Note

Zihang

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1 Atomic orbitals

pyscf.pbc.gto.Cell.pbc_eval_ao("GTOval_sph", position, kpts)
Hydrogen.pbc_eval_ao(position)

1.1 Gaussian type orbitals

We use Gaussian type orbitals as basis functions. The basis we used here, as well as in PYSCF, is a little bit different from CP2K. Take gth-dzvp as an example.

```
H DZVP-GTH
    2
    1   0   0   4   2
                8.3744350009   -0.0283380461    0.0000000000
                1.8058681460   -0.1333810052    0.0000000000
                0.4852528328   -0.3995676063    0.0000000000
                0.1658236932   -0.5531027541    1.0000000000
    2   1   1   1   1
                0.7270000000    1.0000000000
```

The file-format used in the .dat file

$$\chi_i(\mathbf{r}) = R_i(r) \cdot Y_{l_i,m_i}(\theta,\phi)$$
$$R_i(r) = r^{l_i} \sum_{j=1}^{N} c_{ij} \exp(-\alpha_j \cdot r^2)$$

$$\chi_i(\mathbf{r}) = \sqrt{4\pi} R_i(r) \cdot Y_{l_i,m_i}(\theta,\phi) \tag{1}$$
$$R_i(r) = r^{l_i} \sum_{j=1}^{N} c_{ij} \left(\frac{2\alpha_j}{\pi}\right)^{\frac{3}{4}} \exp(-\alpha_j \cdot r^2) \tag{2}$$

1.2 PBC orbitals

Crystalline orbitals Gaussian basis function ϕ is a lattice sum over local Gaussians χ

$$\phi_{\mathbf{k},i}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \chi_i(\mathbf{r}-\mathbf{T}) \tag{3}$$

where $\mathbf{k}$ is a vector in the first Brillouin zone and $\mathbf{T}$ is a lattice translational vector.

2 PBC Hartree Fock

Here we use index μ, ν to specify atoms, p, q, r, s to specify orbitals of each atom, i, j, k, l to specify coeffcients of each orbital, c, d to specify cells. Then the p th pbc gaussian type orbital of μ th atom can be described as

$$|\mathbf{R}_{\mu,p}\rangle = \sum_{i,c} c_{pi} \, |\alpha_i \mathbf{R}_{\mu,c}\rangle \tag{4}$$

Here are some commonly used shorthand symbols.

$$\alpha_{ij} = \frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j}$$
$$\alpha_{ij,kl} = \frac{(\alpha_i + \alpha_j)(\alpha_k + \alpha_l)}{\alpha_i + \alpha_j + \alpha_k + \alpha_l}$$
$$\mathbf{R}_{\mu i,\nu j,c} = \frac{\alpha_i \mathbf{R}_\mu + \alpha_j \mathbf{R}_{\nu,c}}{\alpha_i + \alpha_j}$$

2.1 Integtals

General integral on PBC basis is given by

$$\begin{aligned} A_{ij} &= \sum_{m,n} \int_0^T a(x)\chi_i(x + mT)\chi_j(x + nT)dx \\ &= \sum_{m,n} \int_{mT}^{(m+1)T} a(x' - mT)\chi_i(x')\chi_j[x' + (n - m)T]dx' \\ &= \sum_{m,n-m} \int_{mT}^{(m+1)T} a(x')\chi_i(x')\chi_j[x' + (n - m)T]dx' \\ &= \sum_{n'} \int_{-\infty}^{\infty} a(x')\chi_i(x')\chi_j(x' + n'T)dx' \end{aligned}$$

2.1.1 Overlap

The overlap matrix element is given by

$$O_{\mu p,\nu q} = \langle \mathbf{R}_{\mu p} | \mathbf{R}_{\nu q} \rangle = \sum_c \sum_{ij} c_{pi} c_{qj} \left(\frac{2\sqrt{\alpha_i \alpha_j}}{\alpha_i + \alpha_j}\right)^{\frac{3}{2}} \exp\left[-\alpha_{ij}(\mathbf{R}_\mu - \mathbf{R}_{\nu,c})^2\right] \tag{5}$$

$$O_{\mu pi,\nu qj,c} = c_{pi} c_{qj} \left(\frac{2\sqrt{\alpha_i \alpha_j}}{\alpha_i + \alpha_j}\right)^{\frac{3}{2}} \exp\left[-\alpha_{ij}(\mathbf{R}_\mu - \mathbf{R}_{\nu,c})^2\right] \tag{6}$$

