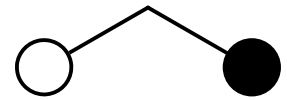
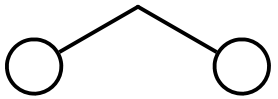
SALCS for Common Geometries *(σ bonding)*

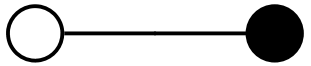
CN = 2

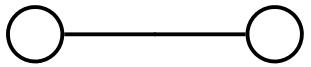
C_{2v}

B_1 

A_1 

$D_{\infty h}$

Σ_u^+ 

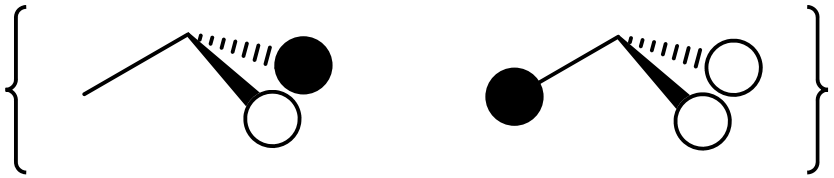
Σ_g^+ 

SALCS for Common Geometries *(σ bonding)*

CN = 3

C_{3v}

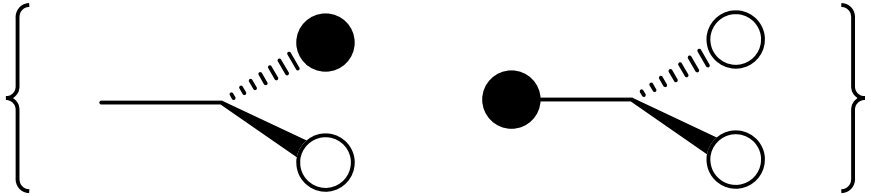
E



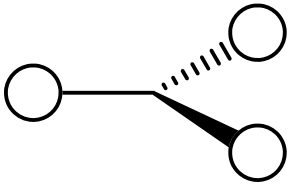
A_1

D_{3h}

E'



A_1'

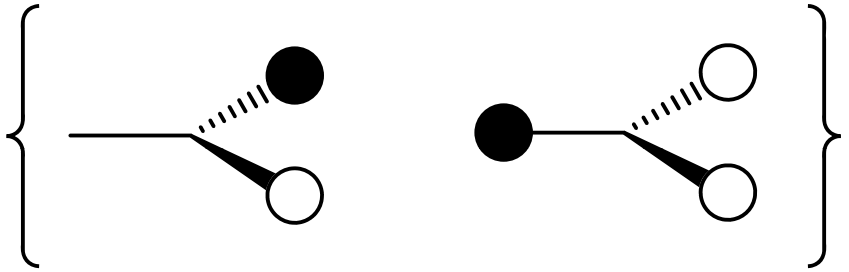


SALCS for Common Geometries *(σ bonding)*

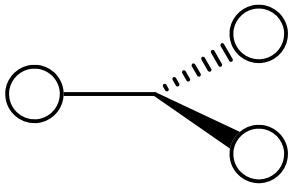
CN = 3

D_{3h}

E



A_1'

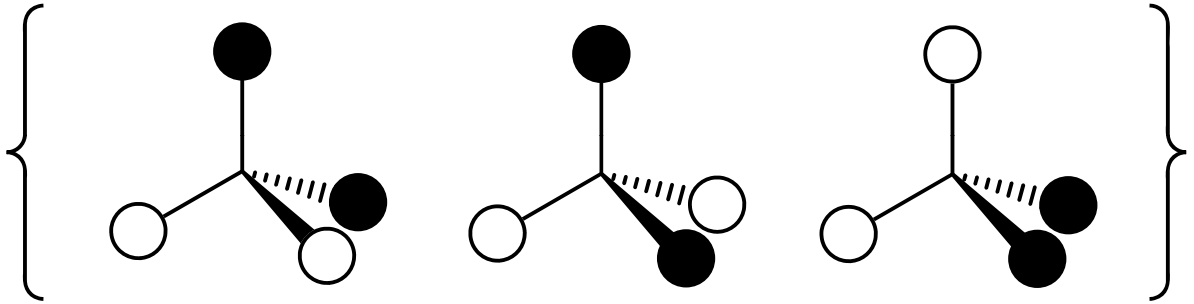


SALCS for Common Geometries *(σ bonding)*

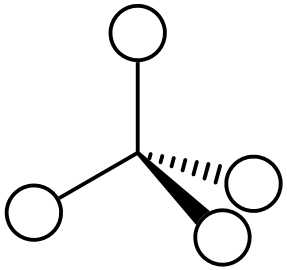
CN = 4

T_d

T_2



A_1

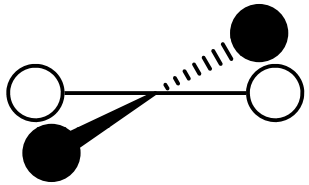


SALCS for Common Geometries *(σ bonding)*

CN = 4

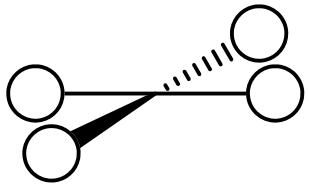
D_{4h}

B_{1g}



E_{u}

A_{1g}

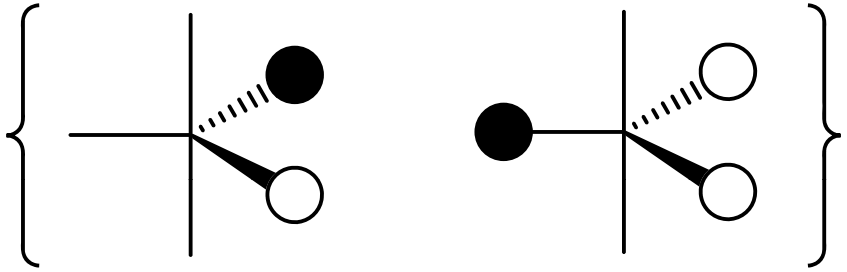


SALCS for Common Geometries *(σ bonding)*

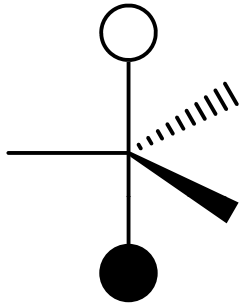
CN = 5

D_{3h}

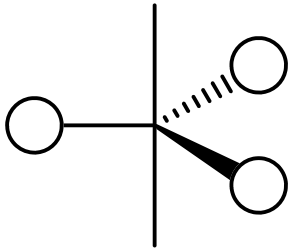
E



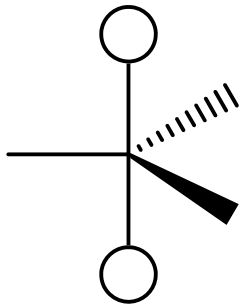
A_2''



A_1'



A_1'

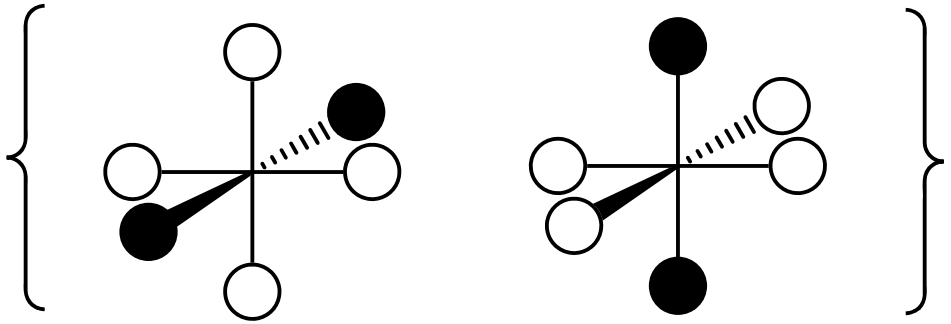


SALCS for Common Geometries *(σ bonding)*

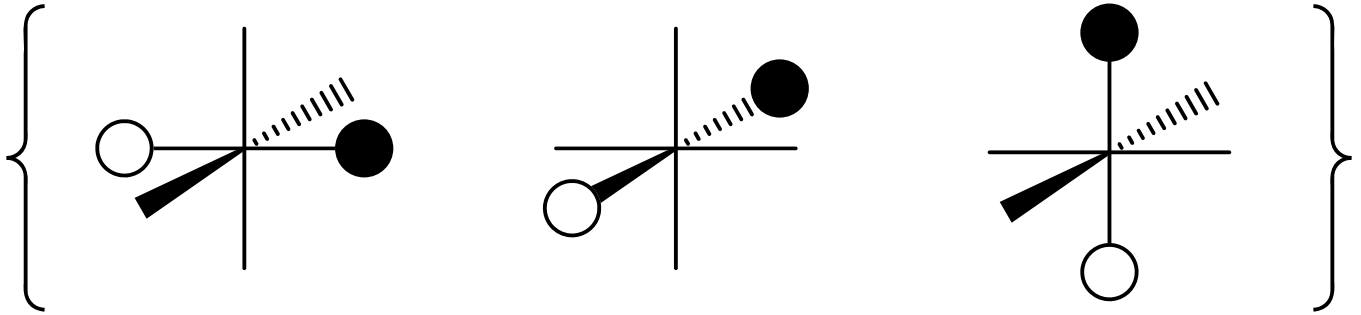
CN = 6

O_h

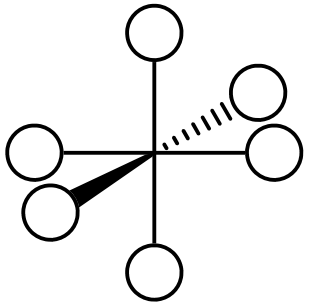
E_g



T_{2g}



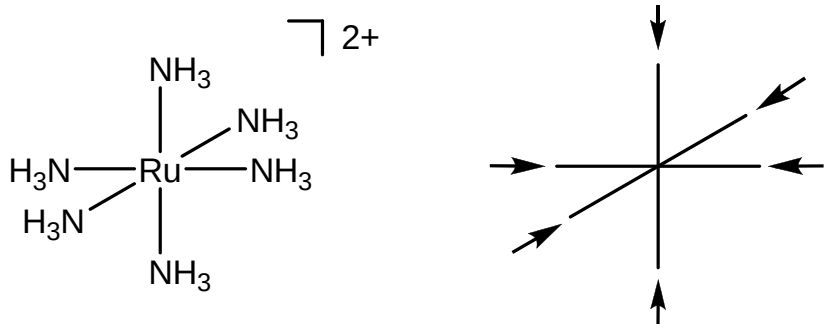
A_{1g}



Construction of MO diagrams for Transition Metal Complexes

σ bonding only scenario

Example: Constructing a MO for Hexammine Ruthenium, $[Ru(NH_3)_6]^{2+}$



point group = O_h

$h = 48$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Σ	Σ/h
Γ_σ	6	0	0	2	2	0	0	0	4	2		
A_{1g}	6	0	0	12	6	0	0	0	12	12	48	1
A_{2g}	6	0	0	-12	6	0	0	0	12	-12	0	0
E_g	12	0	0	0	12	0	0	0	24	0	48	1
T_{1g}	18	0	0	12	-6	0	0	0	-12	-12	0	0
T_{2g}	18	0	0	-12	-6	0	0	0	-12	12	0	0
A_{1u}	6	0	0	12	6	0	0	0	-12	-12	0	0
A_{2u}	6	0	0	-12	6	0	0	0	-12	12	0	0
E_u	12	0	0	0	12	0	0	0	-24	0	0	0
T_{1u}	18	0	0	12	-6	0	0	0	12	12	48	1
T_{2u}	18	0	0	-12	-6	0	0	0	12	-12	0	0

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$

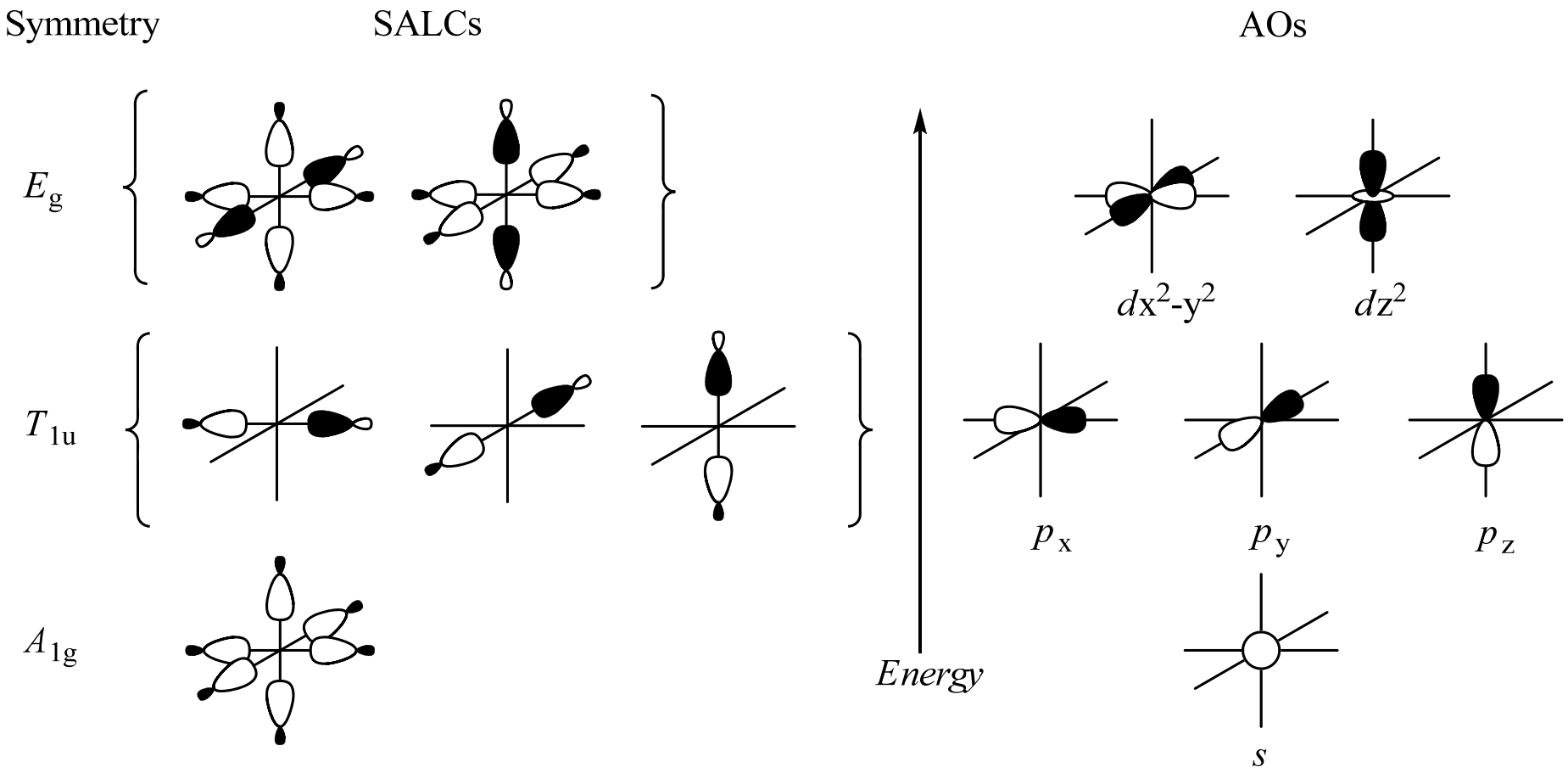
$$d_\Gamma = 1 + 2 + 3 = 6$$

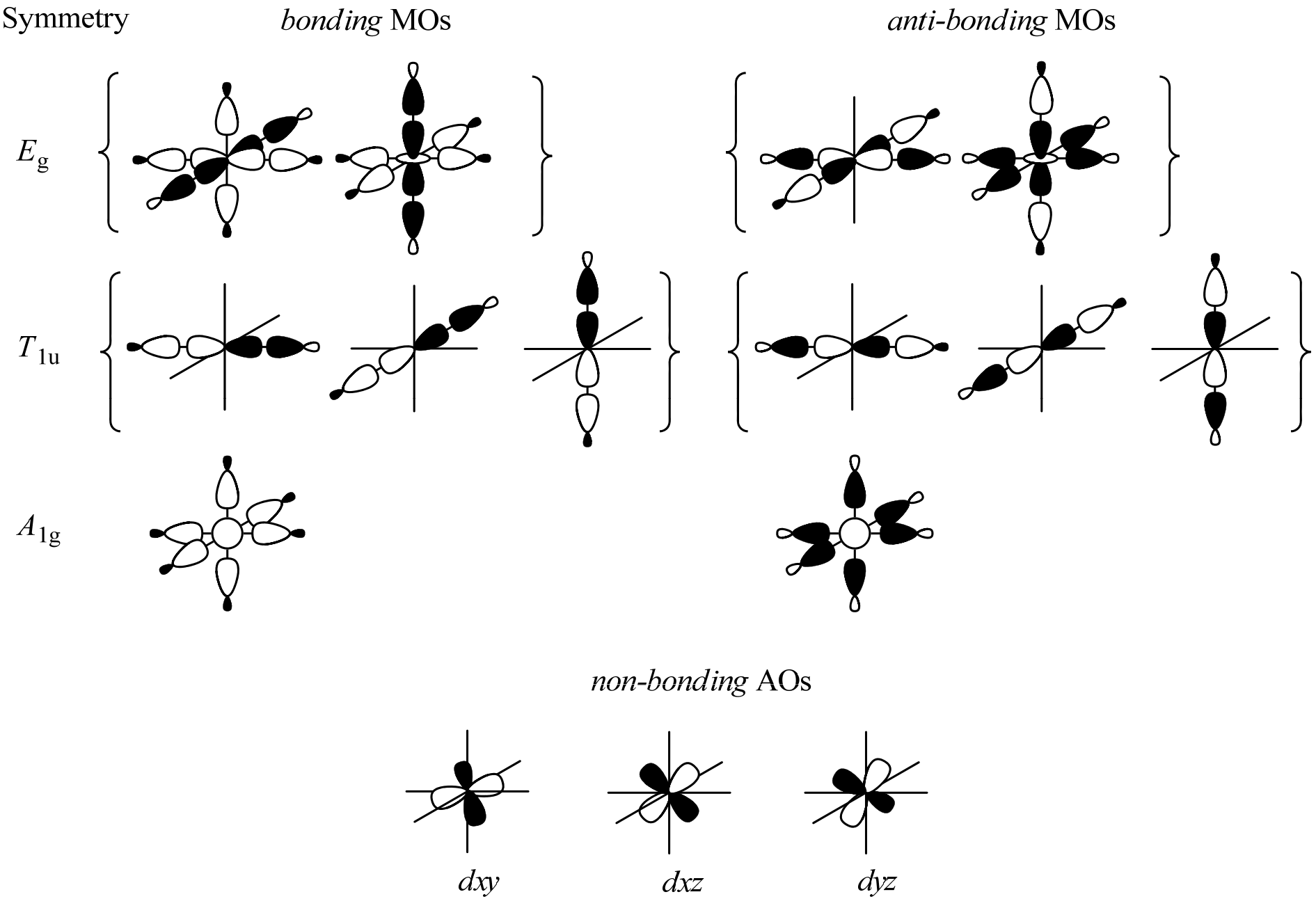
Ru bonding AOs

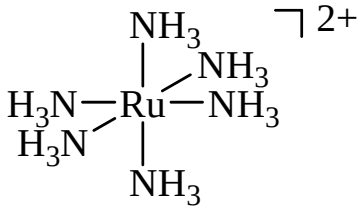
A_{1g} : 5*s*
T_{1u} : (5p_x , 5p_y , 5p_z)
E_g : (4*d*x^2-y^2 , 4*d*z^2)

