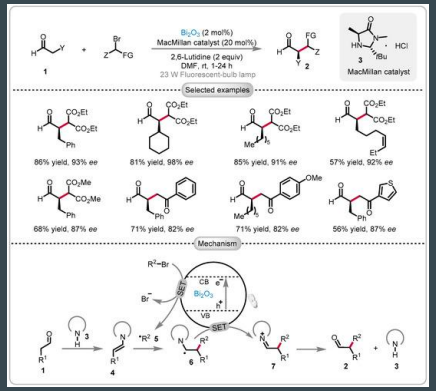
Bismuth goes through different redox catalysis pathways



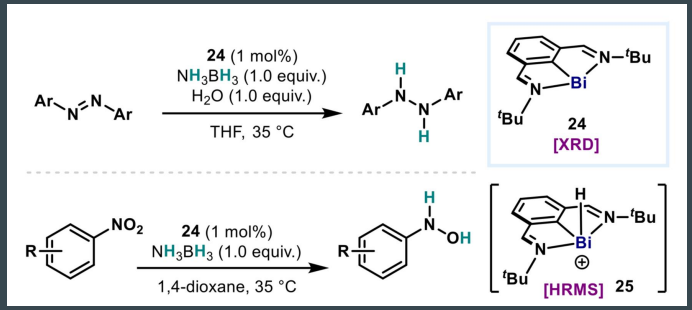
General Scheme of Bismuth Redox Catalysis
(Cornella et al., 2022)



Bismuth-mediated Radical Polymerization via Bi(II) radical
(Cornella et al., 2022)



Bi_2O_3 photocatalyzed α-alkylation of aldehyde
(He et al., 2025)



Bismuth-catalyzed transfer hydrogenation
(Cornella et al., 2022)

Computational Chemistry has several methods

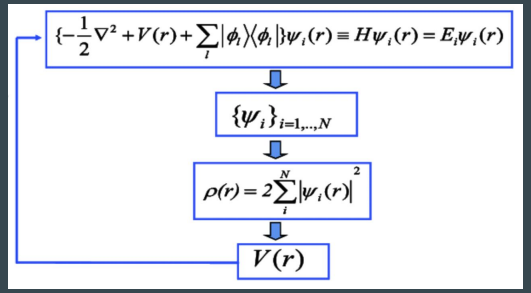
$$\rho(1,2) = \sum_{Aa}\sum_{Bb} |Aa(1)\rangle p_{Aa,Bb} \langle Bb(2)|$$

$$k_{Aa,Bb} = 0.1 p_{Aa,Bb} \langle Aa| -\frac{1}{2}\nabla^2 |Bb\rangle A \neq B$$

Density Bond Orders and Kinetic Bond Orders from QUAO

(Rudenberg et al., 2020)

DBO: density matrix of the total molecular wave function expanded in terms of QUAOs
KBO: interatomic kinetic energy between QUAO a on atom A and QUAO b on atom B



Basics of Density Functional Theory (DFT)

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\chi_1, \chi_2, \cdots, \chi_N\rangle$$

$$E[\psi^{HF}] = \left\langle \psi^{HF} | \hat{H}^e | \psi^{HF} \right\rangle$$

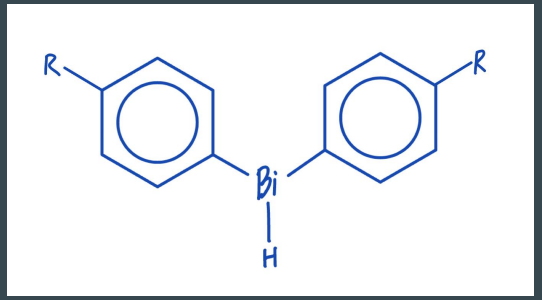
$$|\psi_i\rangle \approx \sum_\mu c_{\mu i} |\mu\rangle,$$

Basics of Hartree-Fock Method

- Slater Determinant to calculate total electronic molecular wave function from each one-particle wavefunction
- Hartree-Fock energy derived from expectation value of Hamiltonian of total electronic molecular wave function
- Optimization of coefficients for linear combination of basis sets of atomic orbitals

