Python与机器学习

——机器学习经典案例1

华算科技 黄老师

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目录

重现文献案例

利用机器学习方法预测金属与双金属的d带中心

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Machine-learning prediction of the d-band center for metals and bimetals

Ichigaku Takigawa,*[ab] Ken-ichi Shimizu,[cd] Koji Tsuda[efg] and Satoru Takakusagi[c]

The d-band center for metals has been widely used in order to understand activity trends in metal-surface-catalyzed reactions in terms of the linear Brønsted–Evans–Polanyi relation and Hammer–Nørskov d-band model. In this paper, the d-band centers for eleven metals (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, Au) and their pairwise bimetals for two different structures (1% metal doped- or overlayer-covered metal surfaces) are statistically predicted using machine learning methods from readily available values as descriptors for the target metals (such as the density and the enthalpy of fusion of each metal). The predictive accuracy of four regression methods with different numbers of descriptors and different test-set/training-set ratios are quantitatively evaluated using statistical cross validations. It is shown that the d-band centers are reasonably well predicted by the gradient boosting regression (GBR) method with only six descriptors, even when we predict 75% of the data from only 25% given for training (average root mean square error (RMSE) < 0.5 eV). This demonstrates a potential use of machine learning methods for predicting the activity trends of metal surfaces with a negligible CPU time compared to first-principles methods.

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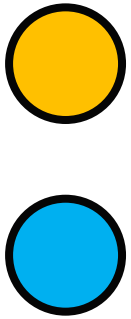
Ichigaku. T, Satoru. T, *et al. RSC Adv.*, **2016**, 6, 52587.

预测模型

输入：主客体金属描述符



原子数

价电子数

周期

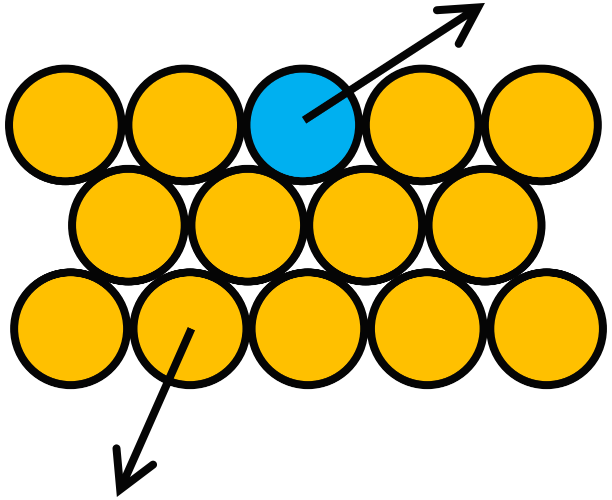
密度

……

机器学习

输出：双金属d带中心数值

客体金属（1%掺杂）

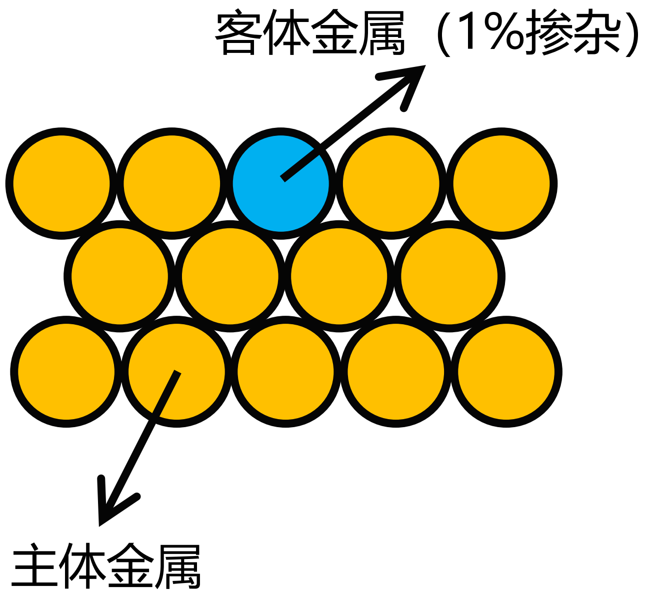


主体金属

d带中心数据集

Table 1
Shifts in d-band centers of surface impurities and overlayers relative to the clean metal values (italic)

	Fe	Co	Ni	Cu	Ru	Rh	Pd	Ag	Ir	Pt	Au
Fe	*−0.92*	0.05	−0.20	−0.13	−0.29	−0.54	−1.24	−0.83	−0.36	−1.09	−1.42
		0.14	−0.04	−0.05	−0.73	−0.72	−1.32	−1.25	−0.95	−1.48	−2.19
Co	0.01	*−1.17*	−0.28	−0.16	−0.24	−0.58	−1.37	−0.91	−0.36	−1.19	−1.56
	−0.01		−0.20	−0.06	−0.70	−0.95	−1.65	−1.36	−1.09	−1.89	−2.39
Ni	0.09	0.19	*−1.29*	0.19	−0.14	−0.31	−0.97	−0.53	−0.14	−0.80	−1.13
	0.96	0.11		0.12	−0.63	−0.74	−1.32	−1.14	−0.86	−1.53	−2.10
Cu	0.56	0.60	0.27	*−2.67*	0.58	0.32	−0.64	−0.70	0.58	−0.33	−1.09
	0.25	0.38	0.18		−0.22	−0.27	−1.04	−1.21	−0.32	−1.15	−1.96
Ru	0.21	0.26	0.01	0.12	*−1.41*	−0.17	−0.82	−0.27	0.02	−0.62	−0.84
	0.30	0.37	0.29	0.30		−0.12	−0.47	−0.40	−0.13	−0.61	−0.86
Rh	0.24	0.34	0.16	0.44	0.04	*−1.73*	−0.54	0.07	0.17	−0.35	−0.49
	0.31	0.41	0.34	0.22	0.03		−0.39	−0.08	0.03	−0.45	−0.57
Pd	0.37	0.54	0.50	0.94	0.24	0.36	*−1.83*	0.59	0.53	0.19	0.17
	0.36	0.54	0.54	0.80	−0.11	0.25		0.15	0.31	0.04	−0.14
Ag	0.72	0.84	0.67	0.47	0.84	0.86	0.14	*−4.30*	1.14	0.50	−0.15
	0.55	0.74	0.68	0.62	0.50	0.67	0.27		0.80	0.37	−0.21
Ir	0.21	0.27	0.05	0.21	0.09	−0.15	−0.73	−0.13	*−2.11*	−0.56	−0.74
	0.33	0.40	0.33	0.56	−0.01	−0.03	−0.42	−0.09		−0.49	−0.59
Pt	0.33	0.48	0.40	0.72	0.14	0.23	−0.17	0.44	0.38	*−2.25*	−0.05
	0.35	0.53	0.54	0.78	0.12	0.24	0.02	0.19	0.29		−0.08
Au	0.63	0.77	0.63	0.55	0.70	0.75	0.17	0.21	0.98	0.46	*−3.56*
	0.53	0.74	0.71	0.70	0.47	0.67	0.35	0.12	0.79	0.43	



data_impurities.csv

A. Ruban, J. K. Nørskov, *et al. J. Mol. Catal. A: Chem.*, ***1997***, *115*, 421.

d带中心数据集

Table 3 Input features (descriptors) used for prediction of d-band centers from ref. 34[a]