Pd non-bonding AOs

T_{2g} : (4*d*xy, 4*d*xz, 4*d*yz)

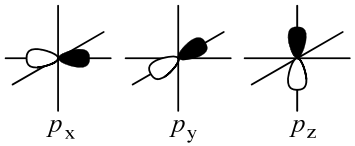

Symmetry
SALCs
AOs
E_g
T_{1u}
A_{1g}
Energy
dx^2-y^2
dz^2
p_x
p_y
p_z
s

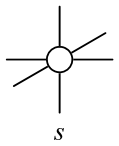

Symmetry
bonding MOs
anti-bonding MOs
E_g
T_{1u}
A_{1g}
non-bonding AOs
dxy
dxz
dyz

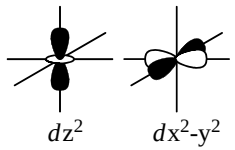

NH3
NH3
H3N
Ru
NH3
H3N
NH3
2+

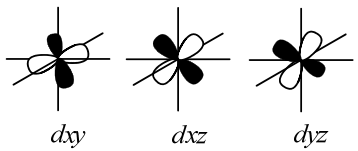
Ru^{2+}

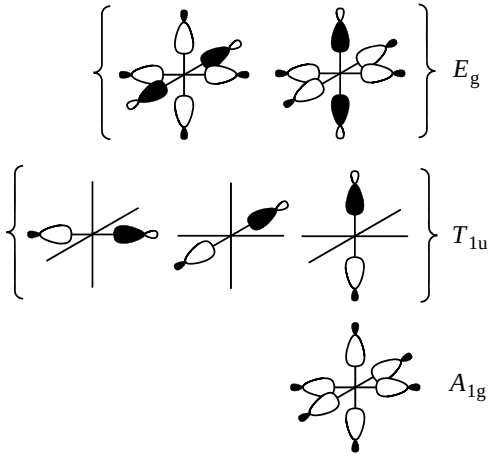
$6NH_3$

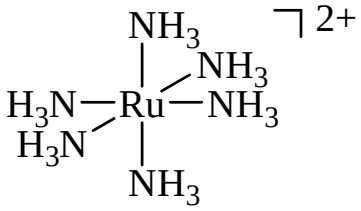

px
py
pz


s


dz2
dx2-y2

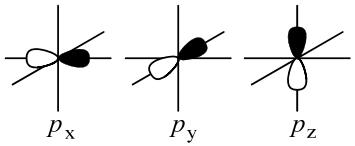

dxy
dxz
dyz


Eg
T1u
A1g

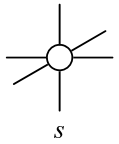


Ru^{2+}

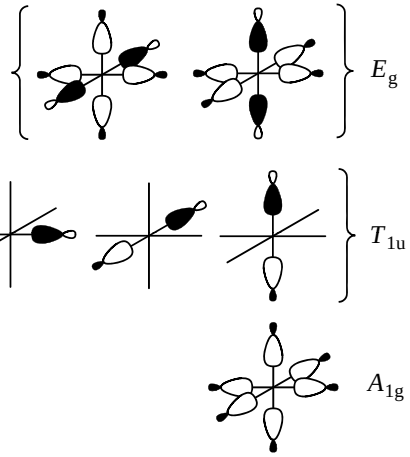
$6NH_3$



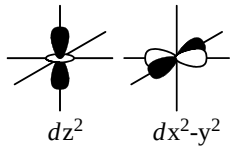
5*p* (t_{1u})

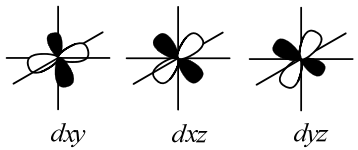


5*s* (a_{1g})



4*d* (t_{2g} , e_g)

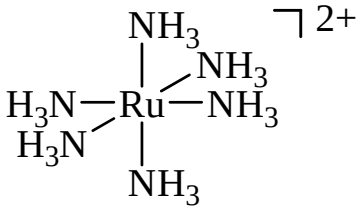




e_g

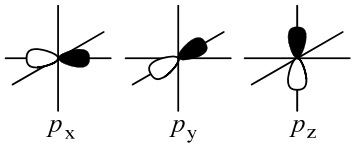
t_{1u}

a_{1g}

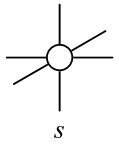


Ru^{2+}

$6NH_3$

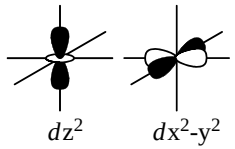


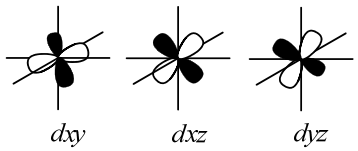
5*p* (t_{1u})

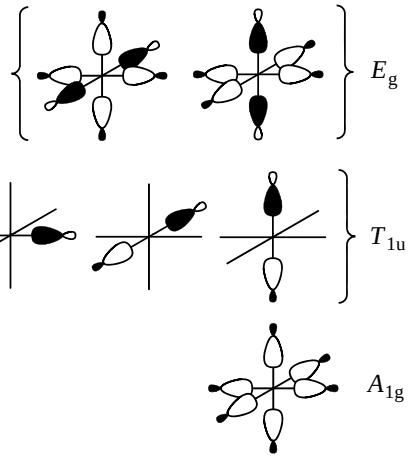


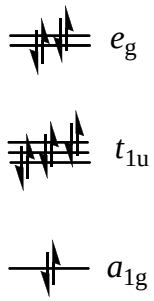
5*s* (a_{1g})

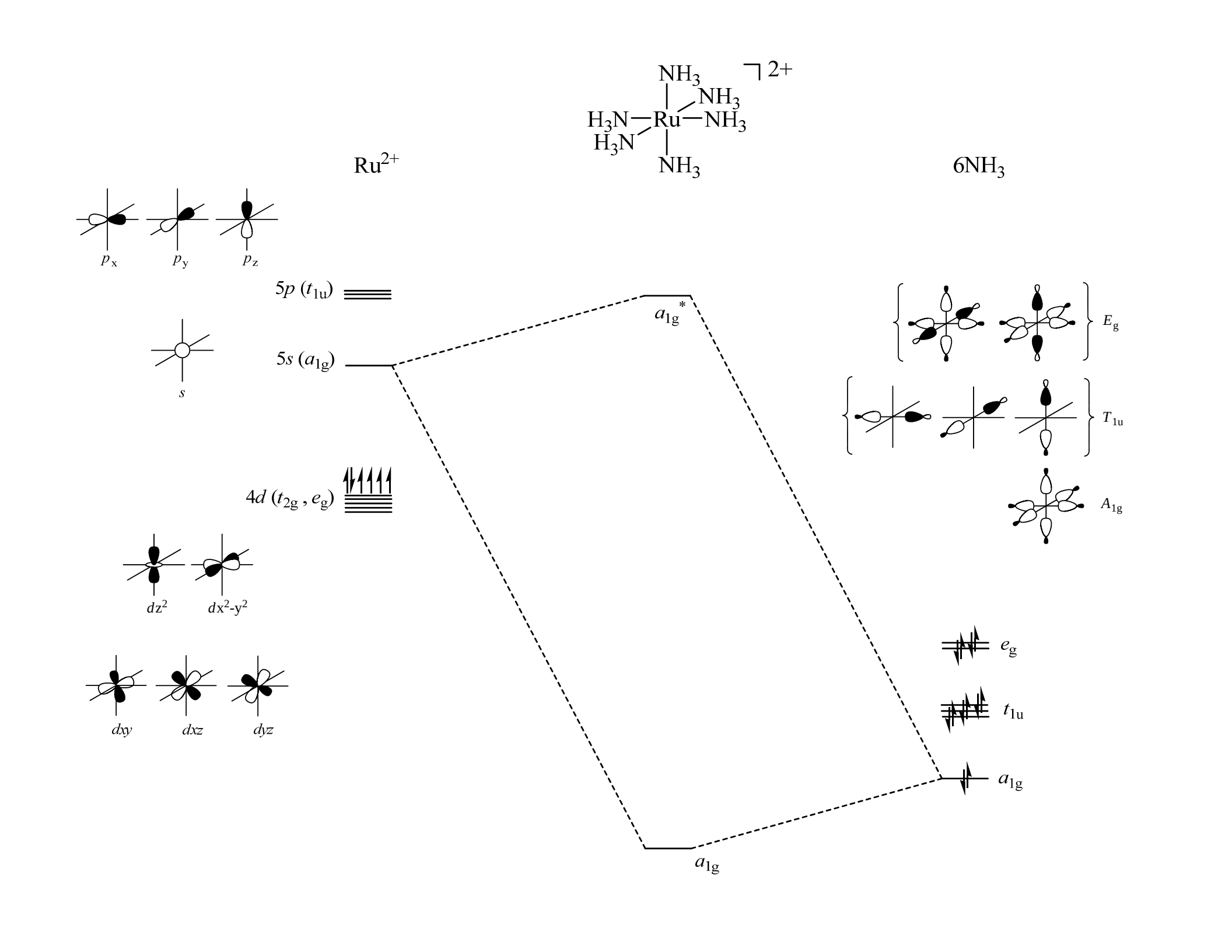
4*d* (t_{2g} , e_g)