Types and positions of substituents on the phenyl rings affect the bonding profiles of organobismth hydrides

Independent Variables



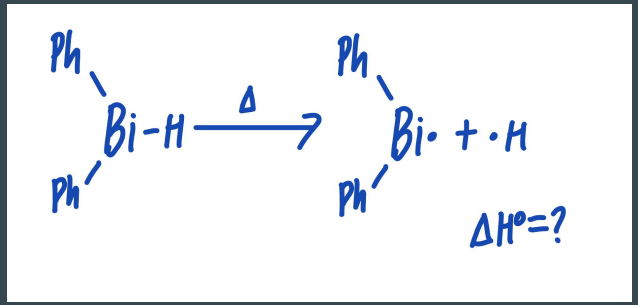
Types of Substituents (e.g., R=F, NH_2, OCH_3, CH_3, SCH_3, NO_2) and **Respective Positions of Substituents**

Dependent Variables

$$\rho(1,2) = \sum_{Aa}\sum_{Bb} |Aa(1)\rangle p_{Aa,Bb} \langle Bb(2)|$$

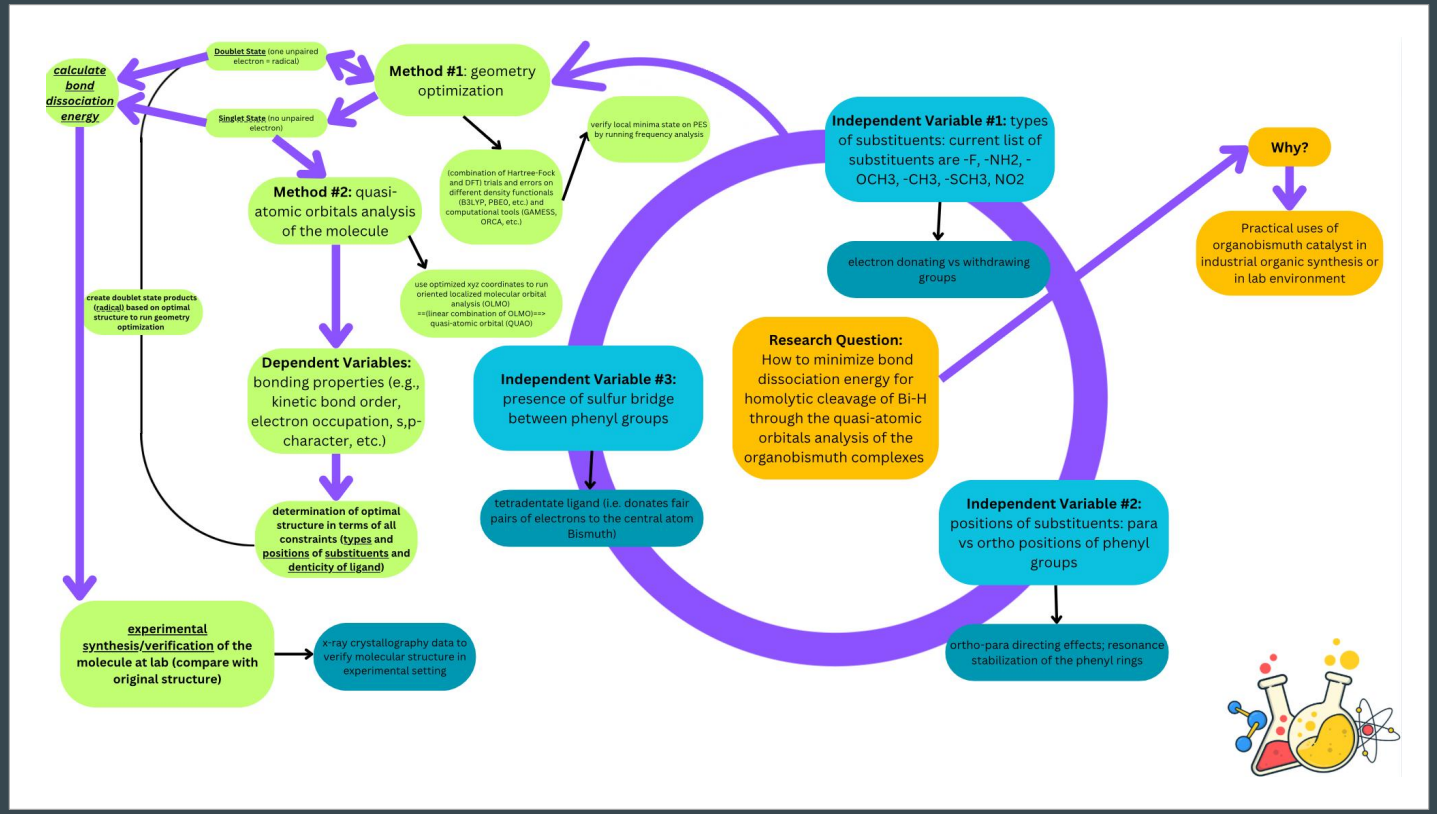
$$k_{Aa,Bb} = 0.1 p_{Aa,Bb} \langle Aa| - \frac{1}{2}\nabla^2 |Bb\rangle A \neq B$$