Metal	G	R/Å	AN	AM/g mol^{-1}	P	EN	IE/eV	$\Delta_{fus}H$/J g^{-1}	ρ/g cm^{-3}
Fe	8	2.66	26	55.85	4	1.83	7.90	247.3	7.87
Co	9	2.62	27	58.93	4	1.88	7.88	272.5	8.86
Ni	10	2.60	28	58.69	4	1.91	7.64	290.3	8.90
Cu	11	2.67	29	63.55	4	1.90	7.73	203.5	8.96
Ru	8	2.79	44	101.07	5	2.20	7.36	381.8	12.10
Rh	9	2.81	45	102.91	5	2.28	7.46	258.4	12.40
Pd	10	2.87	46	106.42	5	2.20	8.34	157.3	12.00
Ag	11	3.01	47	107.87	5	1.93	7.58	104.6	10.50
Ir	9	2.84	77	192.22	6	2.20	8.97	213.9	22.50
Pt	10	2.90	78	195.08	6	2.20	8.96	113.6	21.50
Au	11	3.00	79	196.97	6	2.40	9.23	64.6	19.30

[a] Group (G), bulk Wigner–Seitz radius (R) in Å, atomic number (AN), atomic mass (AM) in g mol^{-1}, period (P) electronegativity (EN), ionization energy (IE) in eV, enthalpy of fusion ($\Delta_{fus}H$) in J g^{-1}, density at 25 °C (ρ) in g cm^{-3}.

data_impurities_features.csv

Ichigaku. T, Satoru. T, *et al. RSC Adv.*, **2016**, 6, 52587.

模型预测

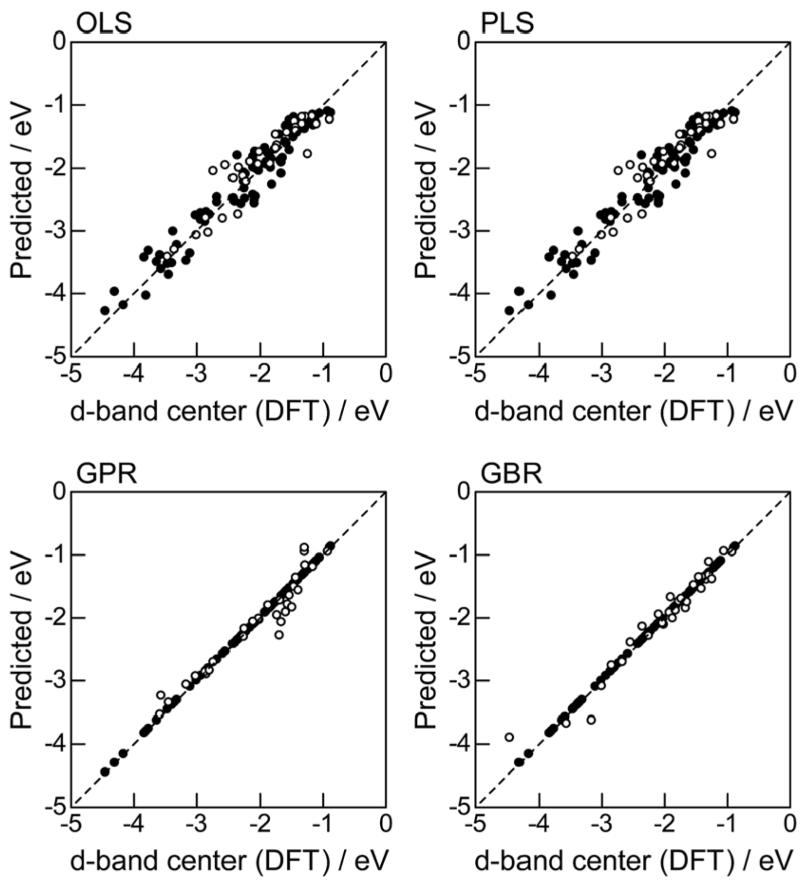


Fig. 1 DFT calculated local d-band center for metals and 1% guest metal-doped metals (Table 1) and the values predicted by linear (OLS, PLS) and nonlinear regression (GPR, GBR): (●) training set = 75%, (○) test set = 25%.

训练集：75%

测试集：25%

模型方法：

OLS：普通最小二乘回归

PLS：偏最小二乘回归

GPR：高斯过程回归

GBR：梯度提升回归

Ichigaku. T, Satoru. T, *et al. RSC Adv.*, **2016**, 6, 52587.

主要步骤

1. 导入待回归数据(data_impurities.csv)
    1.1. 导入数据　　1.2. 将d带中心数据从相对值改为绝对值
2. 导入描述符数据(data_impurities_features.csv)
3. 设置输入输出
4. 线性回归
    4.1. 回归寻找规律　　4.2. 可视化　　4.3. 交叉验证
5. 梯度提升回归
    5.1. 回归寻找规律　　5.2. 可视化　　5.3. 交叉验证
6. 查看数据规律（可选）

导入数据

In [1]:
```python
import numpy as np
import pandas as pd
```

In [2]:
```python
f = open('data_impurities.csv',encoding = 'UTF-8')
df = pd.read_csv(f, index_col = 0)
df
```

Out[2]:

	Fe	Co	Ni	Cu	Ru	Rh	Pd	Ag	Ir	Pt	Au
Fe	-0.92	0.05	-0.20	-0.13	-0.29	-0.54	-1.24	-0.83	-0.36	-1.09	-1.42
Co	0.01	-1.17	-0.28	-0.16	-0.24	-0.58	-1.37	-0.91	-0.36	-1.19	-1.56
Ni	0.09	0.19	-1.29	0.19	-0.14	-0.31	-0.97	-0.53	-0.14	-0.80	-1.13
Cu	0.56	0.60	0.27	-2.67	0.58	0.32	-0.64	-0.70	0.58	-0.33	-1.09
Ru	0.21	0.26	0.01	0.12	-1.41	-0.17	-0.82	-0.27	0.02	-0.62	-0.84
Rh	0.24	0.34	0.16	0.44	0.04	-1.73	-0.54	0.07	0.17	-0.35	-0.49
Pd	0.37	0.54	0.50	0.94	0.24	0.36	-1.83	0.59	0.53	0.19	0.17
Ag	0.72	0.84	0.67	0.47	0.84	0.86	0.14	-4.30	1.14	0.50	-0.15
Ir	0.21	0.27	0.05	0.21	0.09	-0.15	-0.73	-0.13	-2.11	-0.56	-0.74
Pt	0.33	0.48	0.40	0.72	0.14	0.23	-0.17	0.44	0.38	-2.25	-0.05
Au	0.63	0.77	0.63	0.55	0.70	0.75	0.17	0.21	0.98	0.46	-3.56

查看数据

In [3]:
```
df.loc['Co','Ni']
```
Out[3]:
```
-0.28
```

In [4]:
```
df.loc['Co']
```
Out[4]:
```
Fe     0.01
Co    -1.17
Ni    -0.28
Cu    -0.16
Ru    -0.24
Rh    -0.58
Pd    -1.37
Ag    -0.91
Ir    -0.36
Pt    -1.19
Au    -1.56
Name: Co, dtype: float64
```