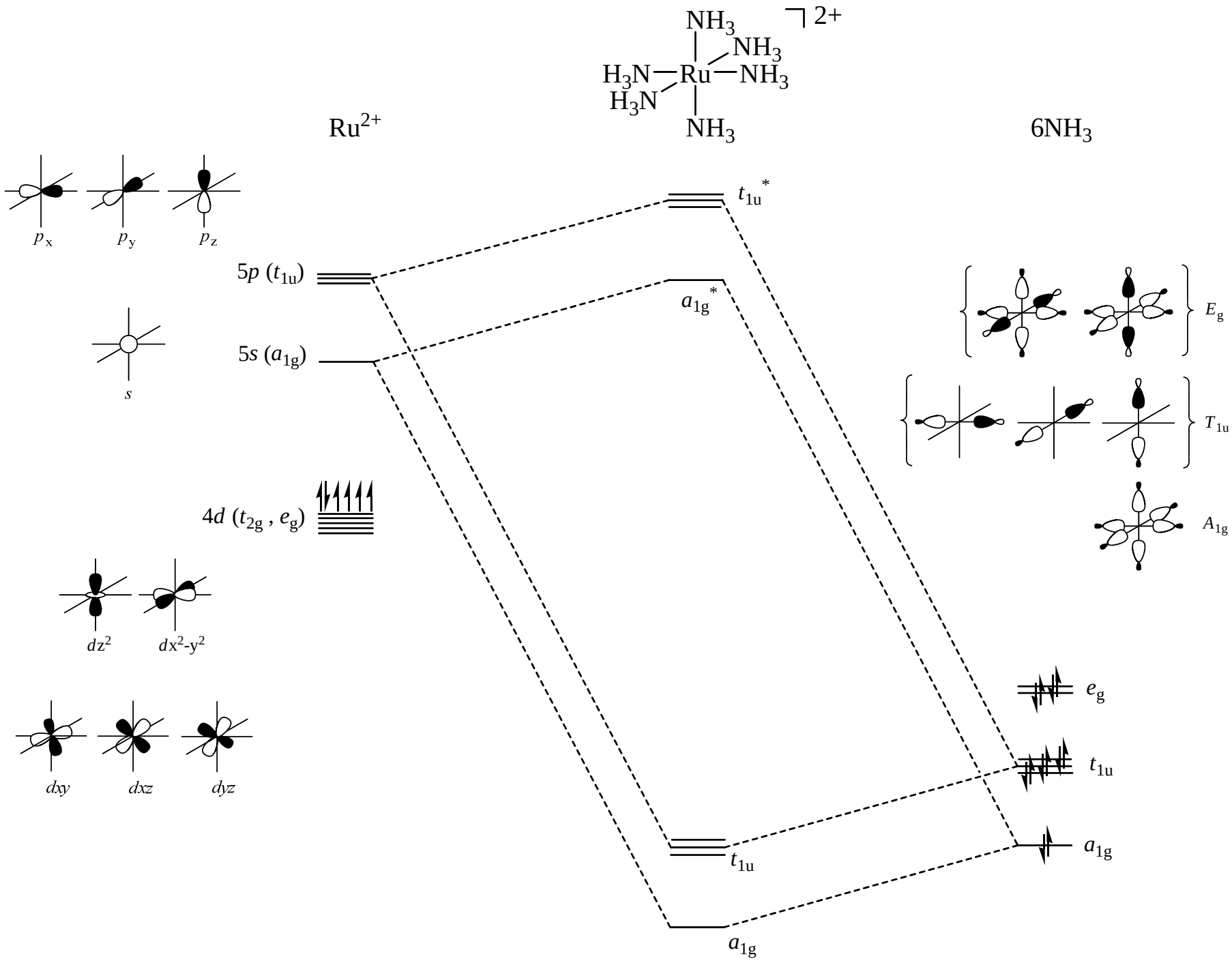


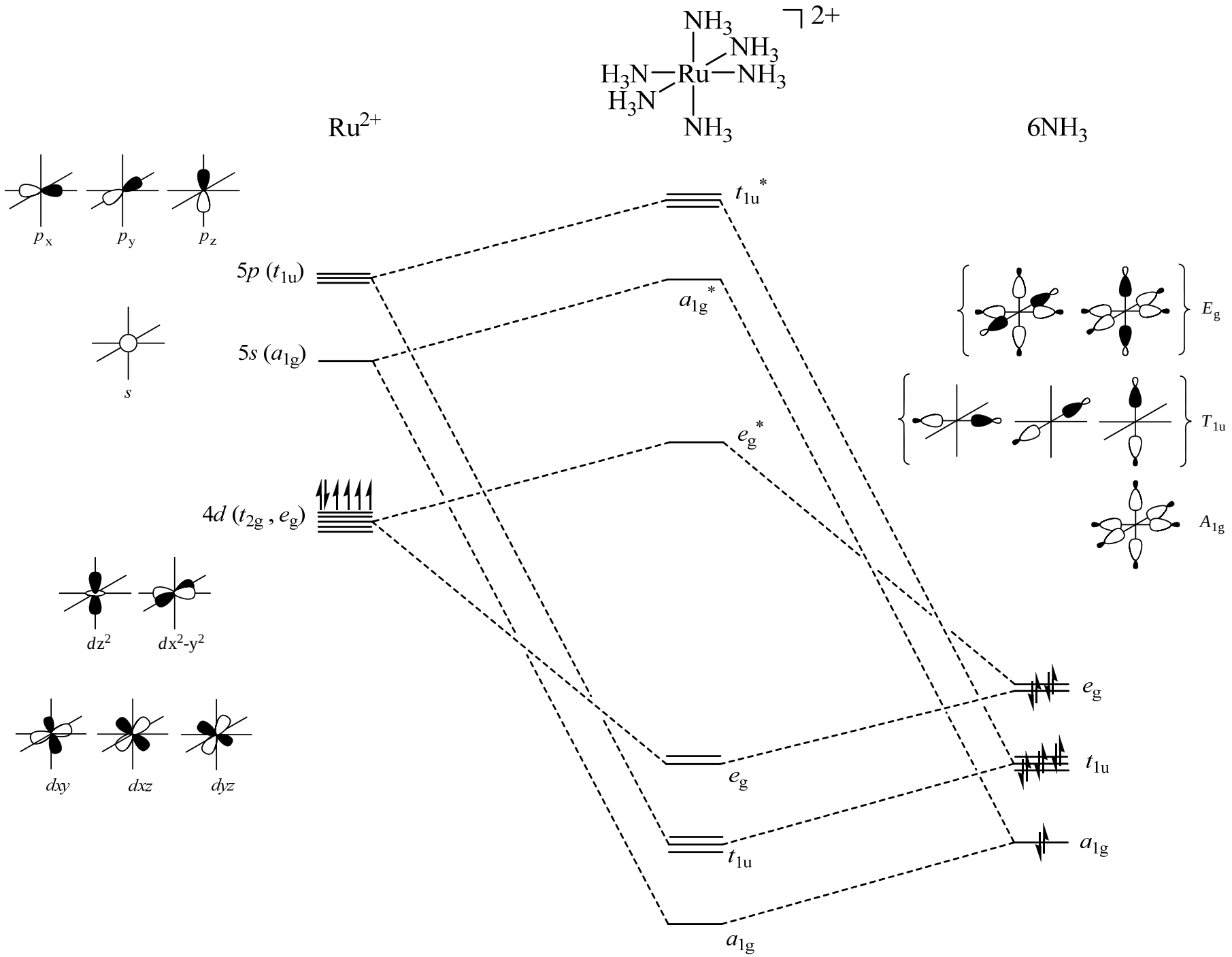


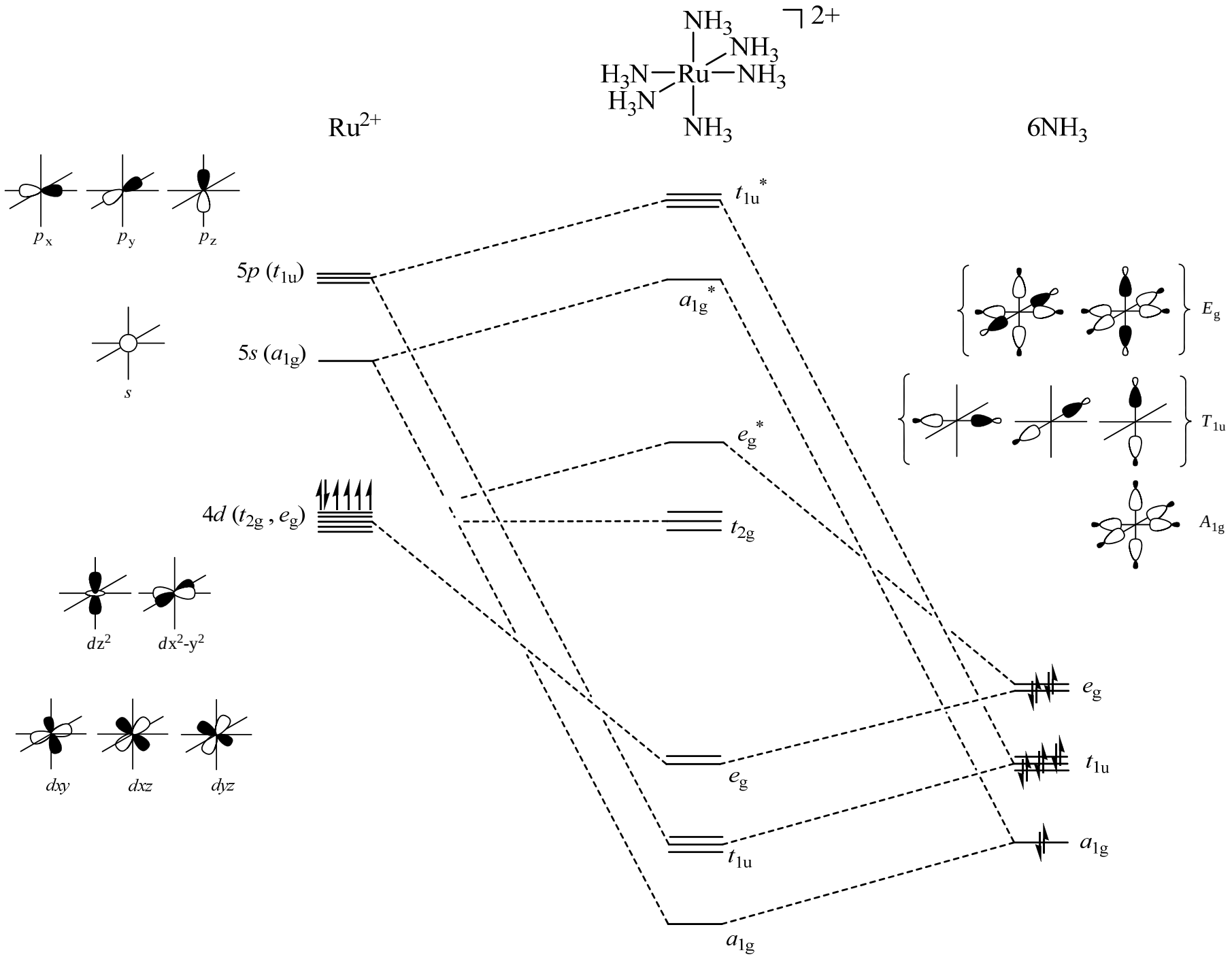


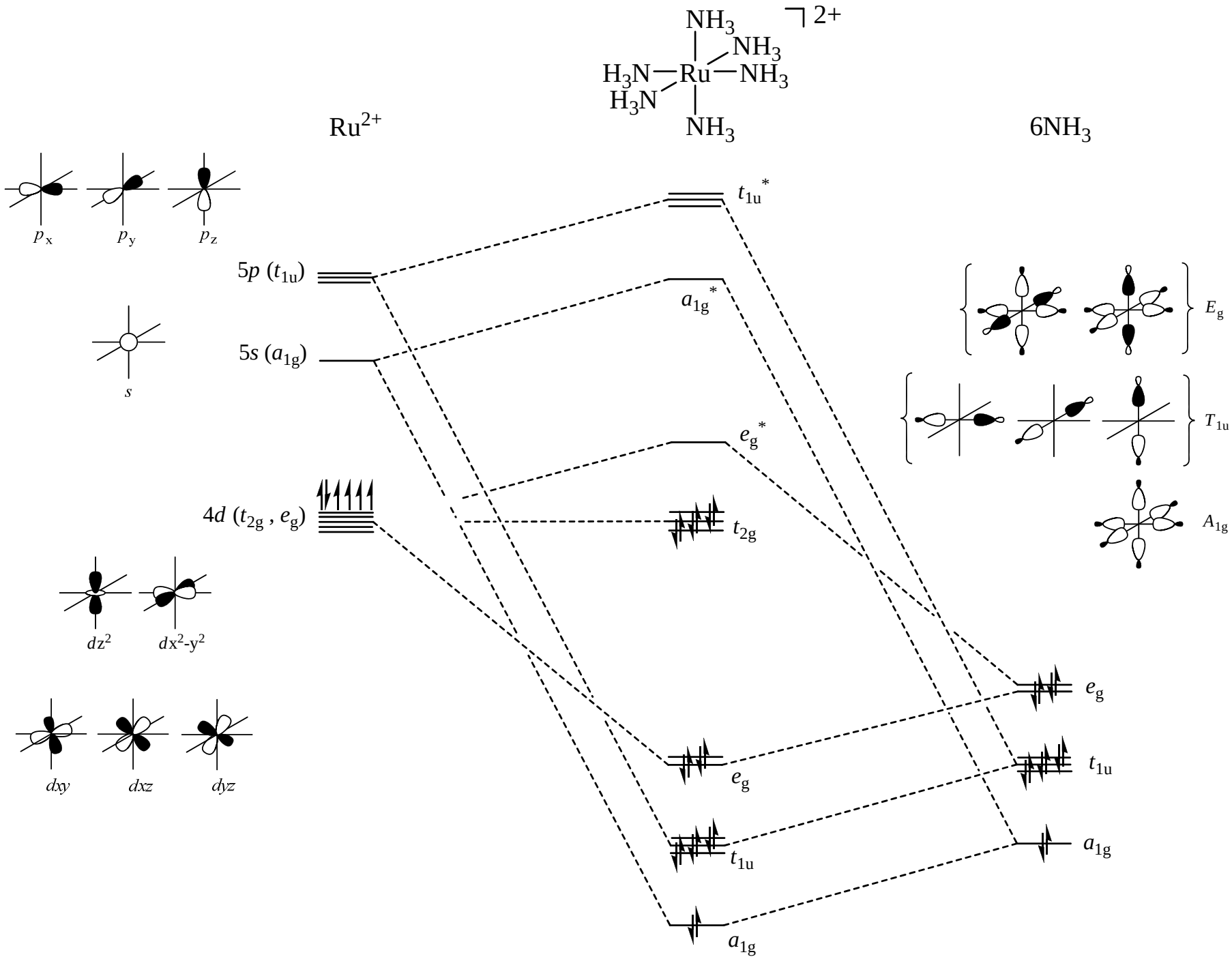


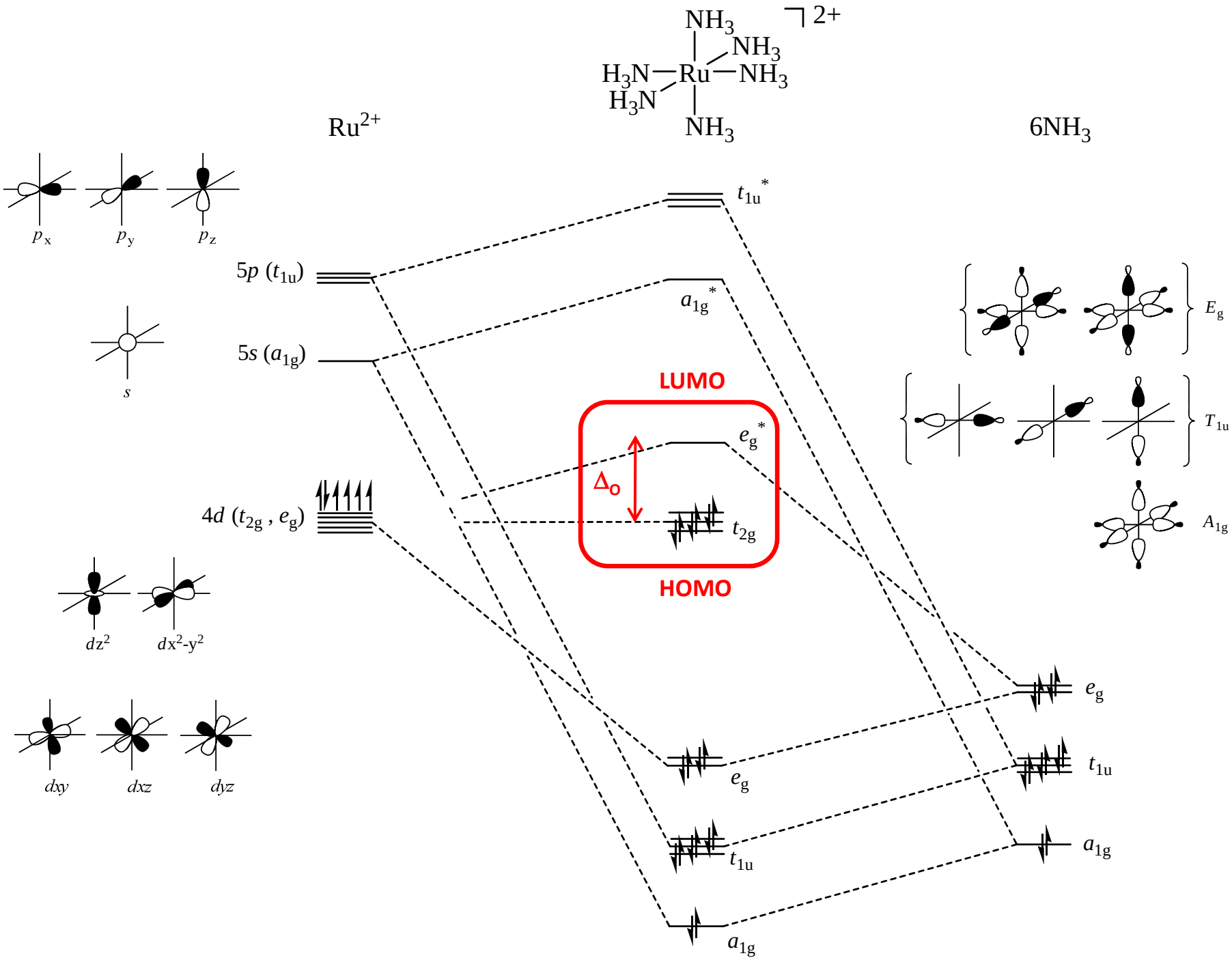

NH3
NH3
H3N—Ru—NH3
H3N
NH3
2+
Ru2+
6NH3
px
py
pz
5p (t1u)
a1g*
Eg
5s (a1g)
s
T1u
A1g
4d (t2g , eg)
dz2
dx2-y2
eg
t1u
a1g
dxy
dxz
dyz
a1g


NH3
NH3
H3N
Ru
NH3
H3N
NH3
2+
Ru2+
6NH3
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
5p (t1u)
5s (a1g)
4d (t2g , eg)
t1u*
a1g*
t1u
a1g
Eg
T1u
A1g
eg
t1u
a1g

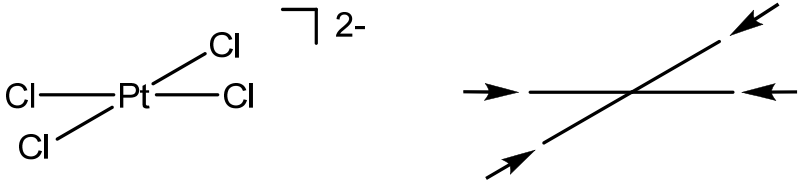

NH3
NH3
H3N—Ru—NH3
H3N
NH3
2+
Ru2+
6NH3
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
5p (t1u)
5s (a1g)
4d (t2g , eg)
t1u*
a1g*
eg*
eg
t1u
a1g
Eg
T1u
A1g
eg
t1u
a1g


NH3
NH3
H3N—Ru—NH3
H3N
NH3
2+
Ru2+
6NH3
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
5p (t1u)
5s (a1g)
4d (t2g , eg)
t1u*
a1g*
eg*
t2g
eg
t1u
a1g
Eg
T1u
A1g
eg
t1u
a1g


NH3
NH3
H3N
Ru
NH3
H3N
NH3
2+
Ru2+
6NH3
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
5p (t1u)
5s (a1g)
4d (t2g , eg)
t1u*
a1g*
eg*
t2g
eg
t1u
a1g
Eg
T1u
A1g
eg
t1u
a1g


NH3
NH3
H3N
Ru
NH3
H3N
NH3
2+
Ru2+
6NH3
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
5p (t1u)
5s (a1g)
4d (t2g , eg)
t1u*
a1g*
eg*
t2g
LUMO
HOMO
Δo
eg
t1u
a1g
Eg
T1u
A1g

Example: Constructing a MO for Platinum Tetrachloride, $[PtCl_4]^{2-}$



point group = D_{4h}

$h = 16$

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	Σ	Σ/h
Γ_σ	4	0	0	2	0	0	0	4	2	0		
A_{1g}	4	0	0	4	0	0	0	4	4	0	16	1
A_{2g}	4	0	0	-4	0	0	0	4	-4	0	0	0
B_{1g}	4	0	0	4	0	0	0	4	4	0	16	1
B_{2g}	4	0	0	-4	0	0	0	4	-4	0	0	0
E_g	8	0	0	0	0	0	0	-8	0	0	0	0
A_{1u}	4	0	0	4	0	0	0	-4	-4	0	0	0
A_{2u}	4	0	0	-4	0	0	0	-4	4	0	0	0
B_{1u}	4	0	0	4	0	0	0	-4	-4	0	0	0
B_{2u}	4	0	0	-4	0	0	0	-4	4	0	0	0
E_u	8	0	0	0	0	0	0	8	0	0	16	1