Density Bond Orders and Kinetic Bond Orders from QUAO
(Rudenberg et al., 2020)



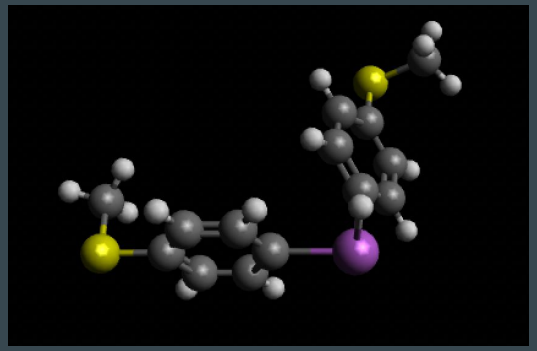
Homolytic Cleavage Energy of Bi-H bond (denoted by ΔH°)

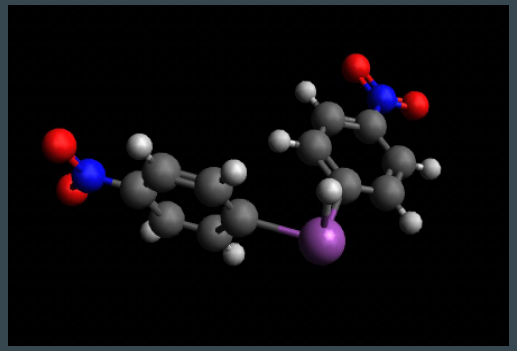
Flow of Computational Analysis



Flow of Computational Analysis

1) Preparation of Initial Input Files for Geometry Optimization





2) Confirmation of Local Minima on Potential Energy Surface (PES)

```
Scaling factor for frequencies =  1.000000000  (already applied!)

    0:       0.00 cm**-1
    1:       0.00 cm**-1
    2:       0.00 cm**-1
    3:       0.00 cm**-1
    4:       0.00 cm**-1
    5:       0.00 cm**-1
    6:     -12.01 cm**-1  ***imaginary mode***
    7:      -5.93 cm**-1  ***imaginary mode***
    8:      29.37 cm**-1
    9:      85.36 cm**-1
   10:     106.00 cm**-1
   11:     148.64 cm**-1
   12:     173.30 cm**-1
   13:     199.04 cm**-1
   14:     202.09 cm**-1
   15:     263.08 cm**-1
   16:     297.87 cm**-1
   17:     303.24 cm**-1
   18:     311.90 cm**-1
   19:     387.82 cm**-1
   20:     389.21 cm**-1
   21:     406.41 cm**-1
   22:     408.50 cm**-1
   23:     497.89 cm**-1
   24:     509.83 cm**-1
   25:     562.92 cm**-1
   26:     567.51 cm**-1
   27:     579.76 cm**-1
   28:     585.93 cm**-1
   29:     590.16 cm**-1
   30:     612.26 cm**-1
   31:     639.65 cm**-1
```