In [5]:
```
for i in df.index:
    for j in df.columns:
        if(i == 'Fe' and j == 'Fe'):
            print('host ' + i + ', guest ' + j + ', val ' + str(df.loc[i, j]))
```
```
host Fe, guest Fe, val -0.92
```

转换数据

In [7]:
```
for i in df.index:
    for j in df.columns:
        if i != j:
            df.loc[i, j] += df.loc[i, i]

df
```

Out[7]:

	Fe	Co	Ni	Cu	Ru	Rh	Pd	Ag	Ir	Pt	Au
Fe	-0.92	-0.87	-1.12	-1.05	-1.21	-1.46	-2.16	-1.75	-1.28	-2.01	-2.34
Co	-1.16	-1.17	-1.45	-1.33	-1.41	-1.75	-2.54	-2.08	-1.53	-2.36	-2.73
Ni	-1.20	-1.10	-1.29	-1.10	-1.43	-1.60	-2.26	-1.82	-1.43	-2.09	-2.42
Cu	-2.11	-2.07	-2.40	-2.67	-2.09	-2.35	-3.31	-3.37	-2.09	-3.00	-3.76
Ru	-1.20	-1.15	-1.40	-1.29	-1.41	-1.58	-2.23	-1.68	-1.39	-2.03	-2.25
Rh	-1.49	-1.39	-1.57	-1.29	-1.69	-1.73	-2.27	-1.66	-1.56	-2.08	-2.22
Pd	-1.46	-1.29	-1.33	-0.89	-1.59	-1.47	-1.83	-1.24	-1.30	-1.64	-1.66
Ag	-3.58	-3.46	-3.63	-3.83	-3.46	-3.44	-4.16	-4.30	-3.16	-3.80	-4.45
Ir	-1.90	-1.84	-2.06	-1.90	-2.02	-2.26	-2.84	-2.24	-2.11	-2.67	-2.85
Pt	-1.92	-1.77	-1.85	-1.53	-2.11	-2.02	-2.42	-1.81	-1.87	-2.25	-2.30
Au	-2.93	-2.79	-2.93	-3.01	-2.86	-2.81	-3.39	-3.35	-2.58	-3.10	-3.56

添加描述符

In [9]:
```python
f = open('data_impurities_features.csv',encoding = 'UTF-8')
feat = pd.read_csv(f, index_col = 0)
feat
```

Out[9]:

	name	group	bulk wigner-seitz radius	atomic number	atomic mass	period	electronegativity	Iionization energy(eV)	H_fus	density
Fe	Iron	8	2.66	26	55.84500	4	1.83	7.9024	247.3	7.87
Co	Cobalt	9	2.62	27	58.93320	4	1.88	7.8810	272.5	8.86
Ni	Nickel	10	2.60	28	58.69340	4	1.91	7.6398	290.3	8.90
Cu	Copper	11	2.67	29	63.54600	4	1.90	7.7264	203.5	8.96
Ru	Ruthenium	8	2.79	44	101.07000	5	2.20	7.3605	381.8	12.10
Rh	Rhodium	9	2.81	45	102.90550	5	2.28	7.4589	258.4	12.40
Pd	Palladium	10	2.87	46	106.42000	5	2.20	8.3369	157.3	12.00
Ag	Silver	11	3.01	47	107.86820	5	1.93	7.5762	104.6	10.50
Ir	Iridium	9	2.84	77	192.21700	6	2.20	8.9670	213.9	22.50
Pt	Platinum	10	2.90	78	195.07800	6	2.20	8.9588	113.6	21.50
Au	Gold	11	3.00	79	196.96655	6	2.40	9.2255	64.6	19.30

查看描述符

```
In [10]: feat.head(4)
```

Out[10]:

	name	group	bulk wigner-seitz radius	atomic number	atomic mass	period	electronegativity	lionization energy(eV)	H_fus	density
Fe	Iron	8	2.66	26	55.8450	4	1.83	7.9024	247.3	7.87
Co	Cobalt	9	2.62	27	58.9332	4	1.88	7.8810	272.5	8.86
Ni	Nickel	10	2.60	28	58.6934	4	1.91	7.6398	290.3	8.90
Cu	Copper	11	2.67	29	63.5460	4	1.90	7.7264	203.5	8.96

```
In [11]: feat.loc['Co']
```

```
Out[11]:
name                        Cobalt
group                            9
bulk wigner-seitz radius      2.62
atomic number                   27
atomic mass                58.9332
period                           4
electronegativity             1.88
Iionization energy(eV)       7.881
H_fus                        272.5
density                       8.86
Name: Co, dtype: object
```

设置输入输出

In [14]:
```
x = list()
y = list()
for i in df.index:
    for j in df.columns:
        vec_i = feat.loc[i].to_numpy()
        vec_j = feat.loc[j].to_numpy()
        x_val = np.concatenate((vec_i, vec_j))
        y_val = df.loc[i][j]
        x.append(x_val)
        y.append(y_val)
        if i == 'Fe' and j =='Co':
            print('host ' + i + ', guest ' + j + ', input = ' + str(x_val) + ', output = ' + str(y_val))
```

```
host Fe, guest Co, input = [  8.        2.66     26.        55.845     4.        1.83      7.9024 247.3
   7.87      9.        2.62     27.        58.9332   4.        1.88      7.881
 272.5       8.86   ], output = -0.87
```

随机

In [18]:
```
from sklearn.utils import shuffle
X_r, y_r = shuffle(X,y)
X_train, y_train = X_r[:-30, :], y_r[:-30]
X_test, y_test = X_r[-30:, :], y_r[-30:]
```

In [19]:
```
from sklearn.linear_model import LinearRegression
lr = LinearRegression()
lr.fit(X_train, y_train)
y_pred_train_lr = lr.predict(X_train)
y_pred_test_lr = lr.predict(X_test)
```

shuffle()

打乱函数

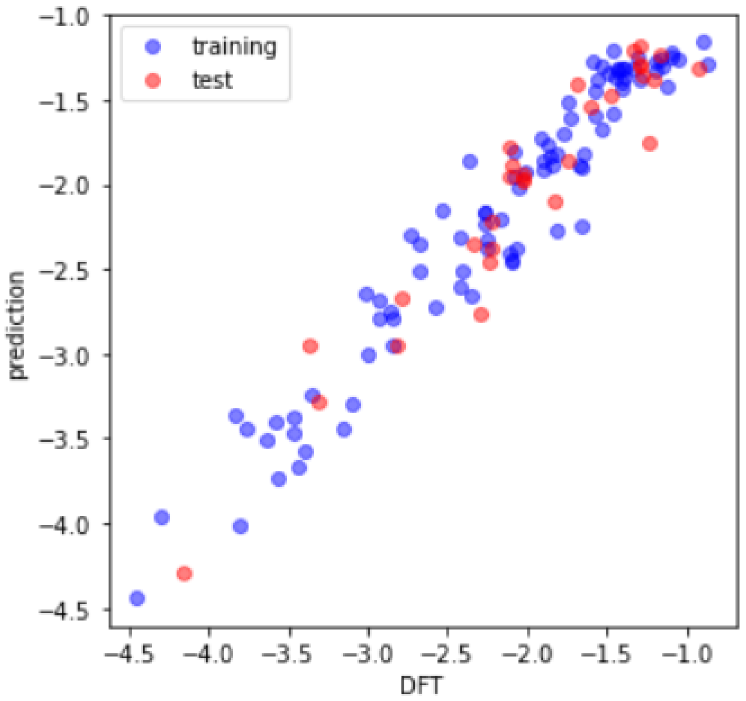
线性回归

In [21]:

```
import matplotlib.pyplot as plt

plt.figure(figsize = (5, 5))
plt.scatter(y_train, y_pred_train_lr, alpha=0.5, color = 'blue', label = 'training')
plt.scatter(y_test, y_pred_test_lr, alpha=0.5, color = 'red', label = 'test')
plt.legend()
plt.xlabel('DFT')
plt.ylabel('prediction')
```