$$\Gamma_\sigma = A_{1g} + B_{1g} + E_u$$

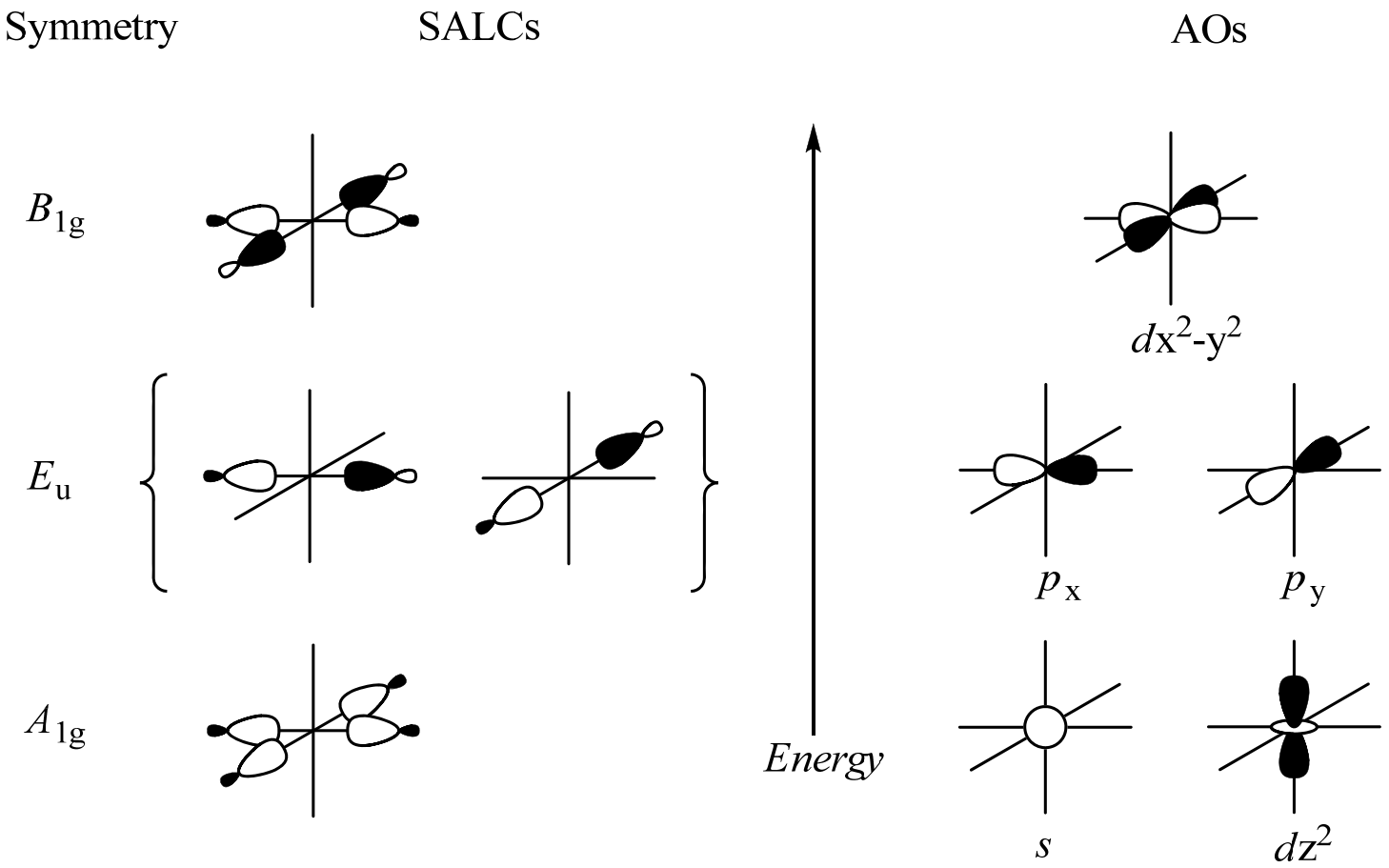
$$d_\Gamma = 1 + 1 + 2 = 4$$

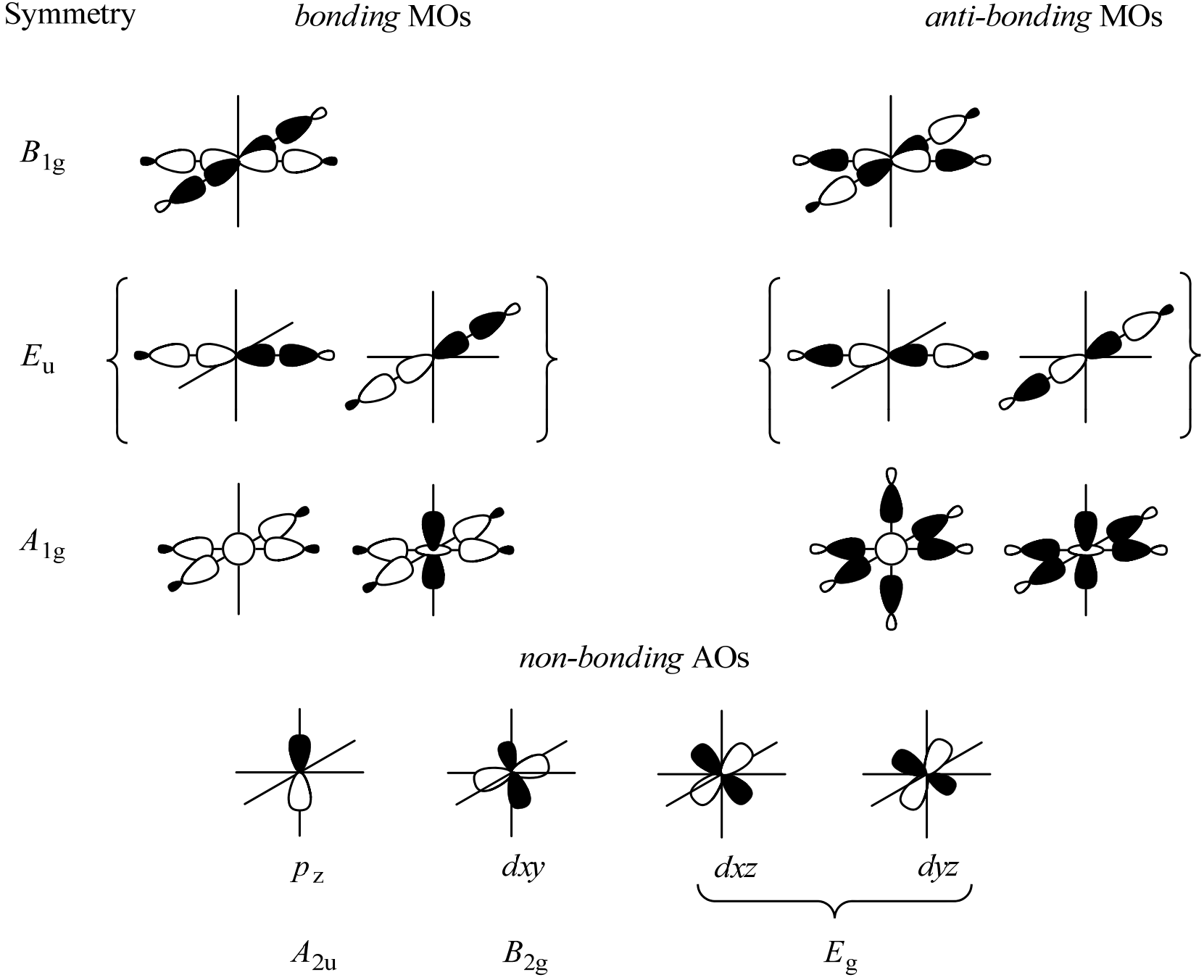
Pt bonding AOs

A_{1g} : 5*s* , 4dz^2
E_u : (5p_x , 5p_y)
B_{1g} : 4*d*x^2-y^2

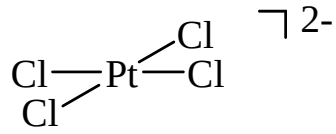
Pd non-bonding AOs

A_{2u} : 5p_z
B_{2g} : 4*d*xy
E_g : (4*dxz*, 4*dyz*)

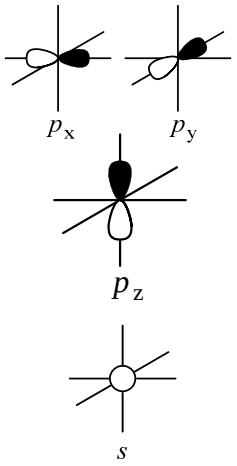

Symmetry
SALCs
AOs
B_{1g}
E_u
A_{1g}
Energy
dx^2-y^2
p_x
p_y
s
dz^2

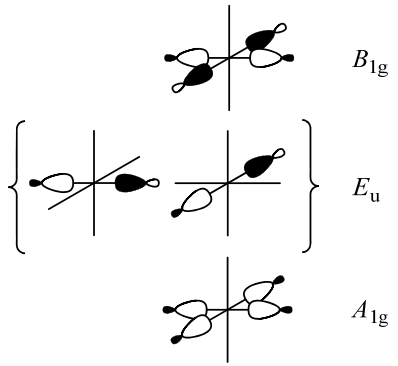

Symmetry
bonding MOs
anti-bonding MOs
B_{1g}
E_u
A_{1g}
non-bonding AOs
p_z
dxy
dxz
dyz
A_{2u}
B_{2g}
E_g

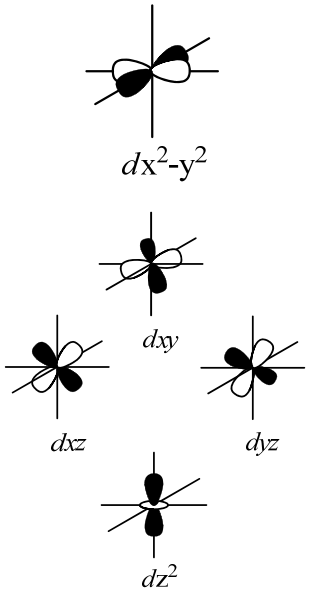
Pt^{2+}



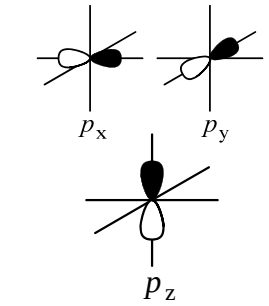
$4Cl^-$



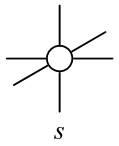




Pt^{2+}

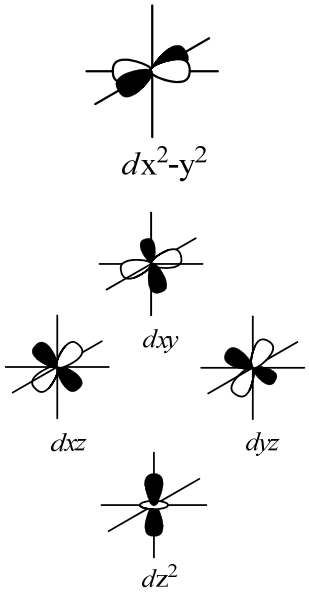


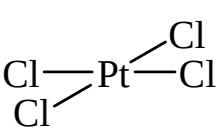
5*p* (a_{2u} , e_u)



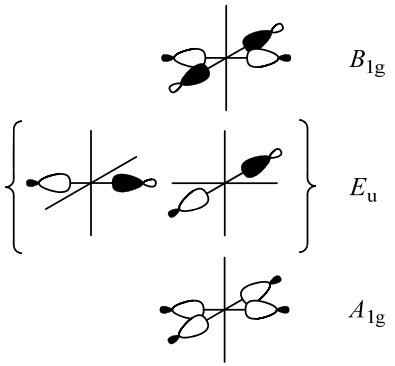
5*s* (a_{1g})

4*d* (a_{1g} , b_{1g} , b_{2g} , e_g)