$$O_{\mu p,\nu q} = \sum_c \sum_{ij} O_{\mu pi,\nu qj,c} \tag{7}$$

2.1.2 Kinetic

The kinetic matrix element

$$T_{\mu p,\nu q} = \langle \mathbf{R}_{\mu p} | -\frac{1}{2}\nabla^2 | \mathbf{R}_{\nu q} \rangle = \sum_c \sum_{ij} c_{pi} c_{qj} \left(\frac{2\sqrt{\alpha_i \alpha_j}}{\alpha_i + \alpha_j}\right)^{\frac{3}{2}} \exp\left[-\alpha_{ij}(\mathbf{R}_\mu - \mathbf{R}_{\nu,c})^2\right] \alpha_{ij} \left[3 - 2\alpha_{ij}(\mathbf{R}_\mu - \mathbf{R}_{\nu,c})^2\right] \tag{8}$$

$$T_{\mu p,\nu q} = \sum_c \sum_{ij} O_{\mu pi,\nu qj,c} \alpha_{ij} \left[3 - 2\alpha_{ij}(\mathbf{R}_\mu - \mathbf{R}_{\nu,c})^2\right] \tag{9}$$

2.1.3 Potential

The potential matrix element

$$V_{\mu p,\nu q,N} = \langle \mathbf{R}_{\mu p}| \sum_d \frac{1}{|r - R_{N,d}|} |\mathbf{R}_{\nu q}\rangle = 2 \sum_{cd} \sum_{ij} O_{\mu pi,\nu qj,c} \sqrt{\frac{\alpha_i + \alpha_j}{\pi}} F_0 \left[(\alpha_i + \alpha_j)(\mathbf{R}_{N,d} - \mathbf{R}_{\mu i,\nu j,c})^2\right] \tag{10}$$

$$V_{\mu p,\nu q} = \sum_{\mathbf{G}\neq 0} \sum_N \sum_c \sum_{ij} V(\mathbf{G}) O_{\mu pi,\nu qj,c} \exp\left[-i\mathbf{G}\cdot(\mathbf{R}_N - \mathbf{R}_{\mu i,\nu j,c})\right] \exp\left[-\frac{G^2}{4(\alpha_i + \alpha_j)}\right] \tag{11}$$

where

$$V(\mathbf{G}) = \frac{4\pi}{L^3}\frac{1}{G^2} \tag{12}$$

2.1.4 Electron interaction

The interaction matrix element

$$E_{p\mu q\nu,r\gamma s\eta} = \langle \alpha_p \mathbf{R}_\mu \alpha_q \mathbf{R}_\nu| \frac{1}{|r - r'|} |\alpha_r \mathbf{R}_\gamma \alpha_s \mathbf{R}_\eta\rangle = 2 O_{p\mu,r\gamma} O_{q\nu,s\eta} \sqrt{\frac{\alpha_{pr,qs}}{\pi}} F_0\left[\alpha_{pr,qs}(\mathbf{R}_{p\mu,r\gamma} - \mathbf{R}_{q\nu,r\eta})^2\right] \tag{13}$$

Where

$$F_0[x] = \frac{\sqrt{\pi} erf(\sqrt{x})}{2\sqrt{x}} \quad \& \quad F_0[0] = 1 \tag{14}$$

2.1.5 Hcore

Hamiltonian matrix element without interaction

$$h_{p\mu,q\nu} = T_{p\mu,q\nu} - \sum_N V_{p\mu,q\nu,N} \tag{15}$$

2.1.6 Fock matrix

Fock operator matrix element

$$F_{p\mu,q\nu} = \langle \alpha_p \mathbf{R}_\mu| \hat{H} |\alpha_q \mathbf{R}_\nu\rangle = h_{p\mu,q\nu} + \sum_k \sum_{r\gamma,s\eta} (2E_{p\mu r\gamma,q\nu s\eta} - E_{p\mu r\gamma,s\eta q\nu}) C^*_{r\gamma,k} C_{s\eta,k} \tag{16}$$

2.2 Solution of Roothaan equation

Roothaan equation

$$\mathbf{F}\mathbf{C}_k = \epsilon_k \mathbf{S}\mathbf{C}_k \tag{17}$$

Energy

$$E_g = 2\sum_k \sum_{p\mu,q\nu} h_{p\mu,q\nu} C^*_{p\mu,k} C_{q\nu,k} + \sum_k \sum_{p\mu,q\nu,r\gamma,s\eta} (2E_{p\mu r\gamma,q\nu s\eta} - E_{p\mu r\gamma,s\eta q\nu}) C^*_{p\mu,k} C_{q\nu,k} C^*_{r\gamma,k} C_{s\eta,k} \tag{18}$$

3 Molecule orbitals

4 Wave function

5 Density

6 Gradient logpsi

7 Laplacian logpsi