Out[21]: Text(0, 0.5, 'prediction')



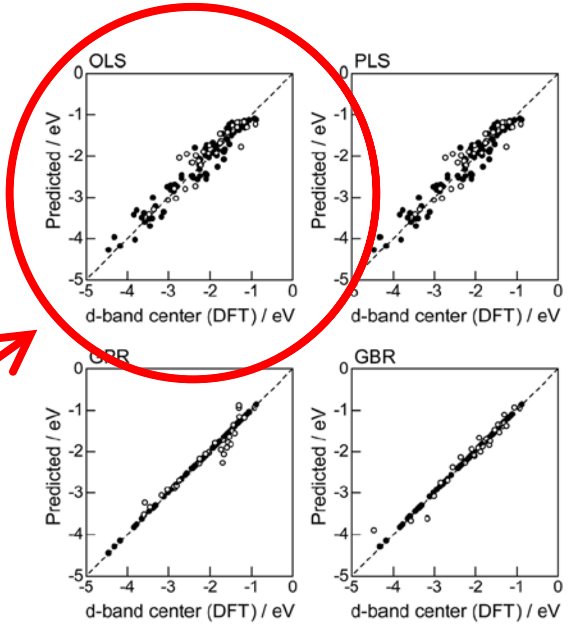


Fig. 1 DFT calculated local d-band center for metals and 1% guest metal-doped metals (Table 1) and the values predicted by linear (OLS, PLS) and nonlinear regression (GPR, GBR): (●) training set = 75%, (○) test set = 25%.

交叉验证

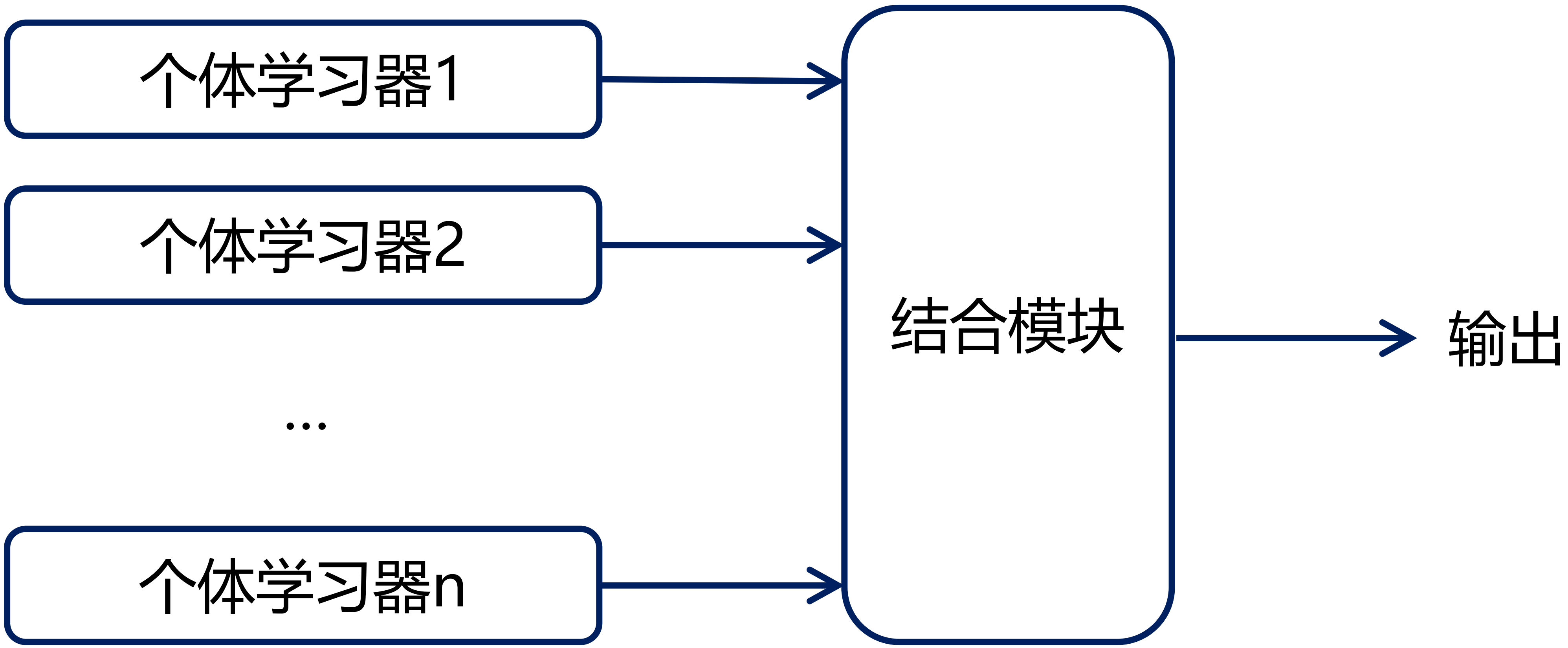
In [22]:
```
from sklearn.metrics import mean_squared_error
rmse_tr_lr = mean_squared_error(y_train, y_pred_train_lr, squared=False)
rmse_te_lr = mean_squared_error(y_test, y_pred_test_lr, squared=False)
print('RMSE(training)%.3f' % rmse_tr_lr)
print('RMSE(test)%.3f' % rmse_te_lr)
```

```
RMSE(training)0.214
RMSE(test)0.213
```

In [23]:
```
from sklearn.model_selection import cross_val_score, ShuffleSplit
cvf = ShuffleSplit(n_splits=100, test_size=0.25)
r2_lr = cross_val_score(lr, X, y, cv=cvf)
scores_lr = cross_val_score(lr, X, y, cv=cvf, scoring = 'neg_root_mean_squared_error')
print('100 times mean r2: %.3f' % r2_lr.mean())
print('100 times mean RMSE: %.3f' % -scores_lr.mean())
```

```
100 times mean r2: 0.897
100 times mean RMSE: 0.250
```