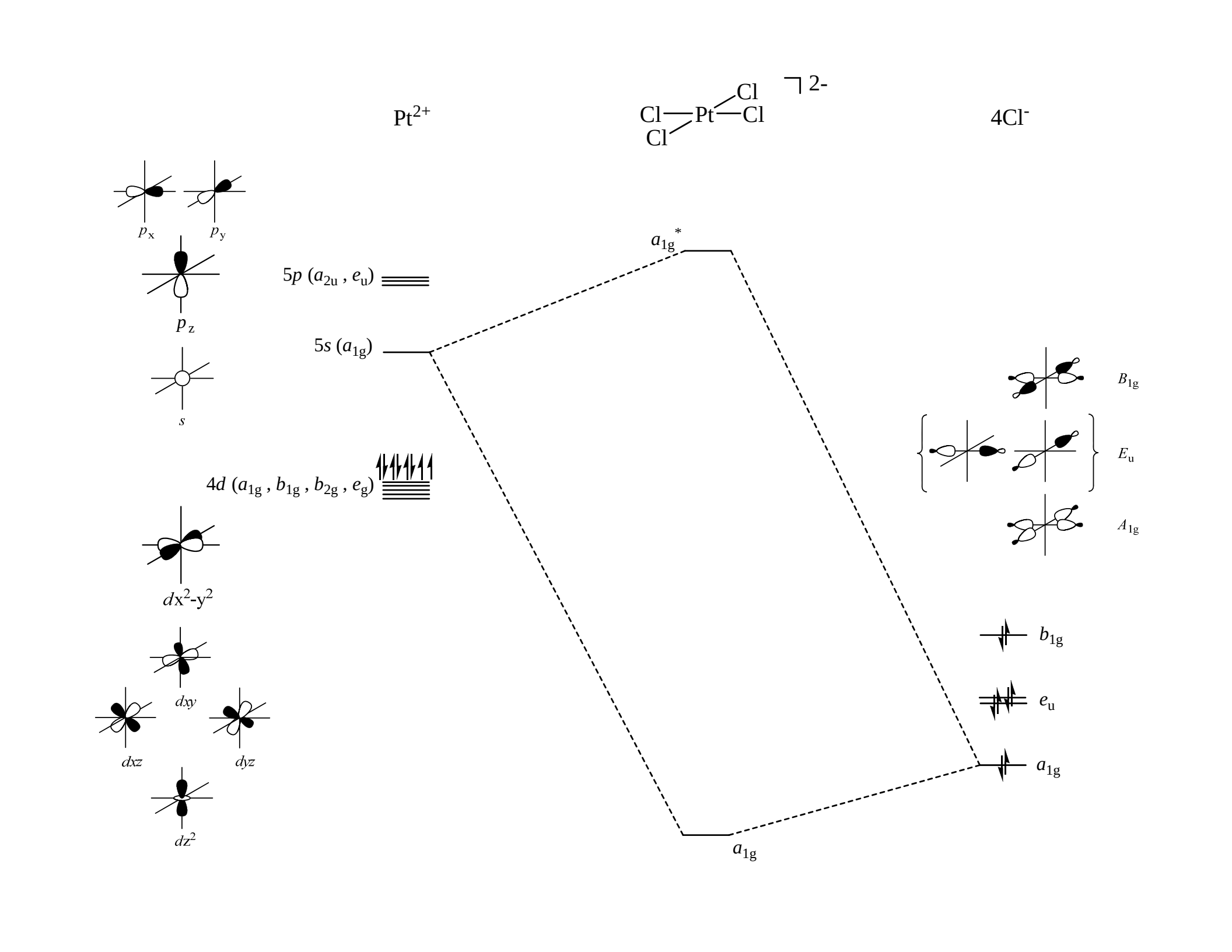
$4Cl^-$

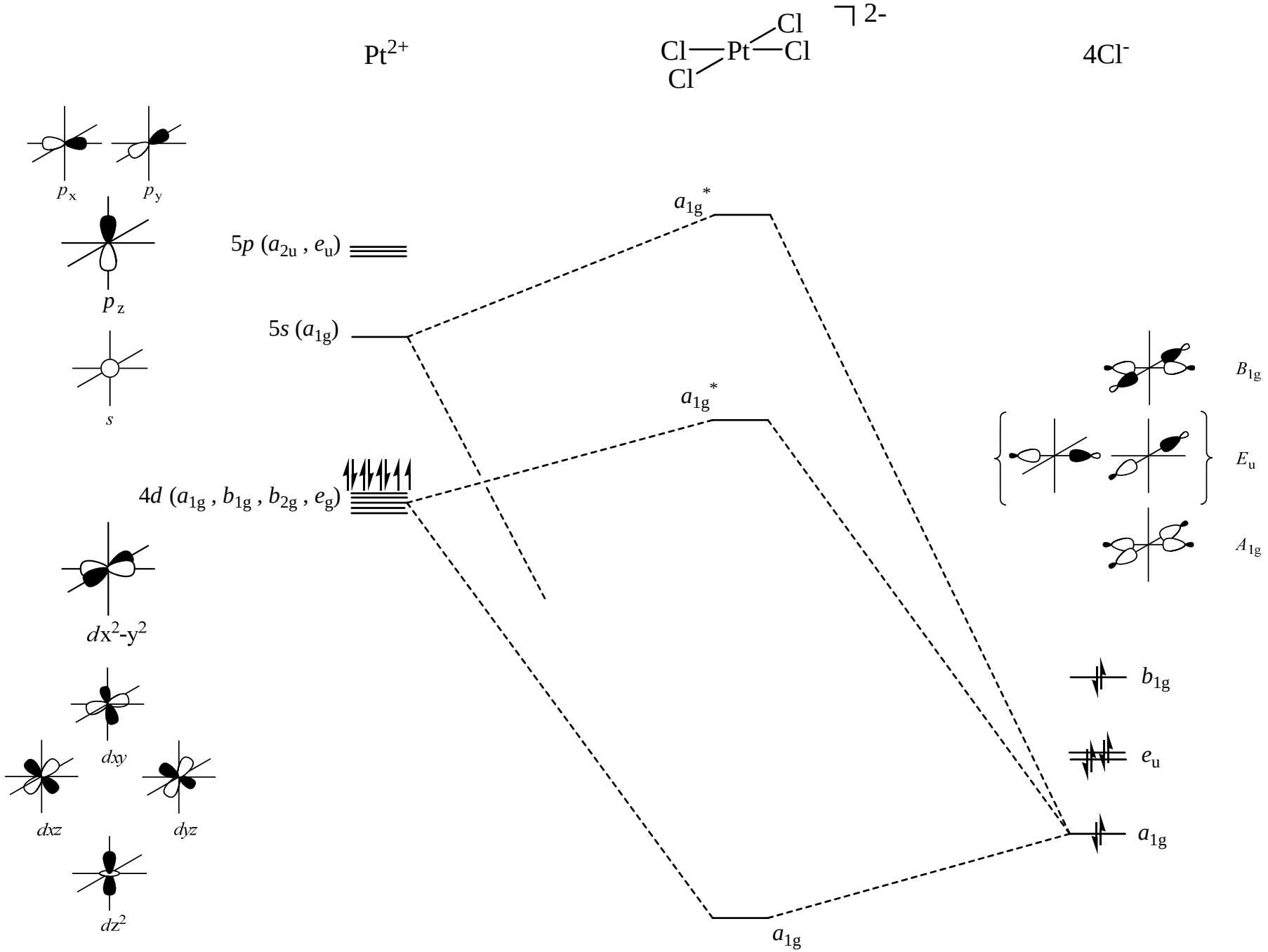


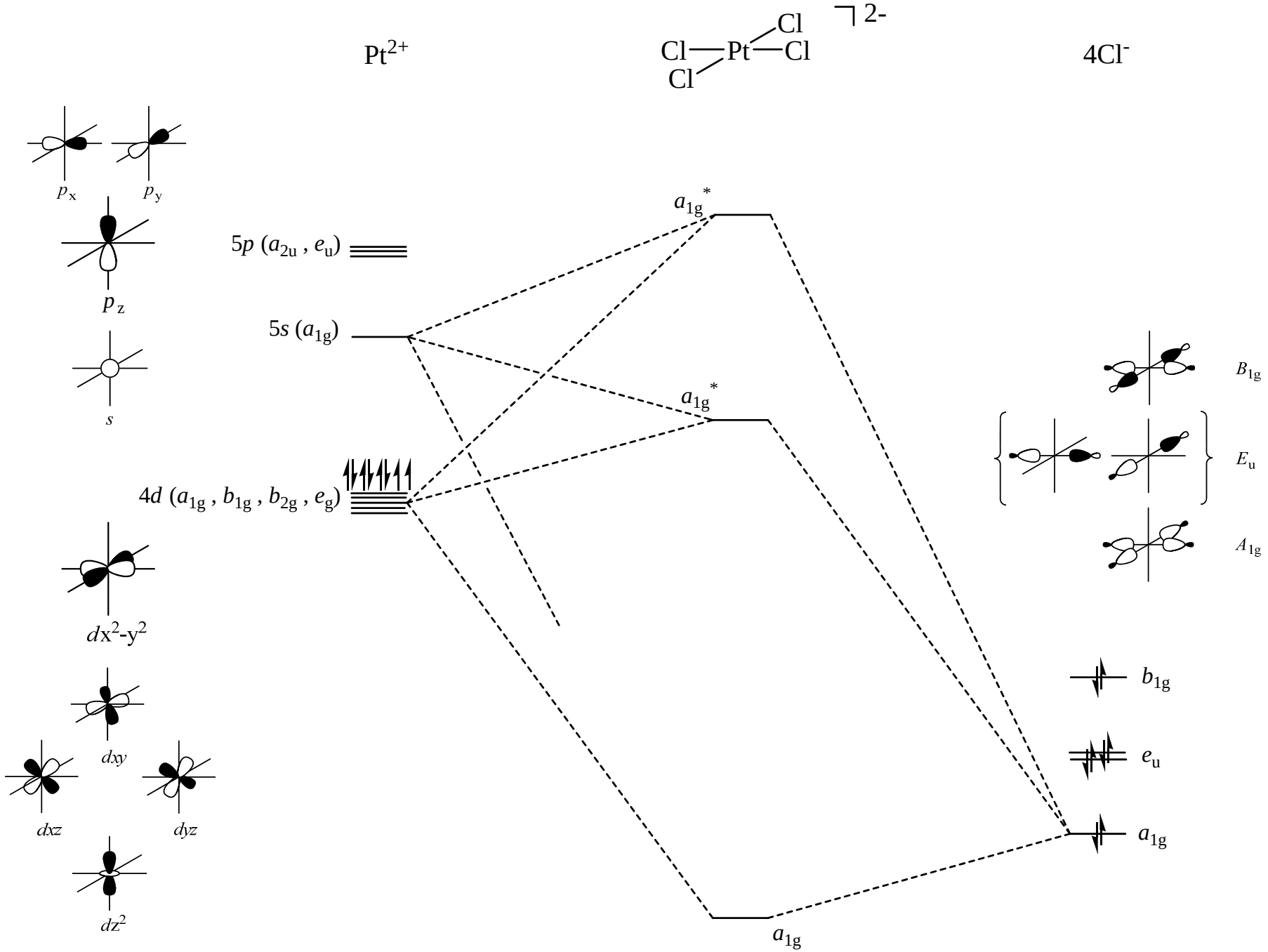
b_{1g}

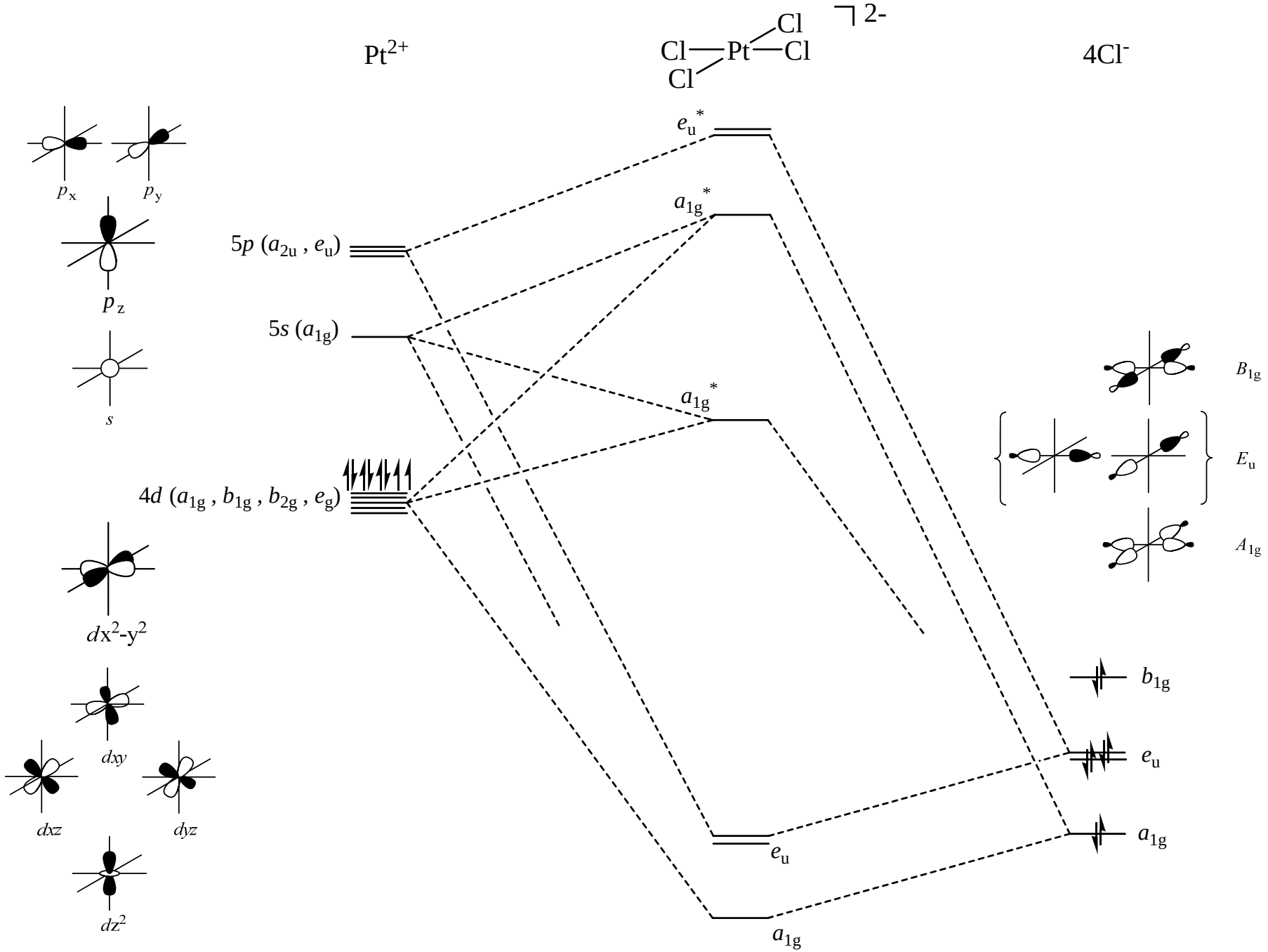
e_u

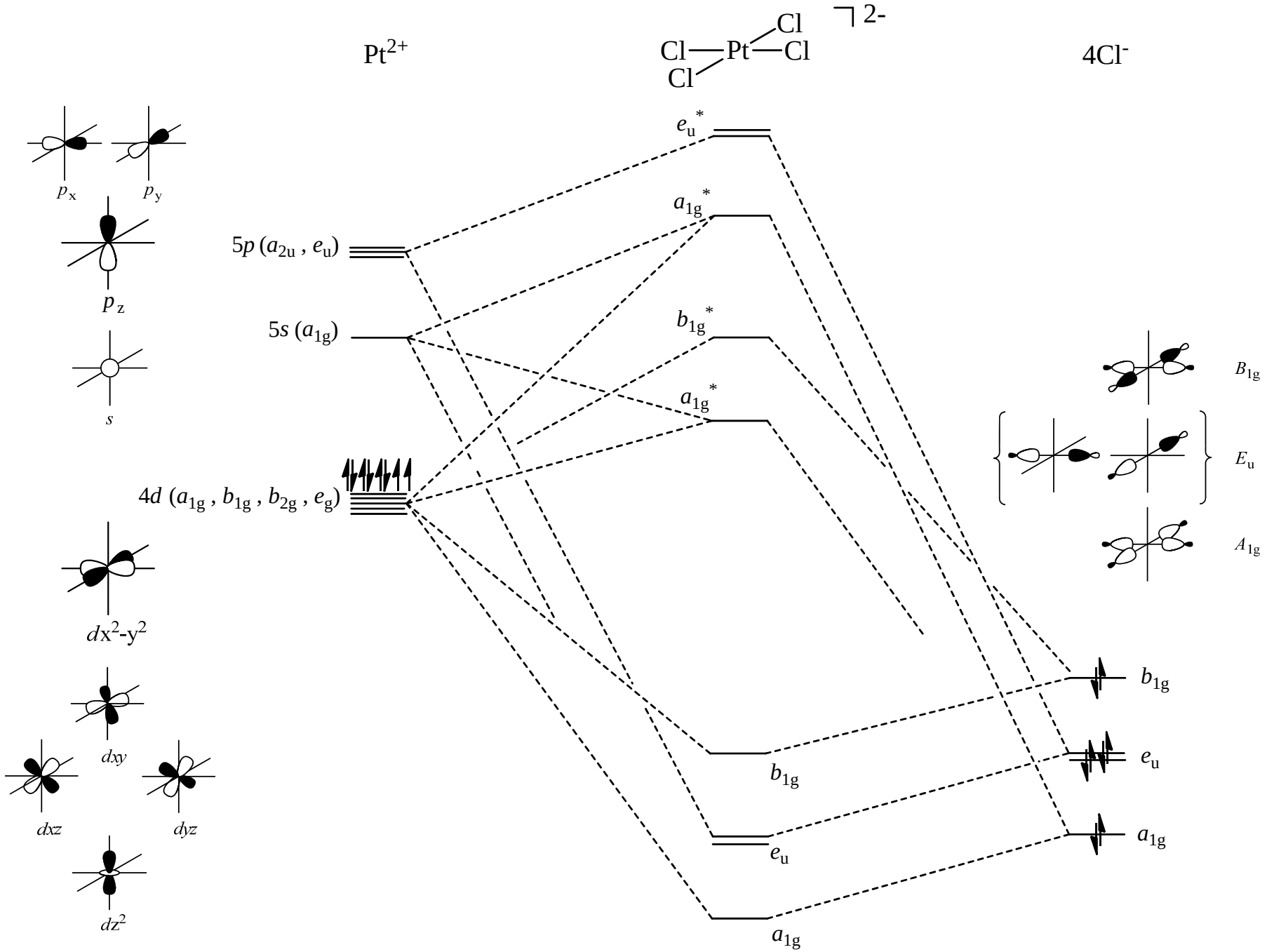
a_{1g}

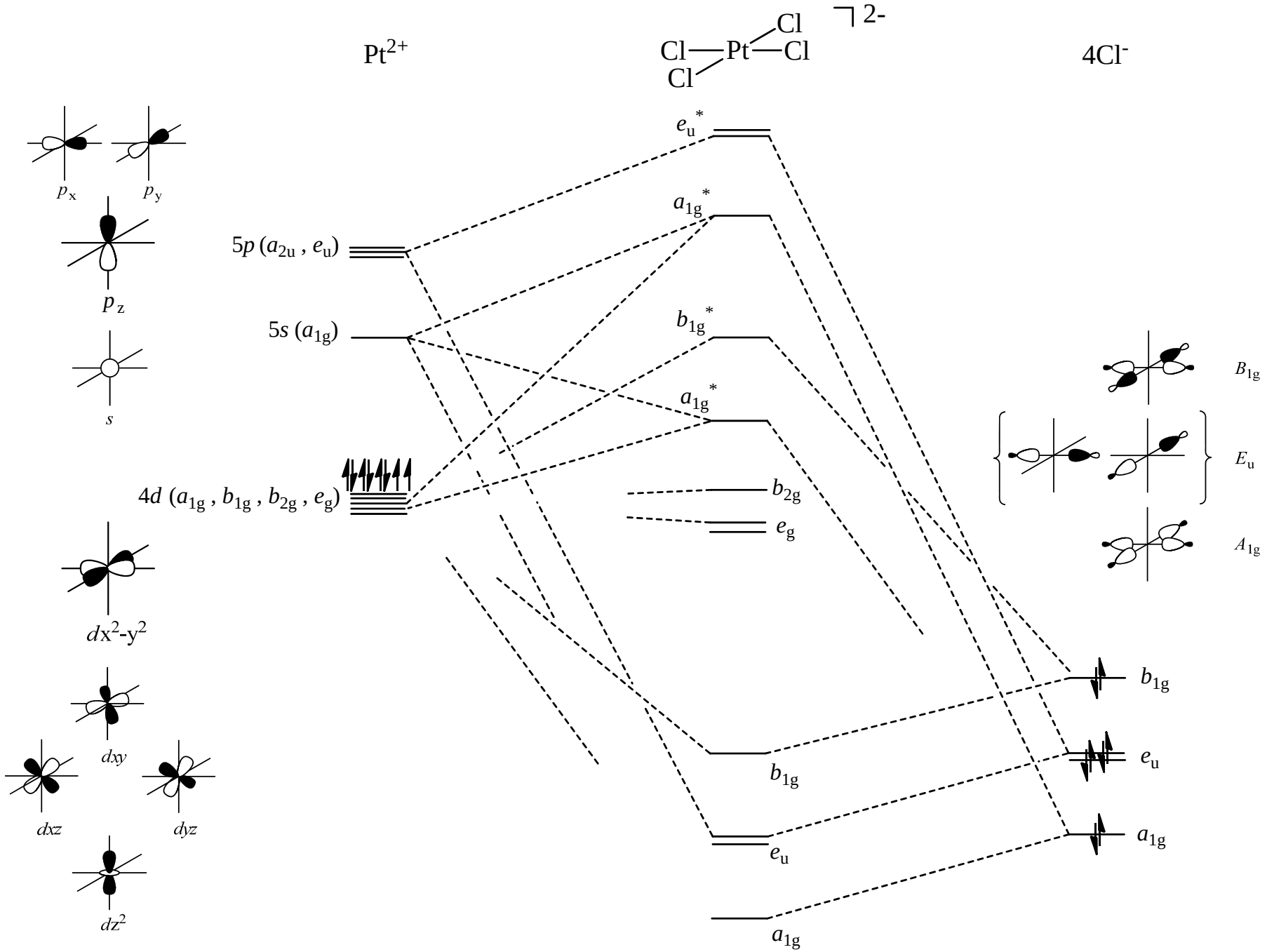

Pt2+
Cl
Cl
Pt
Cl
Cl
2-
4Cl-
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2
5p (a2u , eu)
5s (a1g)
4d (a1g , b1g , b2g , eg)
a1g*
a1g
B1g
Eu
A1g
b1g
eu
a1g


Pt2+
Cl
Cl—Pt—Cl
Cl
2-
4Cl-
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2
5p (a2u , eu)
5s (a1g)
4d (a1g , b1g , b2g , eg)
a1g*
a1g*
a1g
B1g
Eu
A1g
b1g
eu
a1g


Pt2+
Cl
Cl
Pt
Cl
Cl
2-
4Cl-
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2
5p (a2u , eu)
5s (a1g)
4d (a1g , b1g , b2g , eg)
a1g*
a1g*
a1g
B1g
Eu
A1g
b1g
eu
a1g


Pt2+
Cl
Cl
Pt
Cl
Cl
2-
4Cl-
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2
5p (a2u , eu)
5s (a1g)
4d (a1g , b1g , b2g , eg)
eu*
a1g*
a1g*
eu
a1g
B1g
Eu
A1g
b1g
eu
a1g