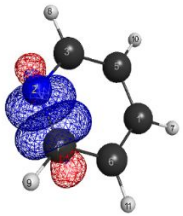
Flow of Computational Analysis

3) QUAO Analysis

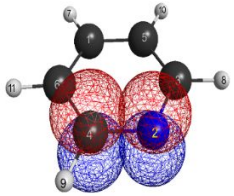
Pyridine

Bond Order	KBO (hartree	QUAO #1	OCC #1 (ele	Orbital I	I	QUAO #2	OCC #2 (ele	Orbital J	J	KBO (kJ/mol	Degeneracy	Total Electron Density
0.979136	-0.974245	22	0.872272	C4N2	SIGMA	13	1.129039	N2C4	SIGMA	-255.7879	Degenerate	2.0013107
0.979136	-0.974244	18	0.872272	C3N2	SIGMA	14	1.129039	N2C3	SIGMA	-255.7878	Orbital #1	2.0013106
0.982876	-0.851352	30	0.991798	C6C1	SIGMA	8	1.00631	C1C6	SIGMA	-223.5224	Degenerate	1.9981073
0.982876	-0.851352	26	0.991798	C5C1	SIGMA	9	1.00631	C1C5	SIGMA	-223.5224	Orbital #2	1.9981073
0.980294	-0.85007	25	1.012803	C5C3	SIGMA	16	1.005509	C3C5	SIGMA	-223.1858	Degenerate	2.0183119
0.980294	-0.850069	29	1.012803	C6C4	SIGMA	20	1.005509	C4C6	SIGMA	-223.1856	Orbital #3	2.0183119
-0.974435	-0.614151	34	0.85311	H10C5	SIGMA	23	1.146795	C5H10	SIGMA	-161.2452	Degenerate	1.9999048
0.974435	-0.61415	35	0.85311	H11C6	SIGMA	27	1.146795	C6H11	SIGMA	-161.2452	Orbital #4	1.9999048
0.973977	-0.612667	31	0.85114	H7C1	SIGMA	7	1.151375	C1H7	SIGMA	-160.8557		2.0025149
0.97181	-0.603532	32	0.854174	H8C3	SIGMA	15	1.155148	C3H8	SIGMA	-158.4572	Degenerate	2.0093218
-0.97181	-0.603531	33	0.854174	H9C4	SIGMA	19	1.155148	C4H9	SIGMA	-158.4571	Orbital #6	2.0093218
0.66177	-0.26156	21	0.925332	C4(C6N2)	PI	12	1.142189	N2(C4C3)	PI	-68.67245	Degenerate	2.0675208
0.661769	-0.261559	17	0.925332	C3(C5N2)	PI	12	1.142189	N2(C4C3)	PI	-68.67224	Orbital #7	2.067521
0.664117	-0.235079	24	1.040311	C5(C1C3)	PI	17	0.925332	C3(C5N2)	PI	-61.71989	Degenerate	1.965643
-0.664116	-0.235078	28	1.040311	C6(C1C4)	PI	21	0.925332	C4(C6N2)	PI	-61.7197	Orbital #8	1.965643
-0.66615	-0.234338	28	1.040311	C6(C1C4)	PI	10	0.926525	C1(C6C5)	PI	-61.52531	Degenerate	1.9668361
0.666149	-0.234337	24	1.040311	C5(C1C3)	PI	10	0.926525	C1(C6C5)	PI	-61.52526	Orbital #9	1.9668359

Degenerate Orbital #1



Degenerate Orbital #6



Sample QUAO Results of Pyridine

Each degenerate orbitals show interaction between QUAOs

4) Calculation of homolytic cleavage energy

Flow of Computational Analysis

5) Determination of optimal organobismuth hydride structure based on QUAO profiles and homolytic cleavage energies

6) Experimental verification