集成学习



集成学习

考虑二分类任务

	测试例1	测试例2	测试例3
h1	√	√	×
h2	√	×	√
h3	×	√	√
集成	√	√	√

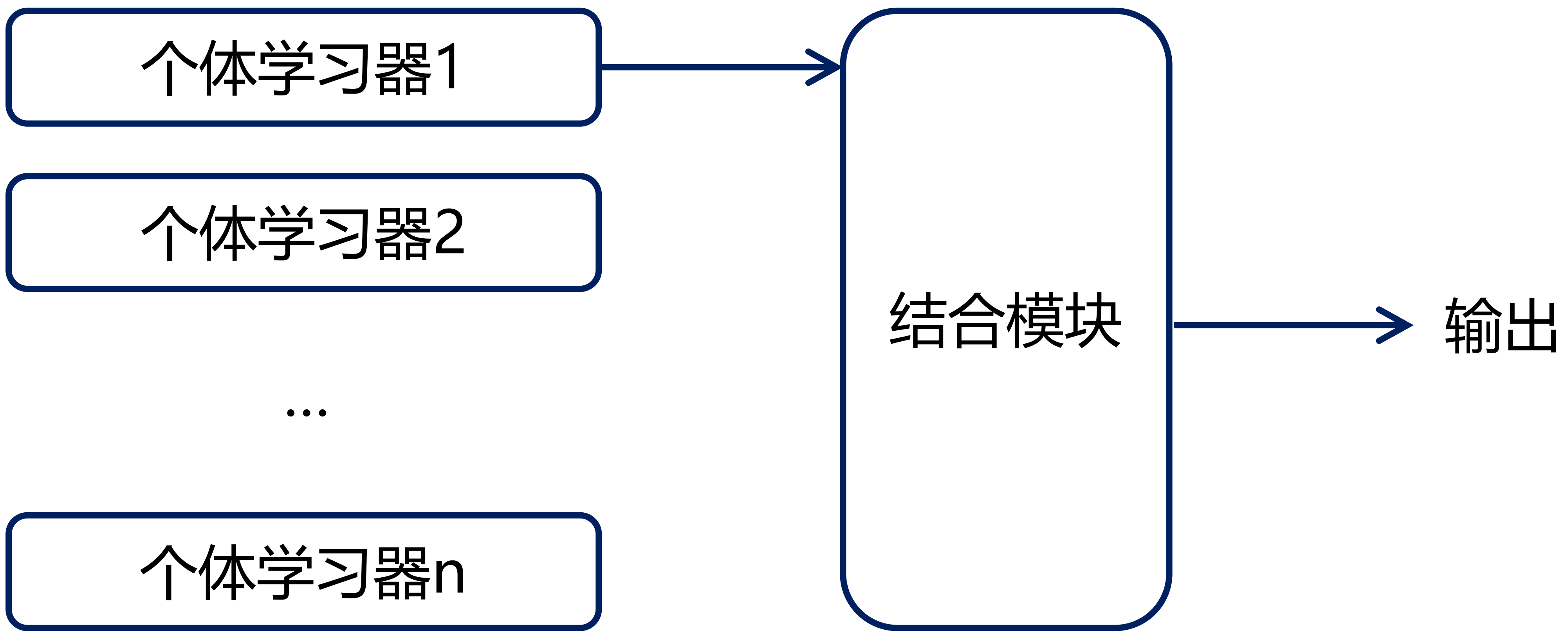
	测试例1	测试例2	测试例3
h1	√	√	×
h2	√	√	×
h3	√	√	×
集成	√	√	×

	测试例1	测试例2	测试例3
h1	√	×	×
h2	×	√	×
h3	×	×	√
集成	×	×	×

集成个体应“好而不同”