Pt2+
Cl
Cl—Pt—Cl
Cl
2-
4Cl-
eu*
a1g*
b1g*
a1g*
5p (a2u , eu)
5s (a1g)
4d (a1g , b1g , b2g , eg)
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2
B1g
Eu
A1g
b1g
eu
a1g
b1g
eu
a1g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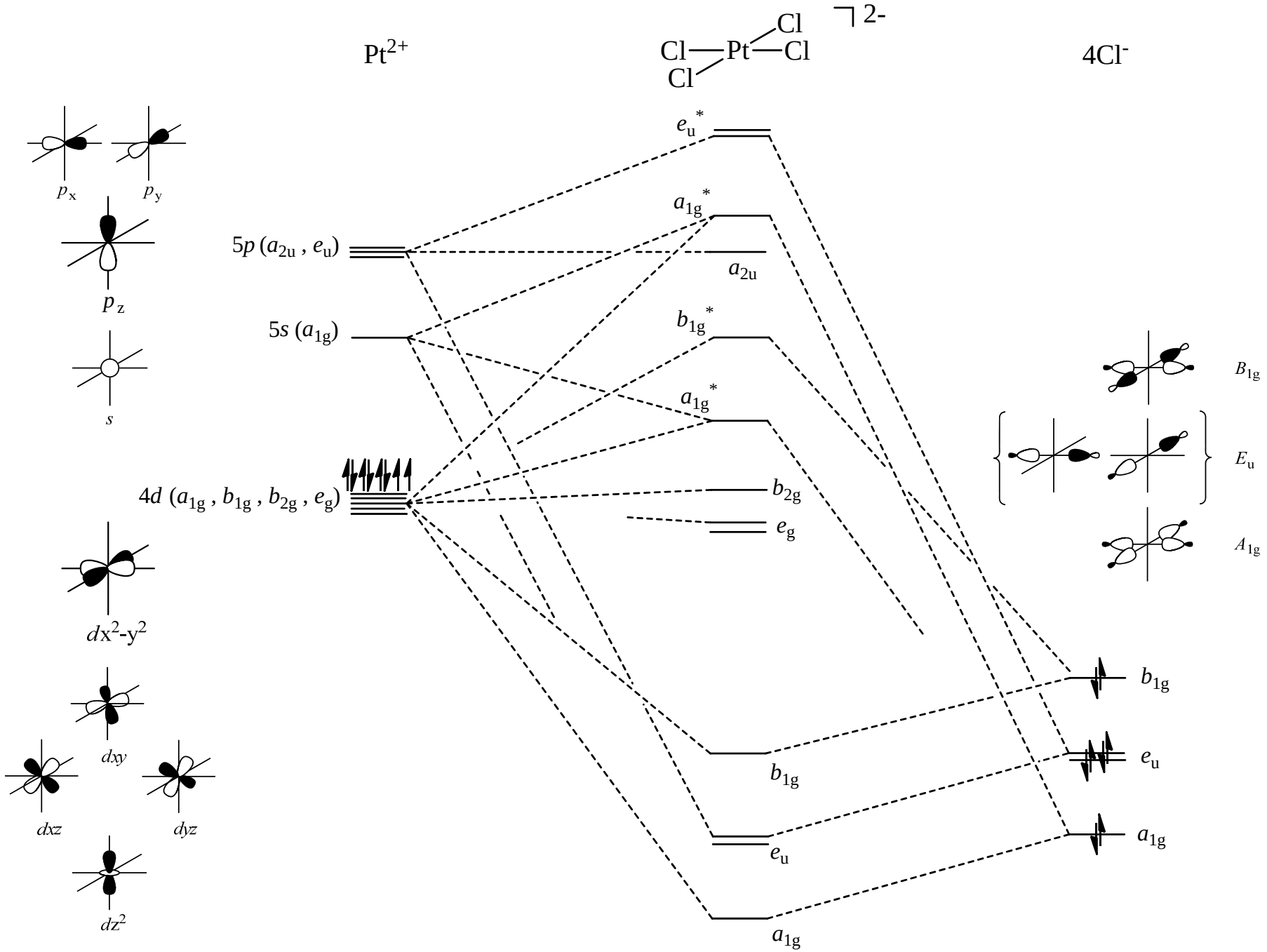
Cl
Cl—Pt—Cl
Cl
2-
4Cl-
eu*
a1g*
5p (a2u , eu)
5s (a1g)
b1g*
a1g*
4d (a1g , b1g , b2g , eg)
b2g
eg
b1g
eu
a1g
B1g
Eu
A1g
b1g
eu
a1g
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2


Pt2+
Cl
Cl—Pt—Cl
Cl
2-
4Cl-
eu*
a1g*
5p (a2u , eu)
a2u
5s (a1g)
b1g*
a1g*
4d (a1g , b1g , b2g , eg)
b2g
eg
b1g
eu
a1g
B1g
Eu
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eu
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dx2-y2
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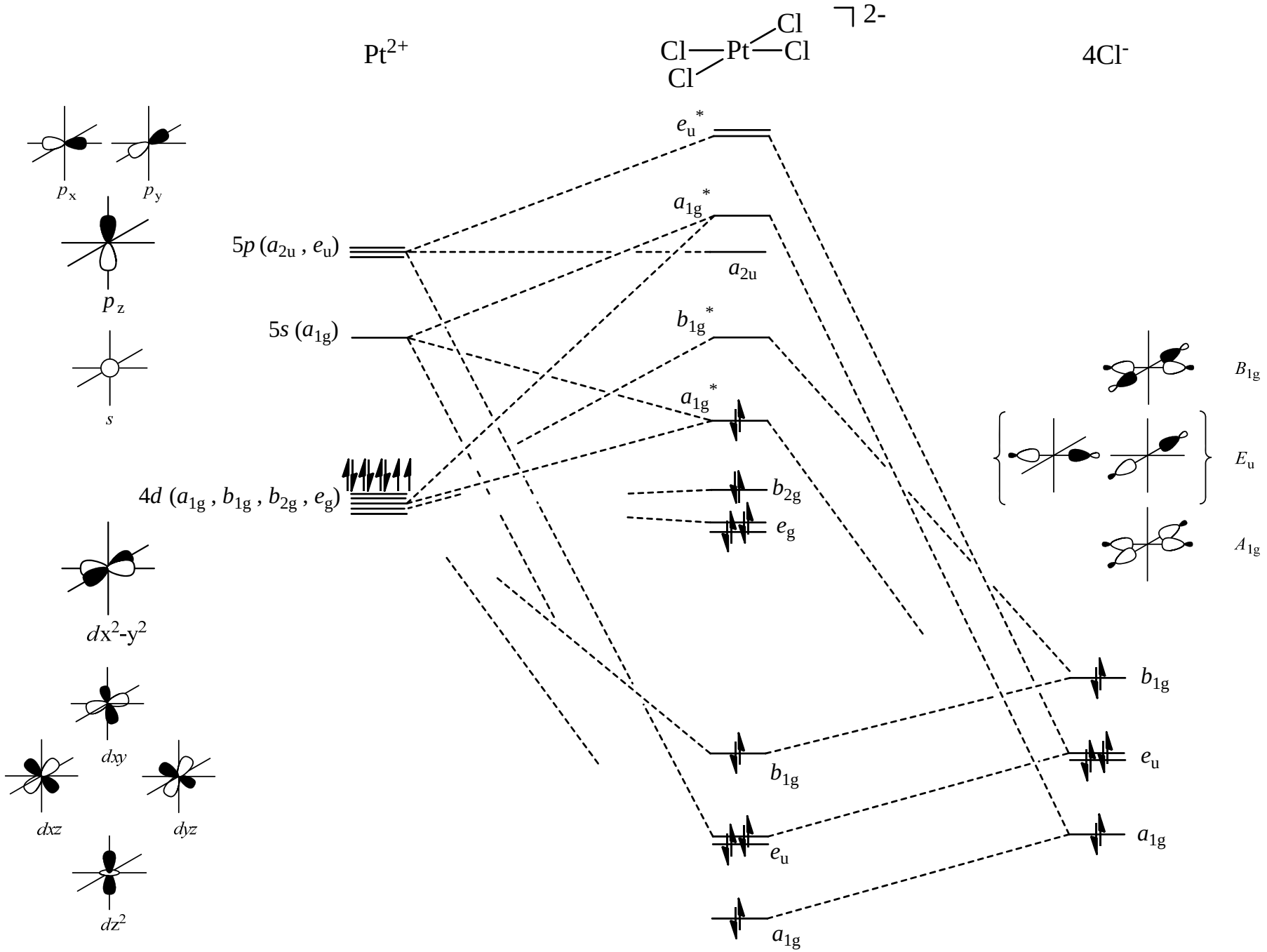
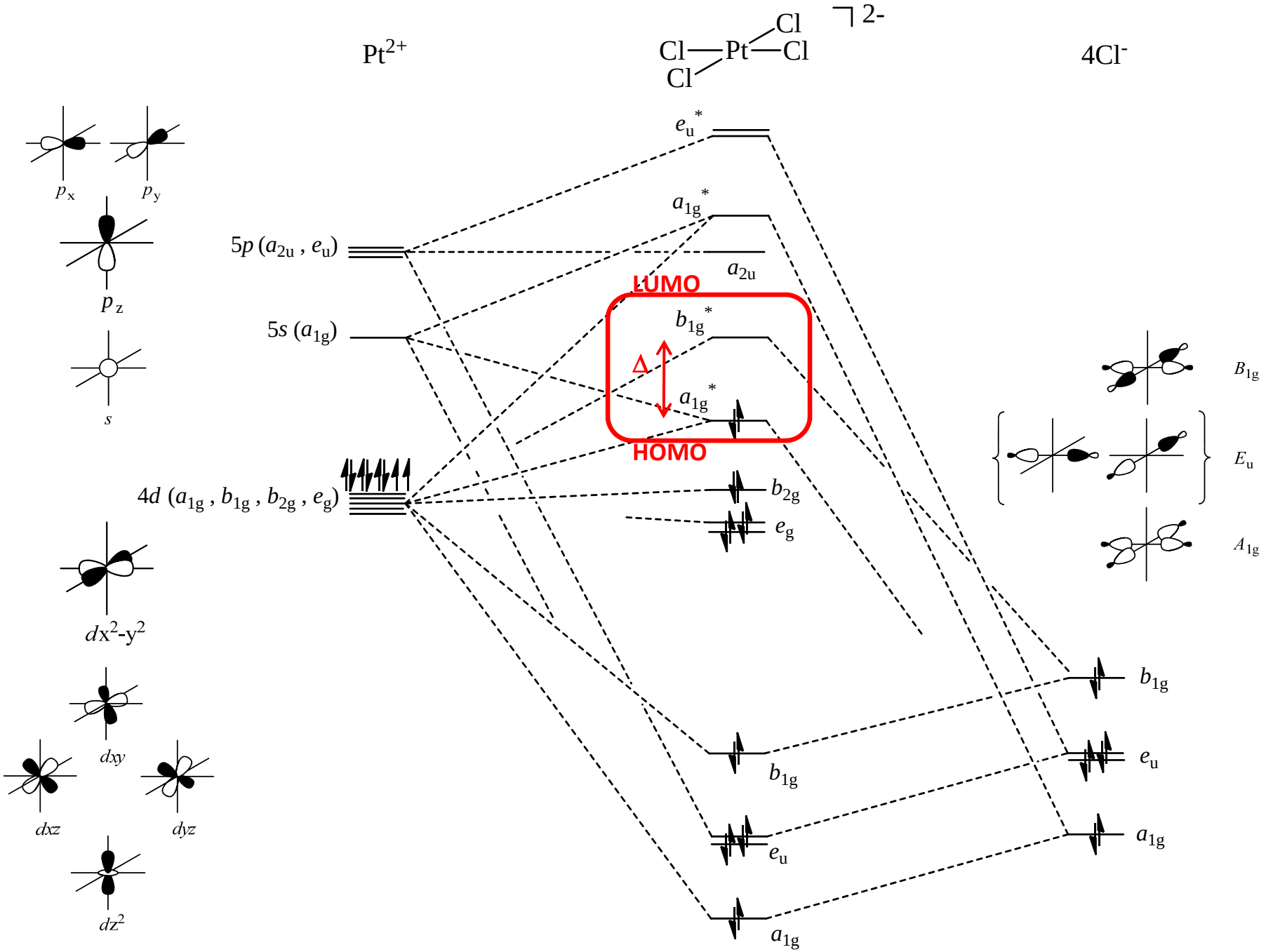
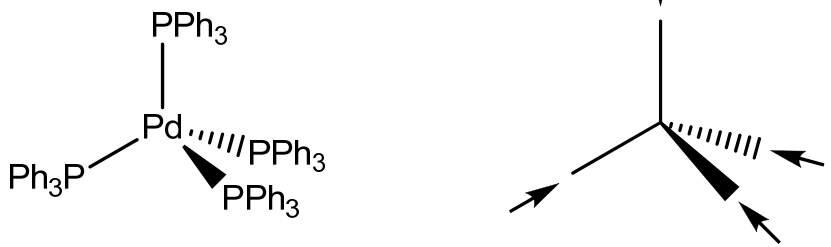
dz2


Pt2+
Cl
Cl—Pt—Cl
Cl
2-
4Cl-
eu*
a1g*
5p (a2u , eu)
a2u
5s (a1g)
b1g*
a1g*
4d (a1g , b1g , b2g , eg)
b2g
eg
b1g
eu
a1g
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2
B1g
Eu
A1g


Pt2+
Cl
Cl—Pt—Cl
Cl
2-
4Cl-
px
py
pz
s
dx2-y2
dxy
dxz
dyz
dz2
5p (a2u , eu)
5s (a1g)
4d (a1g , b1g , b2g , eg)
eu*
a1g*
a2u
LUMO
b1g*
Δ
a1g*
HOMO
b2g
eg
b1g
eu
a1g
B1g
Eu
A1g
b1g
eu
a1g

Example: Constructing a MO for Tetrakis(triphenylphosphine)Palladium, $Pd(PPh_3)_4$



point group = T_d

$$\Gamma_\sigma = A_1 + T_2$$

$$d_\Gamma = 1 + 3 = 4$$

$h = 24$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Σ	Σ/h
Γ_σ	4	1	0	0	2		
A_1	4	8	0	0	12	24	1
A_2	4	8	0	0	-12	0	0
E_1	8	-8	0	0	0	0	0
T_1	12	0	0	0	-12	0	0
T_2	12	0	0	0	12	24	1

Pd bonding AOs

A_1 : 6*s*
T_2 : (6p_x , 6p_y , 6p_z)
(5*d*xy, 5*d*xz, 5*d*yz)

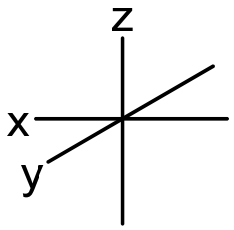
Pd non-bonding AOs

E : (5*d*x^2-y^2 , 5*d*z^2)

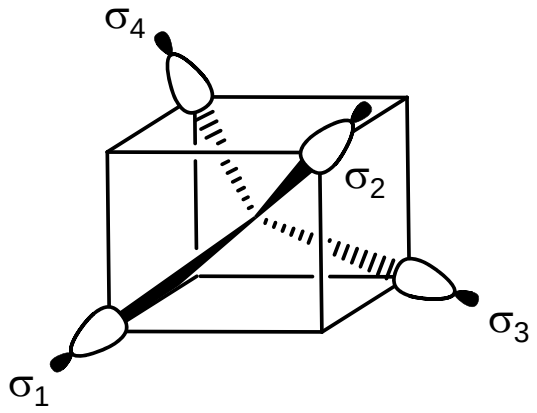
Construction of SALCs for σ bonding in T_d complexes

- Consider first the A_1 SALC. It must have the same symmetry of the *s* orbital on the central metal atom. This requires that it be everywhere positive and unchanged by all symmetry operations

$$\Gamma_\sigma = A_1 + T_2 \qquad A_1 \rightarrow \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$$



A_1
(0 nodes)



Construction of SALCs for σ bonding in T_d complexes

- The T_2 SALC's must match the symmetries of the (p_x , p_y , p_z) and (*d*xy, *d*xz, *d*yz) orbitals, e.g. must have positive amplitude where the *p* orbital is positive and negative amplitude where the p orbitals are negative.

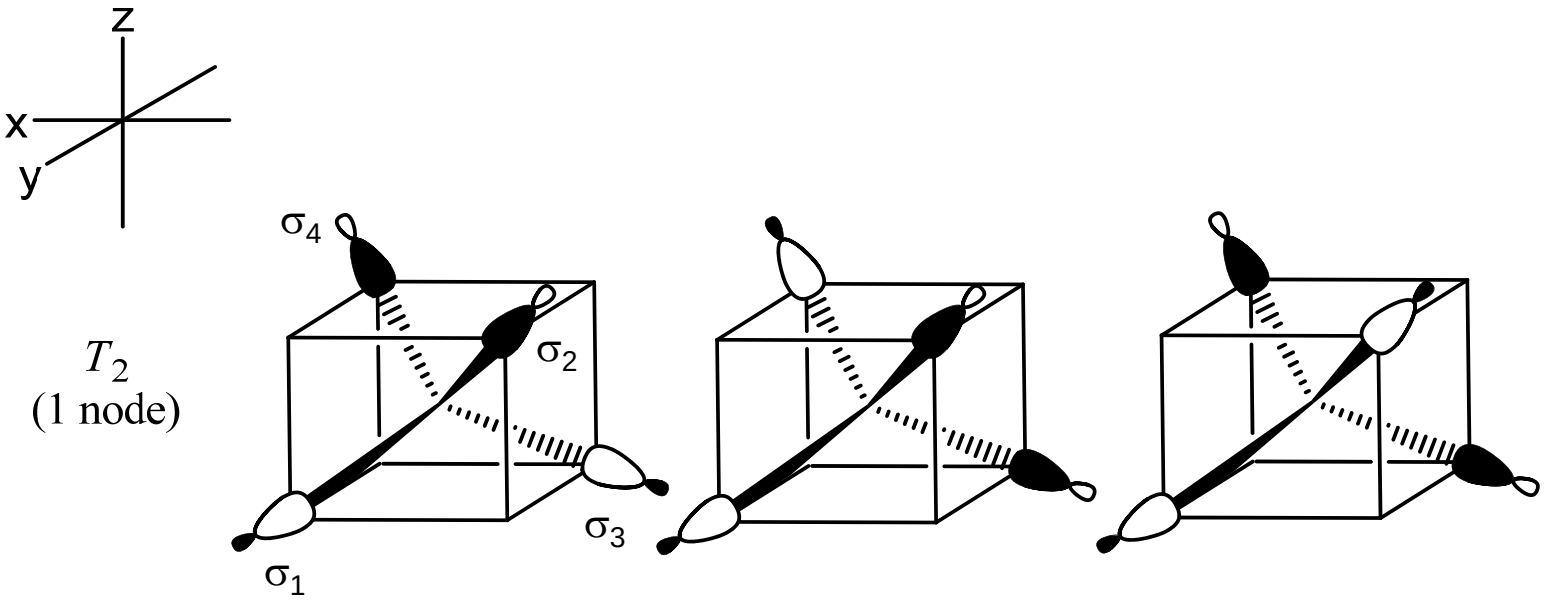
$$\Gamma_\sigma = A_1 + T_2$$

T_2

$\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$

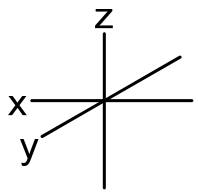
$\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4$