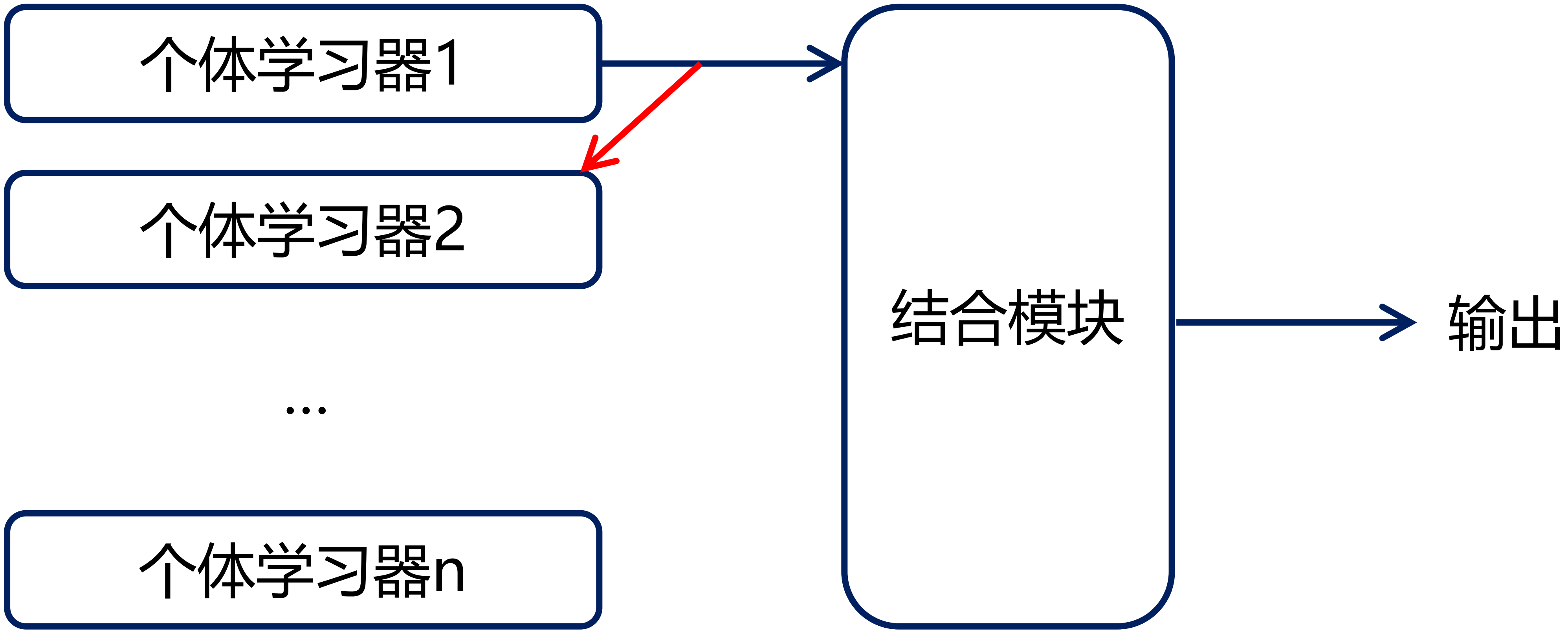
Boosting

① 训练学习器1



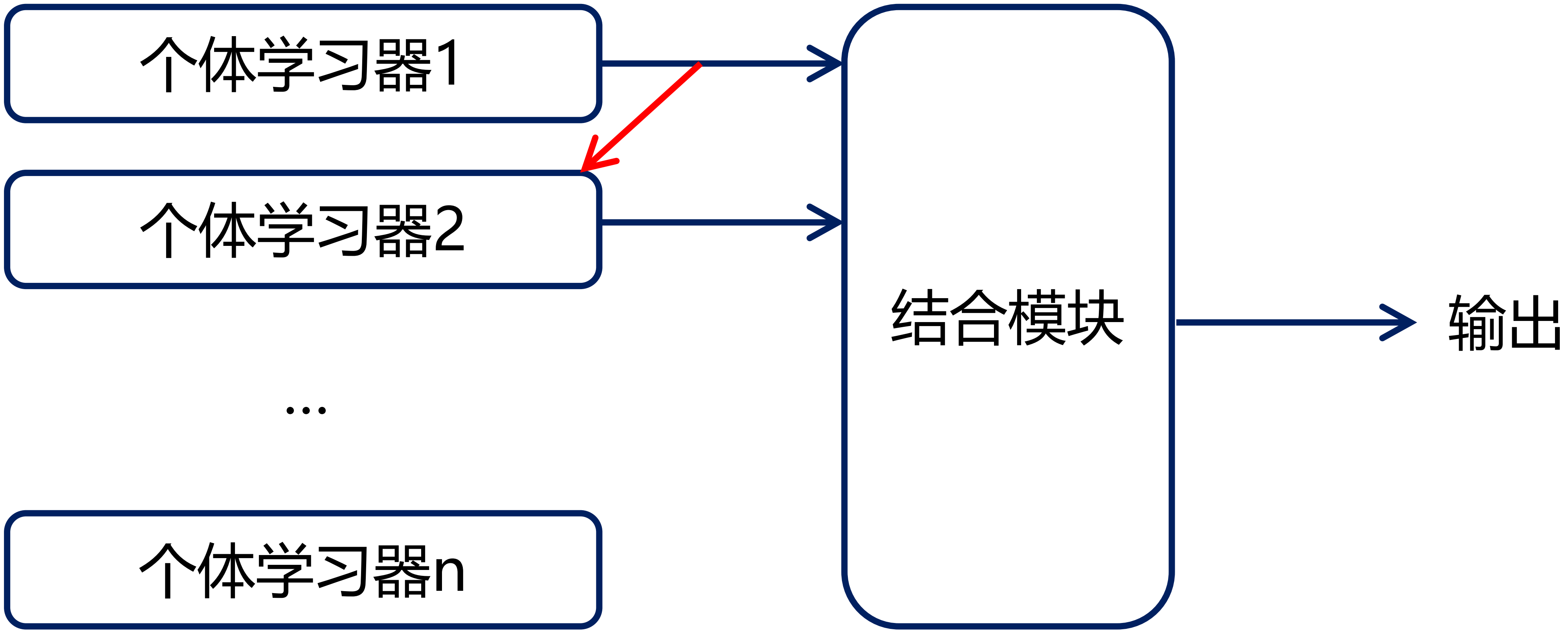
Boosting

② 调整样本权重



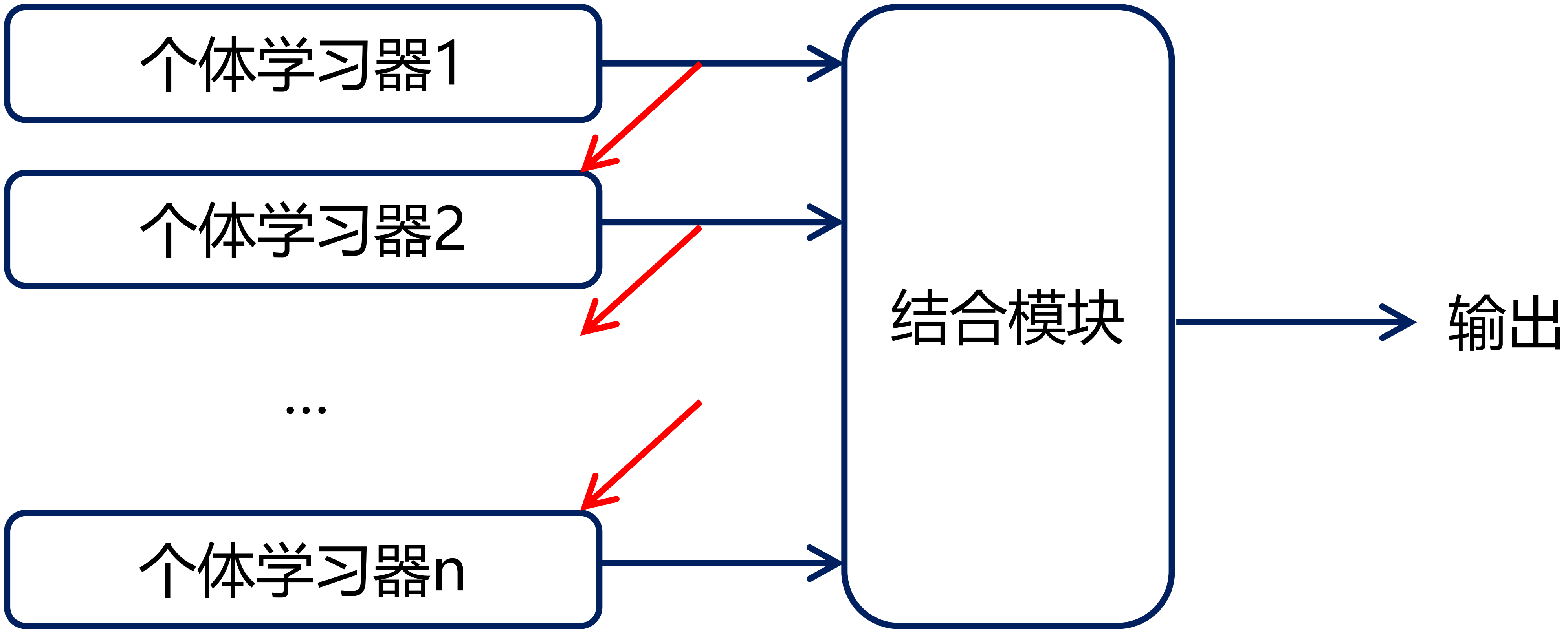
Boosting

③ 训练学习器2



Boosting

得到完整模型

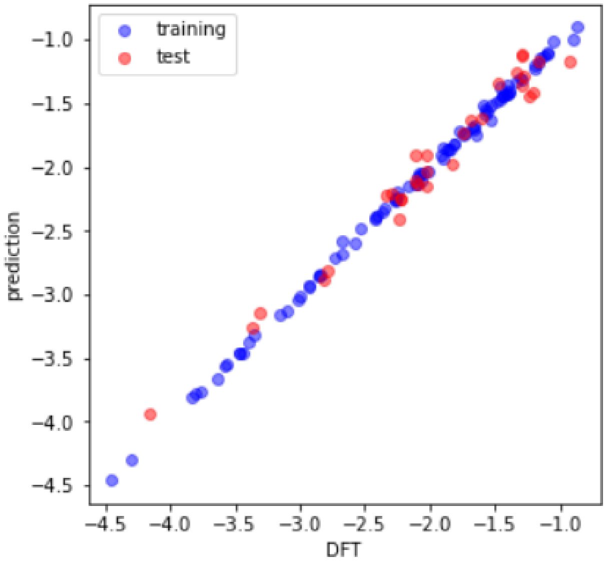


梯度提升回归

In [29]:
```
from sklearn.ensemble import GradientBoostingRegressor
gbr = GradientBoostingRegressor()
gbr.fit(X_train, y_train)
y_pred_train_gbr = gbr.predict(X_train)
y_pred_test_gbr = gbr.predict(X_test)
```

In [30]:
```
plt.figure(figsize = (5,5))
plt.scatter(y_train, y_pred_train_gbr, alpha=0.5, color = 'blue', label = 'training')
plt.scatter(y_test, y_pred_test_gbr, alpha=0.5, color = 'red', label = 'test')
plt.legend()
plt.xlabel('DFT')
plt.ylabel('prediction')
```