$\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$

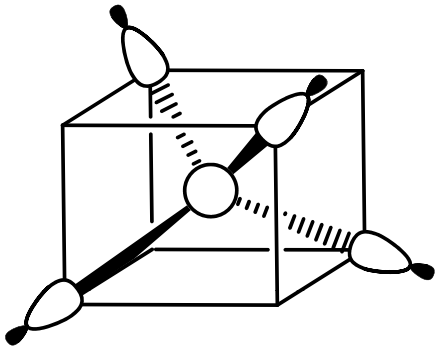


Construction of SALCs for σ bonding in T_d complexes

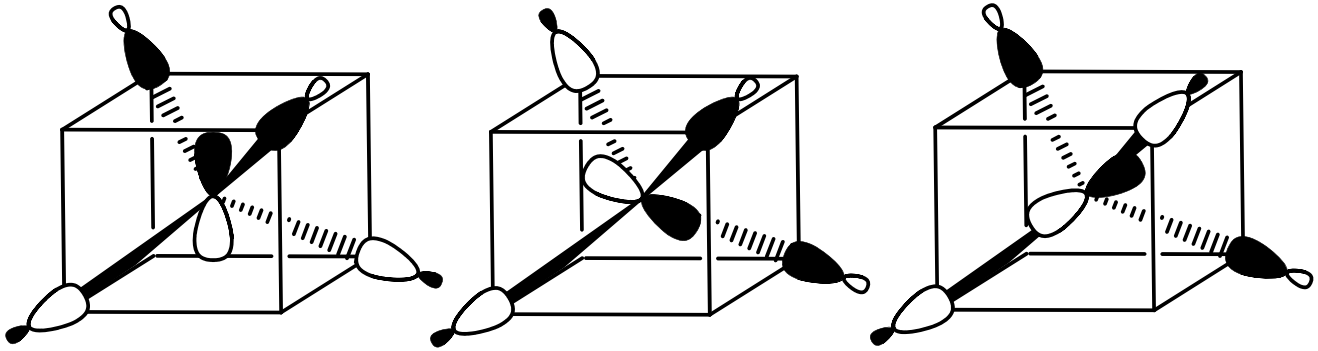
$\Gamma_\sigma = A_1 + T_2$



A_1
(0 nodes)

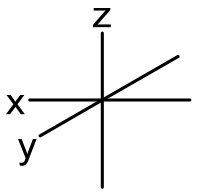


T_2
(1 node)



p_z p_x p_y

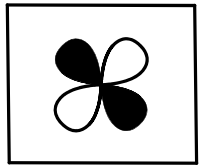
$$\Gamma_\sigma = A_1 + T_2$$



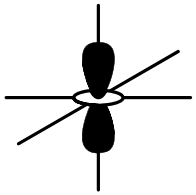
AOs

*d*xy

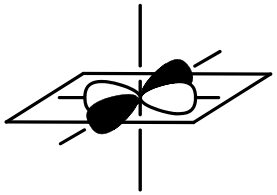
*d*yz



*d*xz



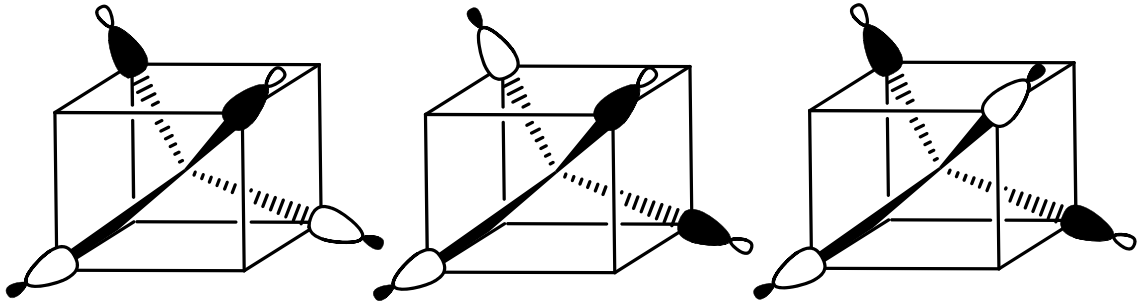
dz^2



dx^2-dy^2

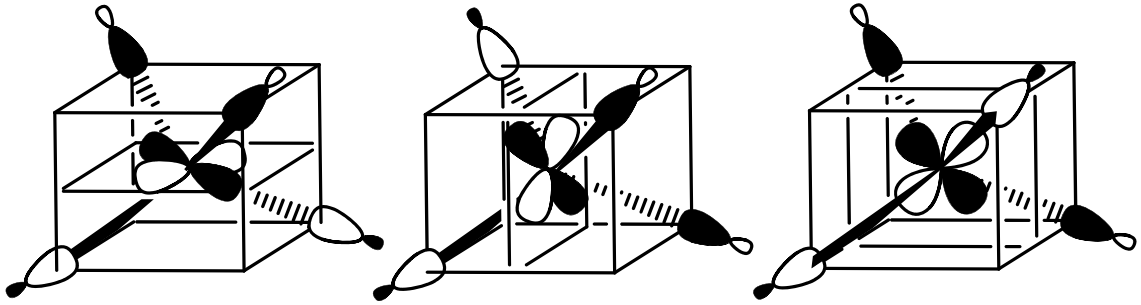
SALCs

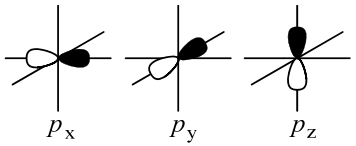
T_2
(1 node)



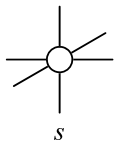
MOs

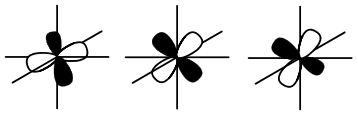
T_2
(1 node)

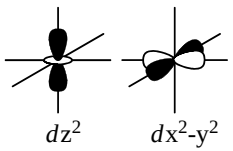


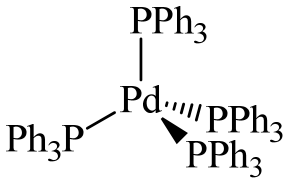


Pd^0

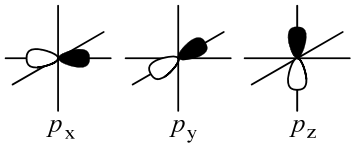




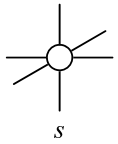




$6PPh_3$

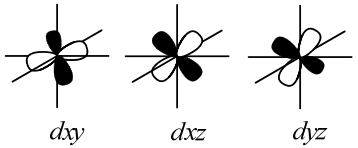


Pd^0

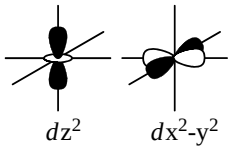


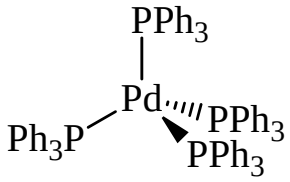
6p (t_2)

6s (a_1)



5d (t_2 , e)

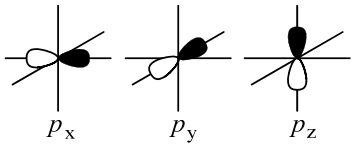




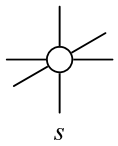
$6PPh_3$

t_2

a_1

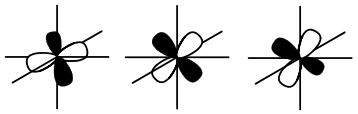


Pd^0

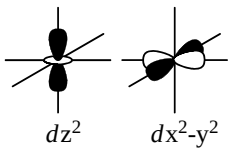


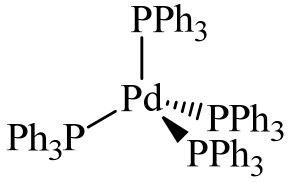
$6p\ (t_2)$

$6s\ (a_1)$



$5d\ (t_2\ ,\ e)$

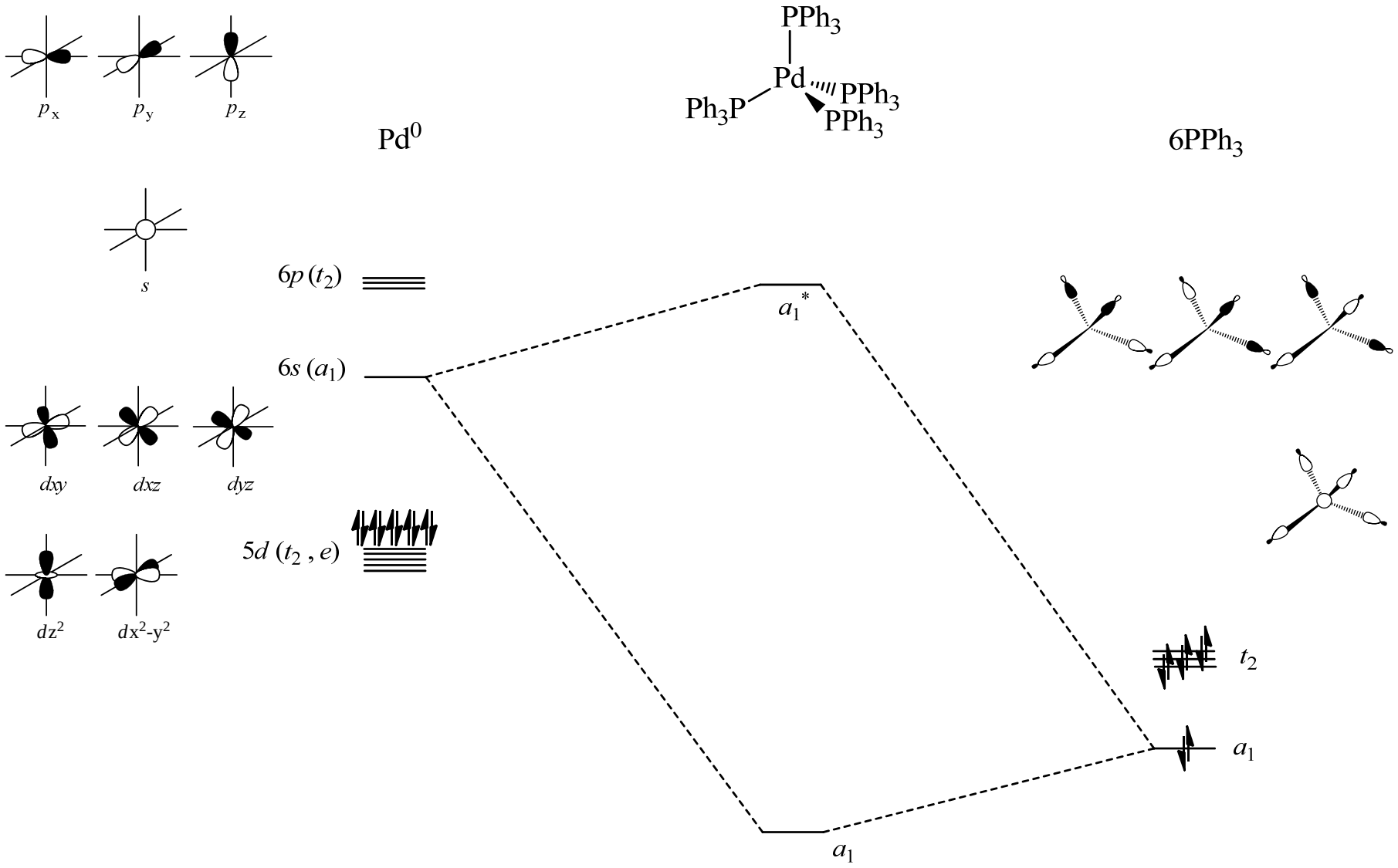


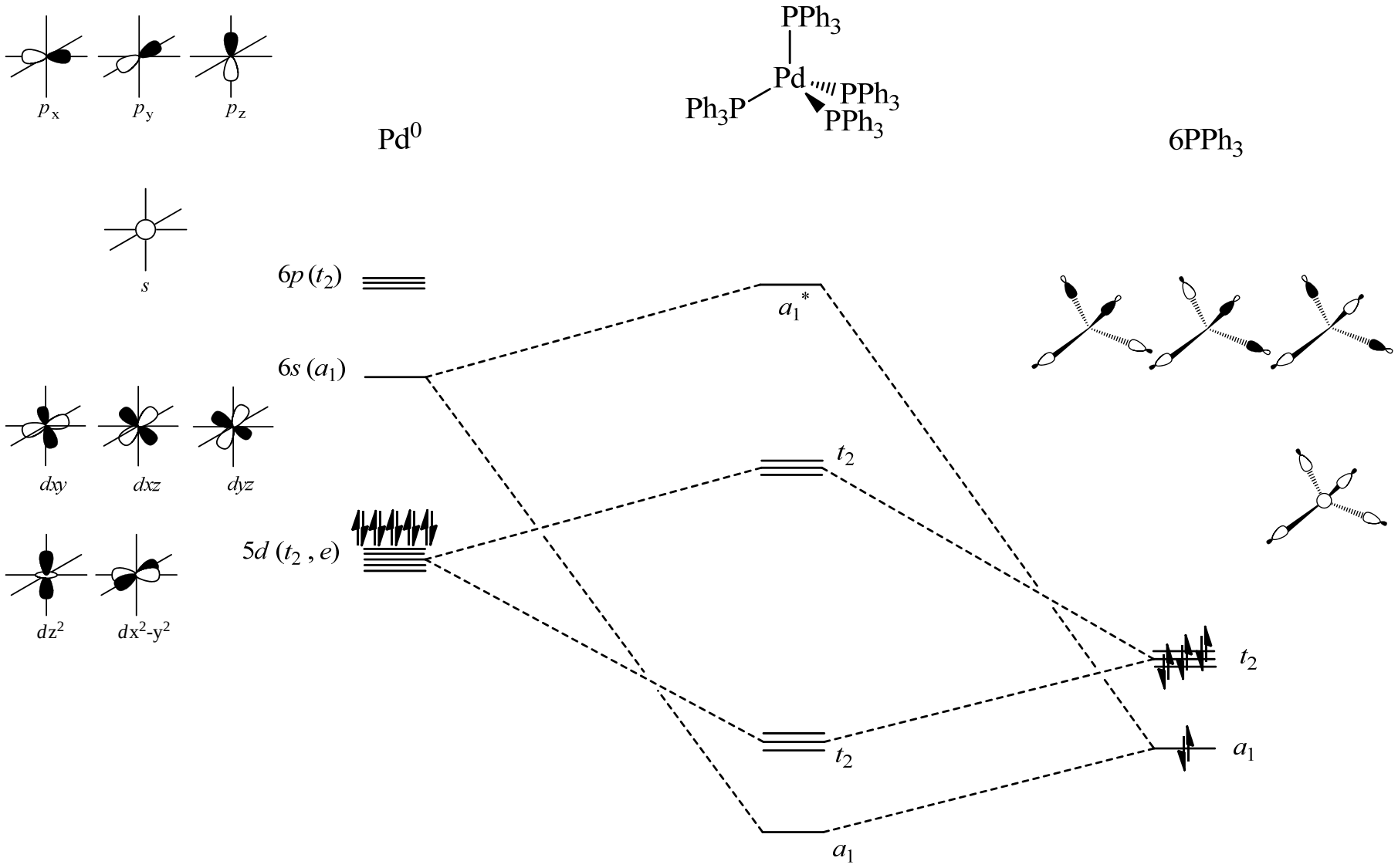


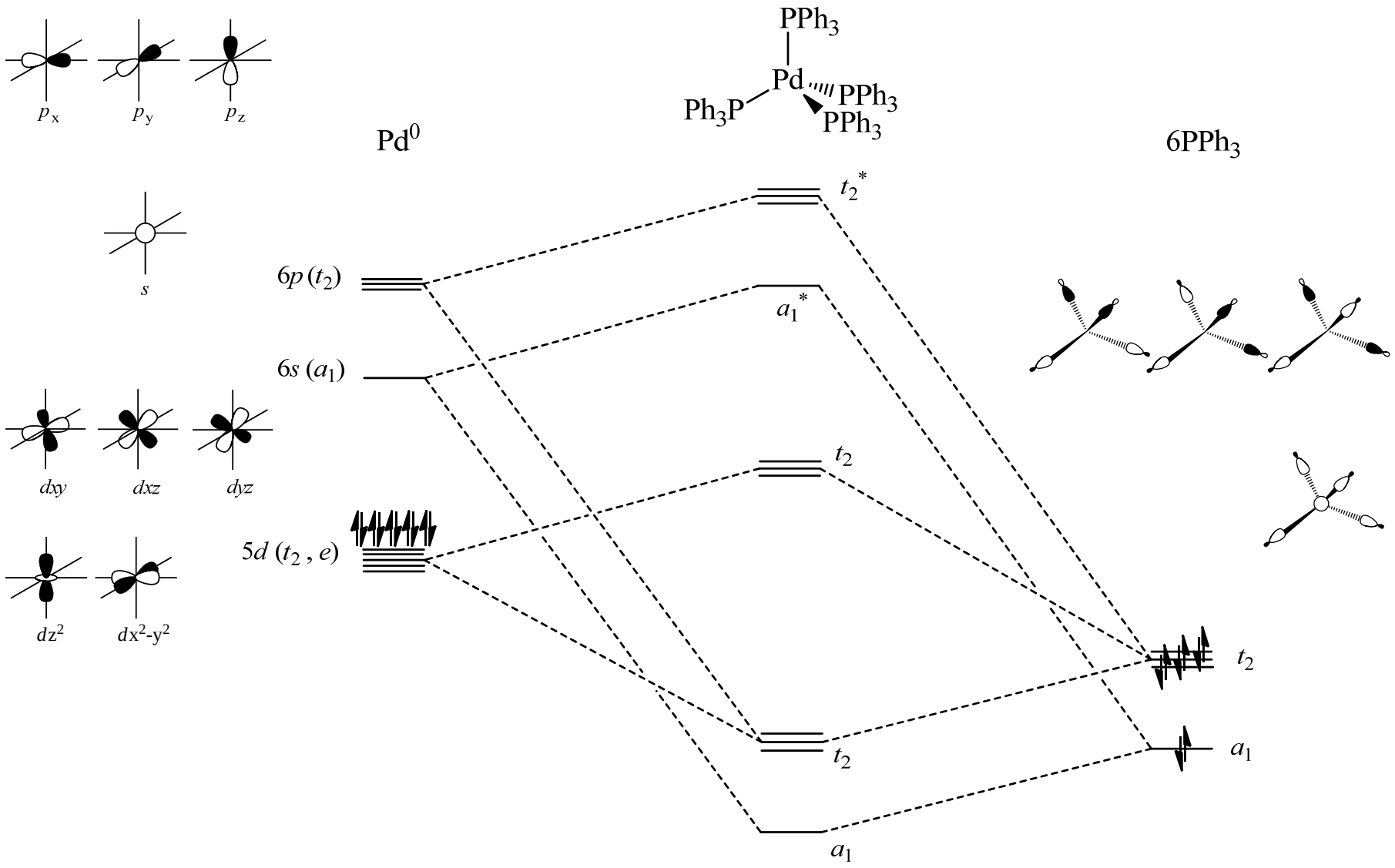
$6PPh_3$

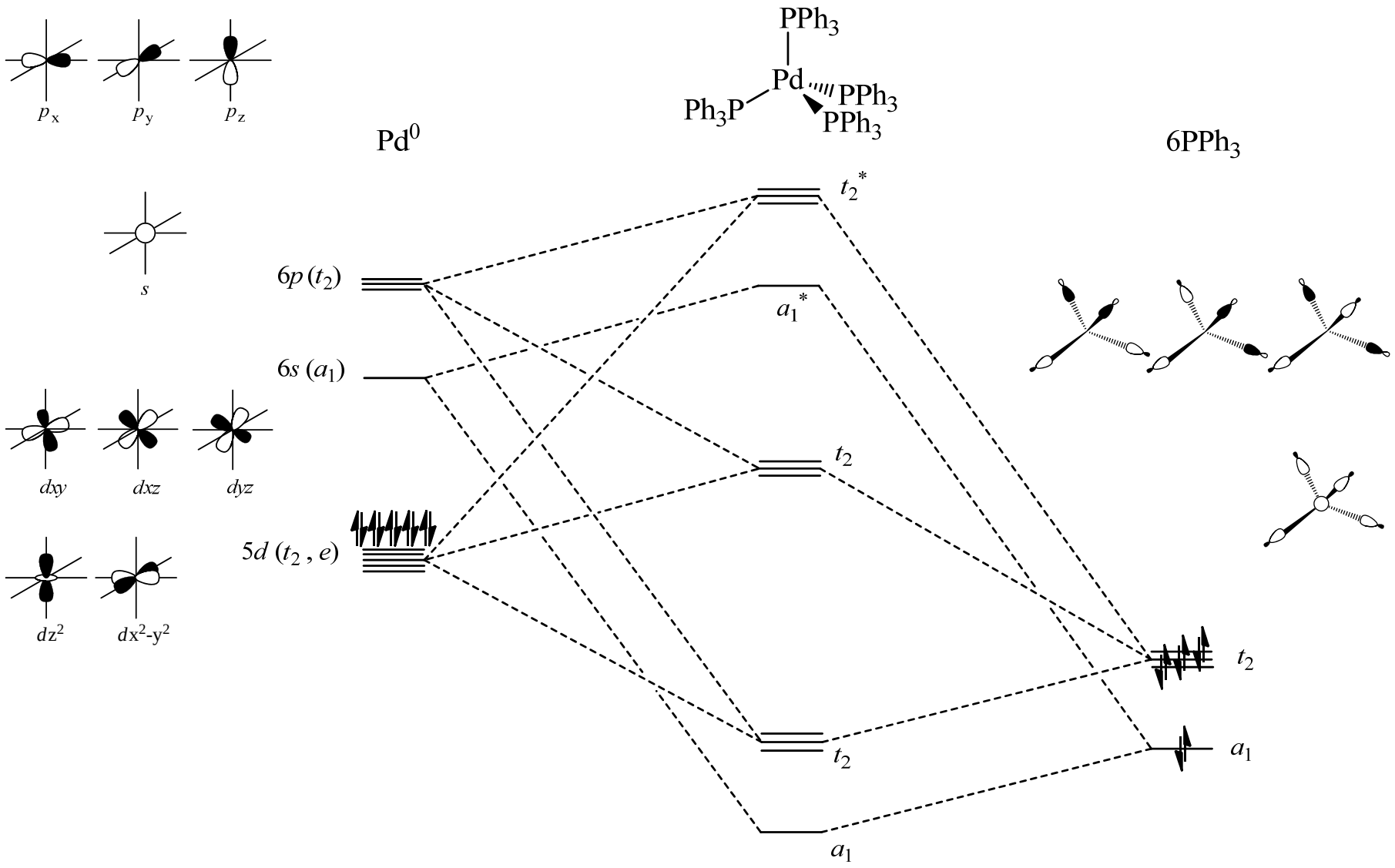
t_2

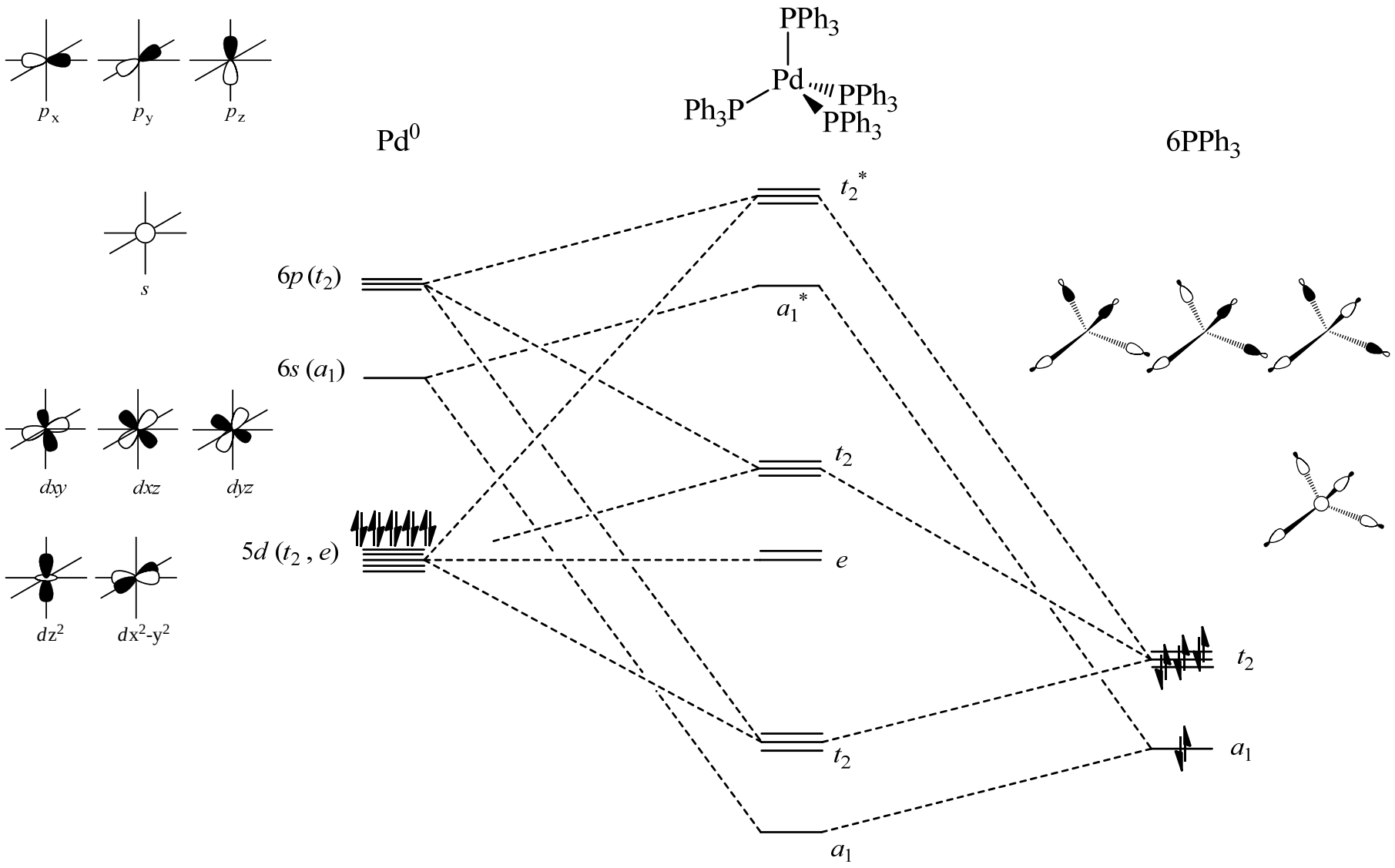
a_1

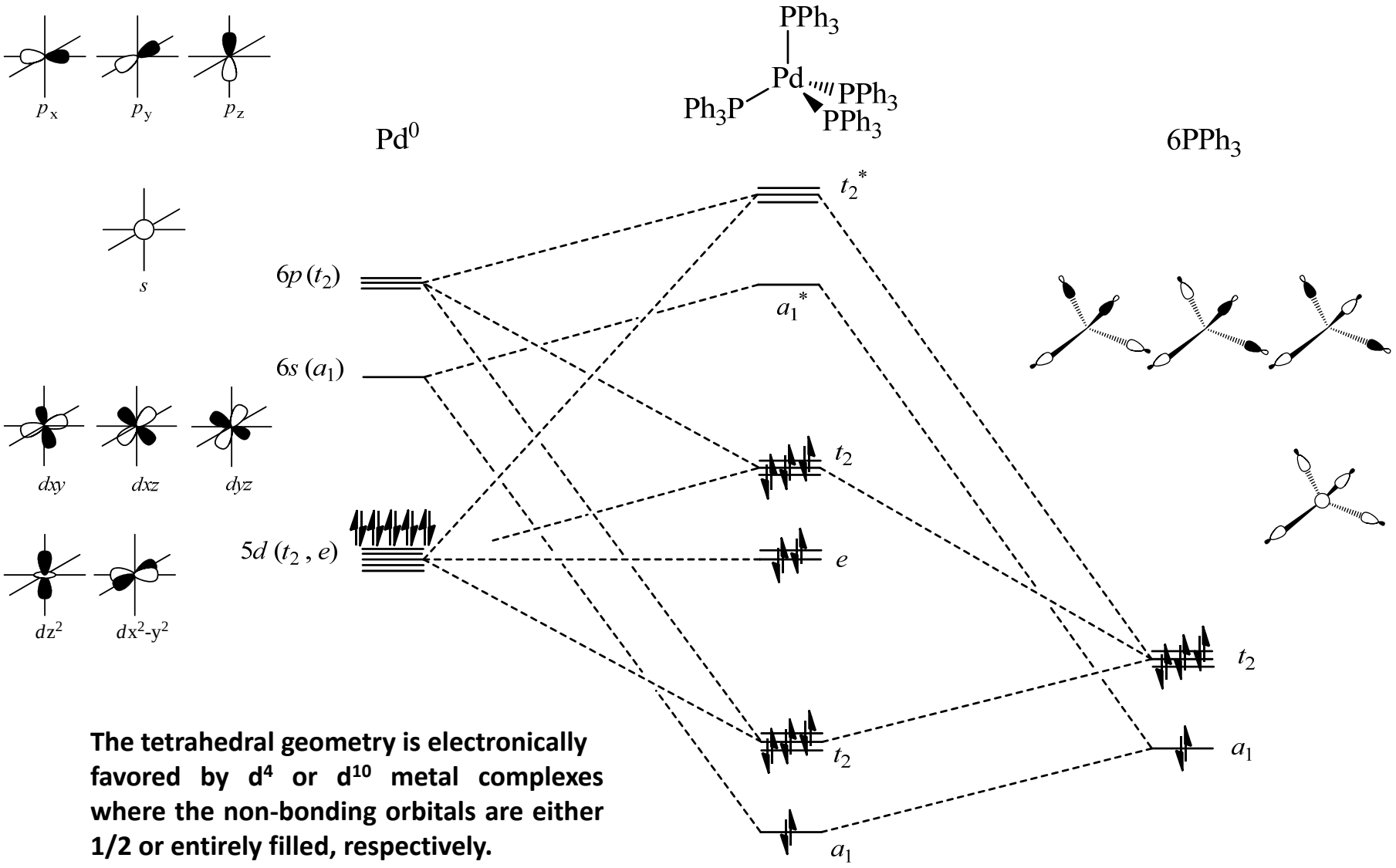

PPh3
Pd
Ph3P
PPh3
PPh3
Pd0
6PPh3
px
py
pz
s
6p (t2)
6s (a1)
5d (t2 , e)
dxy
dxz
dyz
dz2
dx2-y2
a1*
a1
t2
a1


PPh3
Pd
Ph3P
PPh3
PPh3
Pd0
6PPh3
px
py
pz
s
dxy
dxz
dyz
dz2
dx2-y2
6p (t2)
6s (a1)
5d (t2 , e)
a1*
t2
t2
a1
t2
a1

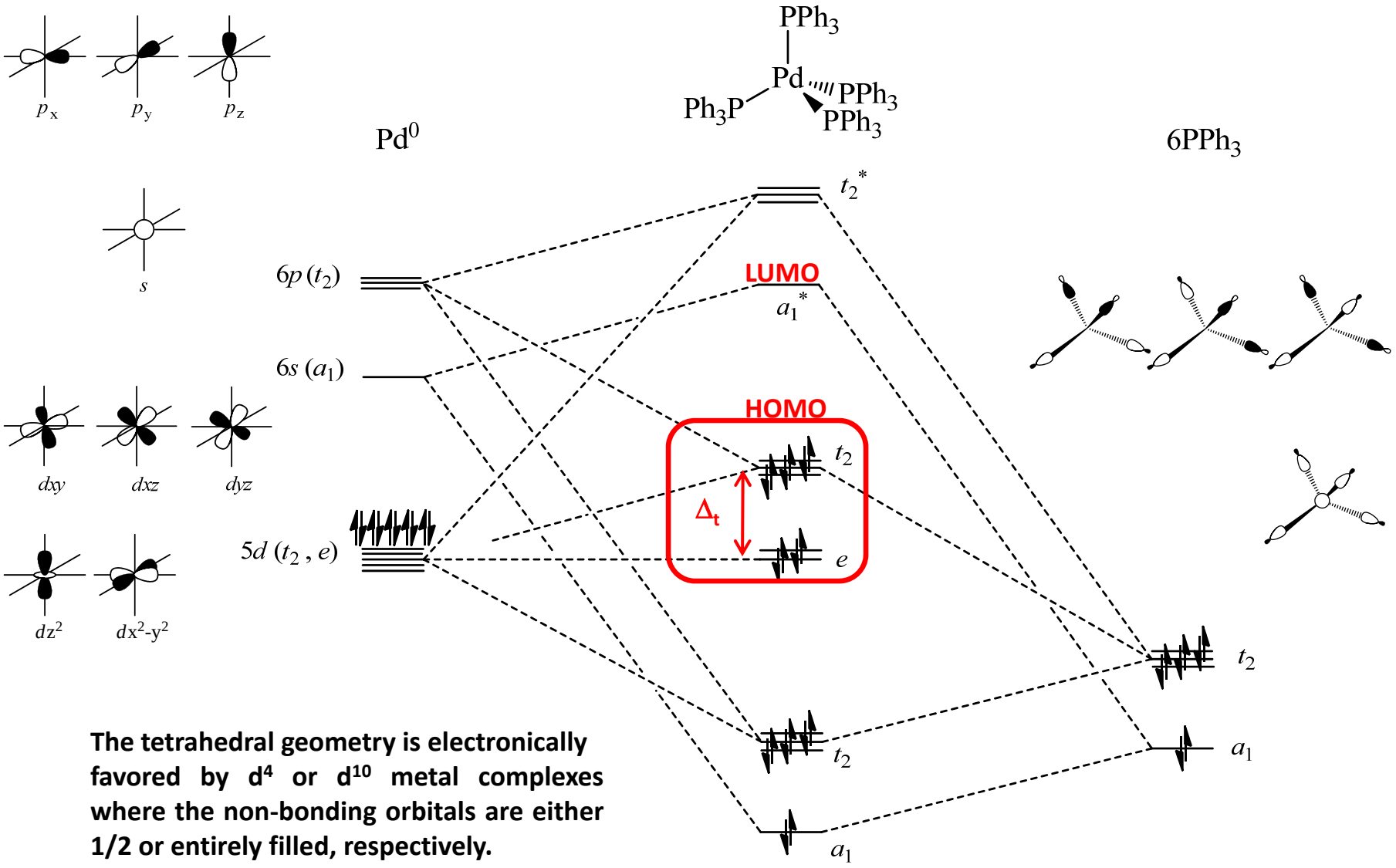

PPh3
Pd
Ph3P
PPh3
PPh3
Pd0
6PPh3
px
py
pz
s
dxy
dxz
dyz
dz2
dx2-y2
6p (t2)
6s (a1)
5d (t2 , e)
t2*
a1*
t2
t2
a1
t2
a1


PPh3
Pd
Ph3P
PPh3
PPh3
Pd0
6PPh3
t2*
6p (t2)
a1*
6s (a1)
t2
5d (t2 , e)
t2
a1
px
py
pz
s
dxy
dxz
dyz
dz2
dx2-y2


PPh3
Pd
Ph3P
PPh3
PPh3
Pd0
6PPh3
px
py
pz
s
dxy
dxz
dyz
dz2
dx2-y2
6p (t2)
6s (a1)
5d (t2 , e)
t2*
a1*
t2
e
t2
a1
t2
a1



The tetrahedral geometry is electronically favored by d^4 or d^{10} metal complexes where the non-bonding orbitals are either 1/2 or entirely filled, respectively.



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