Out[30]: Text(0, 0.5, 'prediction')



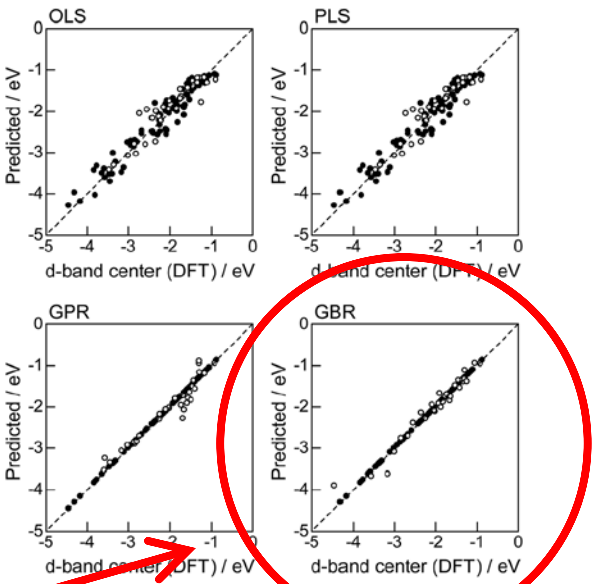


Fig. 1 DFT calculated local d-band center for metals and 1% guest metal-doped metals (Table 1) and the values predicted by linear (OLS, PLS) and nonlinear regression (GPR, GBR): (●) training set = 75%, (○) test set = 25%.

Ichigaku. T, Satoru. T, *et al. RSC Adv.*, **2016**, 6, 52587.

交叉验证

In [31]:
```
rmse_tr_gbr = mean_squared_error(y_train, y_pred_train_gbr, squared=False)
rmse_te_gbr = mean_squared_error(y_test, y_pred_test_gbr, squared=False)
print('RMSE(training)%.3f'%rmse_tr_gbr)
print('RMSE(test)%.3f'%rmse_te_gbr)
```

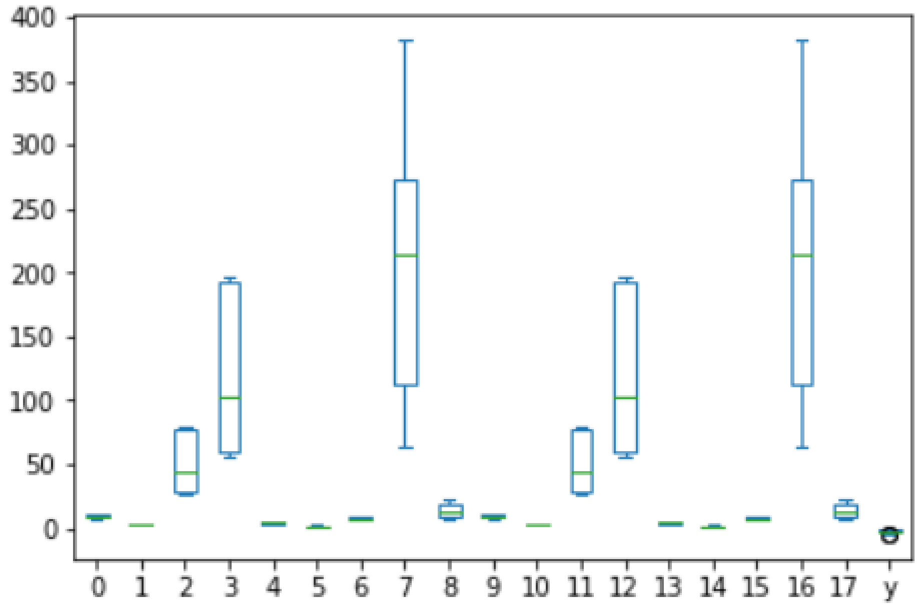
```
RMSE(training)0.032
RMSE(test)0.126
```

In [32]:
```
r2_gbr = cross_val_score(gbr, X, y, cv=cvf, scoring = 'r2')
scores_gbr = cross_val_score(gbr, X, y, cv=cvf, scoring = 'neg_root_mean_squared_error')
print('100 times mean r2: %.3f' % r2_gbr.mean())
print('100 times mean RMSE: %.3f' % -scores_gbr.mean())
```

```
100 times mean r2: 0.965
100 times mean RMSE: 0.152
```

数据可视化

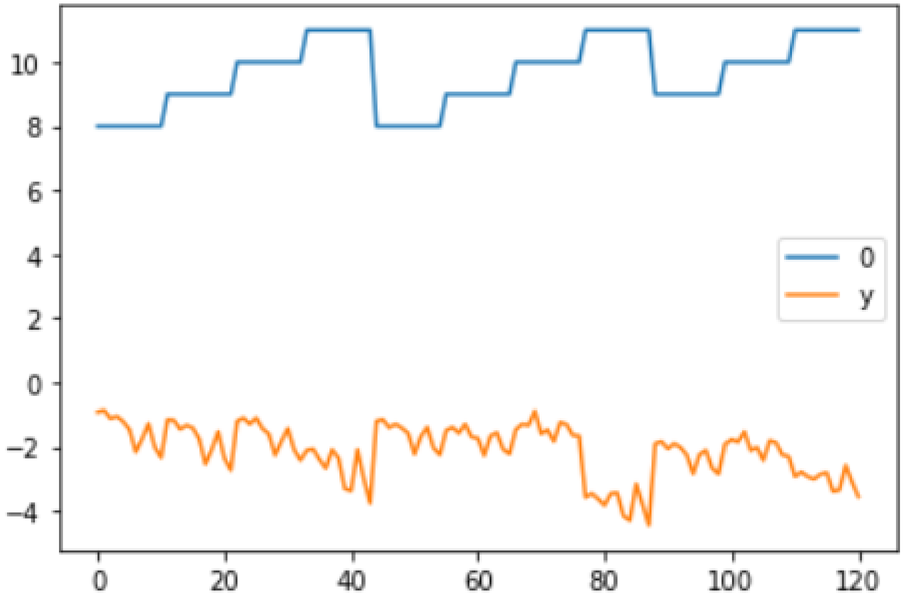
In [34]:
```
df.plot.box()
```
Out[34]: <AxesSubplot:>



数据可视化

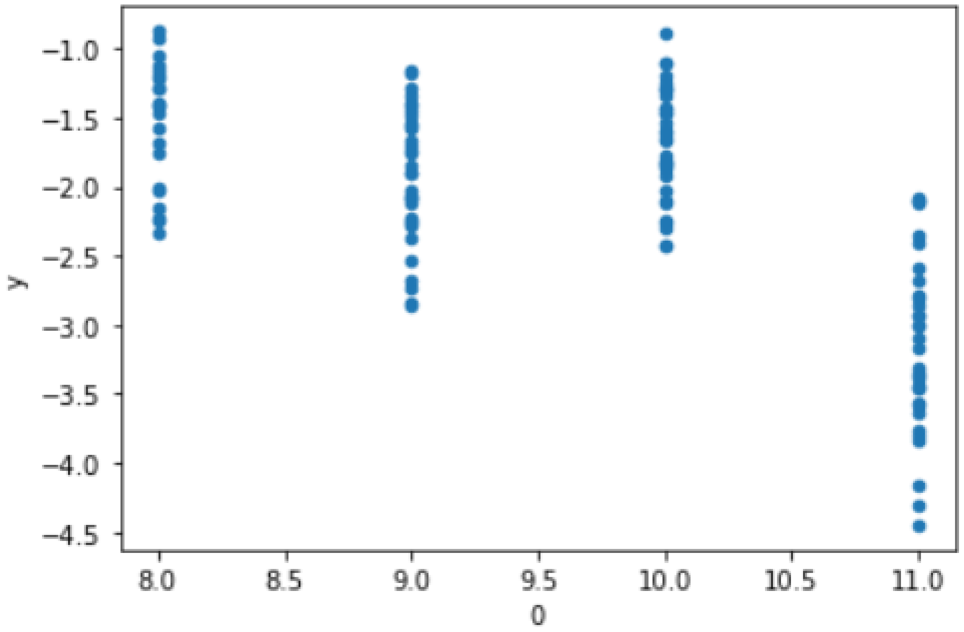
```
In [35]: idx = [0, 'y']
         df[idx].plot()
```

```
Out[35]: <AxesSubplot:>
```



数据可视化

```
In  [36]: df.plot.scatter(x = 0, y = 'y')
Out[36]: <AxesSubplot:xlabel='0', ylabel='y'>
```

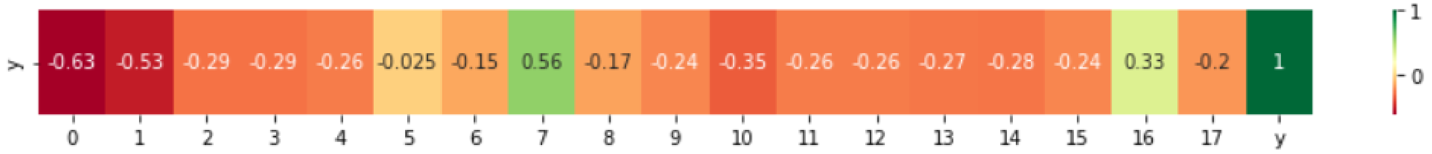


数据可视化

In [39]:
```
df.corr()['y']
```

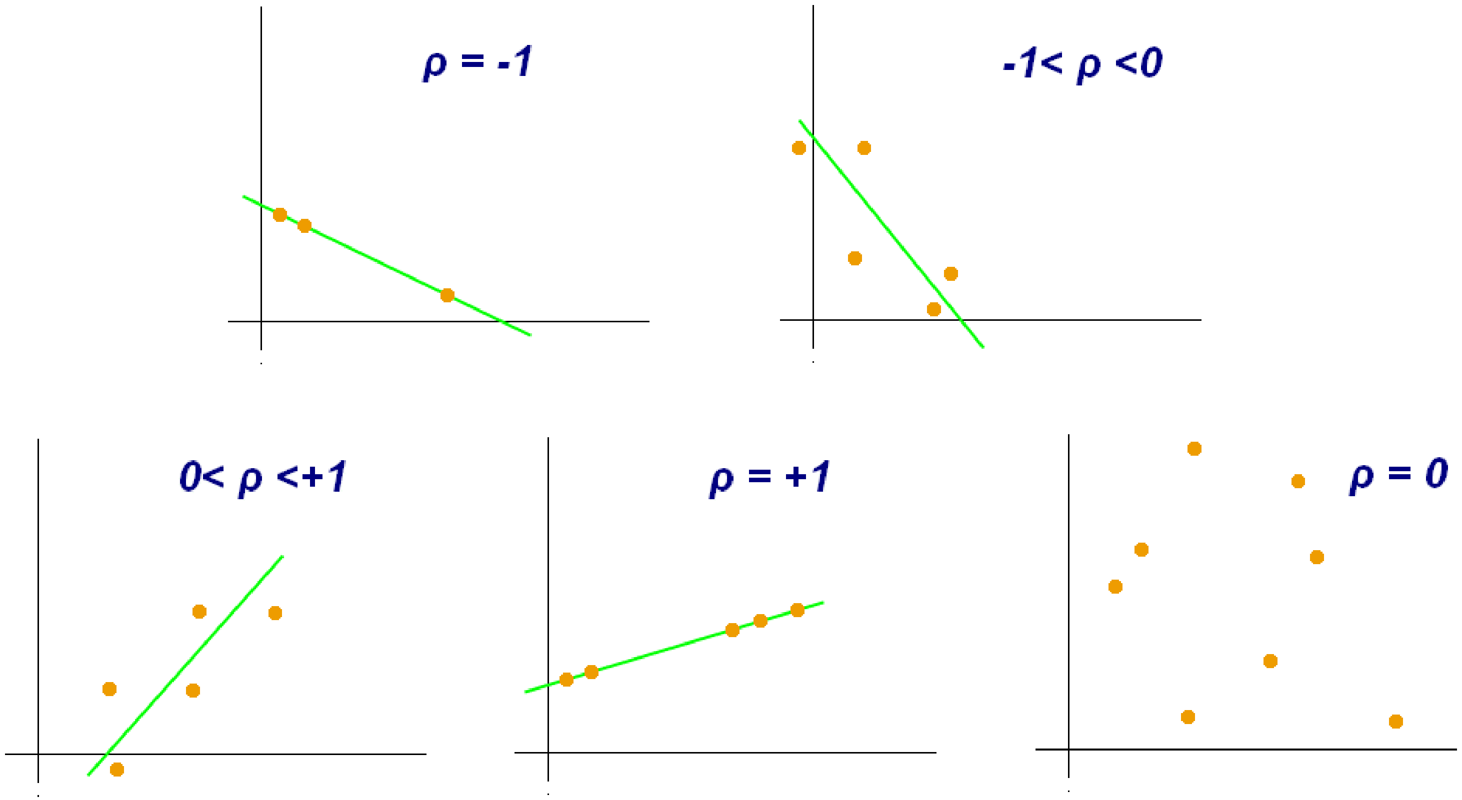
Out[39]:
```
0    -0.628485
1    -0.528149
2    -0.291100
3    -0.286463
4    -0.262104
5    -0.024741
6    -0.152404
7     0.564631
8    -0.169864
9    -0.236039
10   -0.347411
11   -0.264994
12   -0.260405
13   -0.274515
14   -0.279717
15   -0.240431
16    0.329626
17   -0.196517
y     1.000000
Name: y, dtype: float64
```

In [40]:
```
import matplotlib.pyplot as plt
import seaborn as sns
plt.figure(figsize=(15,1))
sns.heatmap(df.corr()['y'].to_frame().T, cmap='RdYlGn',annot=True)
plt.show()
```



Pearson相关系数

$$\rho_{X,Y} = \frac{cov(X,Y)}{\sigma_X \sigma_Y} = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2}\sqrt{\sum(y_i - \bar{y})^2}}$$



数据可视化

In [44]:
```python
plt.figure(figsize=(20,20))
sns.heatmap(df.corr(), cmap='RdYlGn', annot=True)
```

Out[44]: <AxesSubplot:>

数据可视化

In [46]:
```
import plotly.express as px
fig = px.scatter_3d(df, x=0, y=17, z='y', color = y)
fig.show()
```