# 第一次作业答案

## 2. 写出静电场下单个氢气分子的精确哈密顿量（使用原子单位）。

$$
\begin{aligned}
&\hat{H}=\hat{T}_p+\hat{T}_e+\hat{U}_{pp}+\hat{U}_{ep}+\hat{U}_{ep}+\hat{U}_{Ee}\\
&\hat{T}_p=-\frac{1}{2M_a}\nabla_a^2-\frac{1}{2M_b}\nabla_b^2\\
&\hat{T}_e=-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2\\
&\hat{U}_{pp}=\frac{1}{|R_a-R_b|},\hat{U}_{ee}=\frac{1}{|r_1-r_2|}\\
&\widehat{U}_{ep}=-\frac{1}{|R_a-r_1|}-\frac{1}{|R_a-r_2|}-\frac{1}{|R_b-r_1|}-\frac{1}{|R_b-r_2|}\\
&\widehat{U}_{EP}=-ER_a-ER_b,U_{Ee}=Er_1+Er_2
\end{aligned}
$$

## 3. 把上一题中的哈密顿量，利用绝热近似分成原子核部分和电子部分。

$$
\begin{aligned}
&H_e=-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2+\frac{1}{|r_1-r_2|}+E_{r_1}+E_{r_2}\\
&\quad-\frac{1}{|R_a-r_1|}-\frac{1}{|R_a-r_2|}-\frac{1}{|R_b-r_1|}-\frac{1}{|R_b-r_2|}\\
&\widehat{H}_p=-\frac{1}{2M_a}\nabla_a^2-\frac{1}{2M_b}\nabla_b^2+\frac{1}{|R_a-R_b|}-E\cdot R_a-E\cdot R_b
\end{aligned}
$$

## 4. 在$\mathrm{Hartree-Fock}$近似下,推导$\langle\Psi(r_1,r_2)|\frac{1}{|r_1-r_2|}|\Psi(r_1,r_2)\rangle$

$$
\begin{aligned}
&\psi(r_1,r_2)=\frac{1}{\sqrt{2}}(\phi_1(r_1)\phi_2(r_2)-\phi_1(r_2)\phi_2(r_1))\\
&\iint\psi^*(r_1,r_2)\frac{1}{|r_1-r_2|}\psi(r_1,r_2)dr_1dr_2\\
&=\frac{1}{2}\iint\phi^*(r_1)\phi_2^*(r_2)\frac{1}{|r_1-r_2|}\phi_1(r_1)\phi_2(r_2)dr_1dr_2\\
&=\frac{1}{2}\iint\phi^*(r_1)\phi_2^*(r_2)\frac{1}{|r_1-r_2|}\phi_1(r_2)\phi_2(r_1)dr_1dr_2\\
&=\frac{1}{2}\iint\phi^*(r_1)\phi^*(r_1)\frac{1}{|r_1-r_2|}\phi_1(r_1)\phi_2(r_2)dr_1dr_2\\
&+\frac{1}{2}\iint\phi_1^*(r_2)\phi_2^*(r_1)\frac{1}{|r_1-r_2|}\phi_1(r_2)\phi_2(r_1)dr_1dr_2\\
&=\frac{1}{2}\iint\phi_1^*(r_1)\phi_1(r_1)\phi_2^*(r_2)\phi_2(r_2)\frac{1}{|r_1-r_2|}dr_1dr_2\\
&+\frac{1}{2}\iint\phi_1^*(r_1)\phi_1(r_1)\phi_2^*(r_2)\phi_2(r_2)\frac{1}{|r_1-r_2|}dr_1dr_2\\
&-\frac{1}{2}\iint\phi_1^*(r_1)\phi_1(r_2)\phi_2^*(r_2)\phi_2(r_1)\frac{1}{|r_1-r_2|}dr_1dr_2\\
&-\frac{1}{2}\iint\phi_1^*(r_1)\phi_1(r_2)\phi_2^*(r_2)\phi_2(r_1)\frac{1}{|r_1-r_2|}dr_2dr_1dr_2\\
&=\int\phi_1^*(r)\phi_1(r)\phi_2^*(r')\phi_2(r')\frac{1}{|r-r'|}drdr'-\iint\phi_1^*(r)\phi_1(r')\phi_2^*(r')\phi_2(r)\frac{1}{|r-r'|}drdr'
\end{aligned}
$$

## 5. 在 Hartree-Fock 近似下，说明关联能的来源及其定义，说明关联能不会大于零，并列举解决电子关联问题的常用方法

关联：电子波函数不能写成单粒子波函数乘积形式， $\Phi(r_1,r_2,...,r_n)\neq\varphi_1(r_1)\varphi_2(r_2)...\varphi_n(r_n)$

## 6. 利用变分原理推导 Hartree-Fock 方法交换积分的变分导数。

$$\delta\frac{1}{2}\sum_{i,j}k_{ij}=\delta\frac{1}{2}\sum_{i,j}\int\phi_i^*(r_1)\phi_j^*(r_2)\frac{1}{|r_1-r_2|}\phi_i(r_2)\phi_j(r_1)dr_1dr_2$$
$$=\sum_j\int\delta\phi_a^*(r_1)\phi_j^*(r_2)\frac{1}{|r_1-r_2|}\phi_a(r_1)\phi_j(r_1)dr_1dr_2$$
$$\frac{\delta\frac{1}{2}\sum_{ij}k_{ij}}{\delta\phi_a^*}=\sum_j\phi_j(r_1)\int\phi_j^*(r_2)\frac{1}{|r_1-r_2|}\phi_a(r_2)dr_2$$

## 10. 以氢原子为例，根据量子力学求解出来的波函数，计算其在 LDA 下的动能、外势场能、库伦能、交换能和关联能（PW92）

### 交换能

$$\Phi=\frac{1}{\sqrt{\pi}}e^{-r},\rho=\frac{1}{\pi}e^{-2r}$$
$$E_x=\int\rho\epsilon_x(p)dr$$
$$\epsilon_x=\epsilon^0(n)+[\epsilon^1(n)-\epsilon^0(n)]f(\zeta)$$
$$\text{对于氢原子，}\zeta=0,f(\zeta)=0$$
$$\epsilon_x=\epsilon^0\left(n\right)=-\frac{3}{4}\left(\frac{9}{4\pi^2}\right)^{1/3}\frac{1}{r_s}=-\frac{3}{4}\left(\frac{9}{4\pi^2}\right)^{1/3}\frac{1}{\left(\frac{3}{4\pi\rho}\right)^{1/3}}=-\frac{3}{4}\left(\frac{3\rho}{\pi}\right)^{1/3}$$
$$E_x=\int\rho\left(-\frac{3}{4}\right)\left(\frac{3\rho}{\pi}\right)^{1/3}dr$$
$$=-3\left(\frac{3}{\pi^2}\right)^{\frac{1}{3}}\int r^2e^{-\frac{8}{3}r}dr=-0.2127$$

### 关联能

$$E_c=4\pi\int\rho\epsilon_c(p)r^2dr$$
$$\epsilon^0(p)=-2A(1+\alpha_1r_s)\ln\left(1+\frac{1}{2A(\beta_1r_s^{1/2}+\beta_2r_s+\beta_3r_s^{3/2}+\beta_4r_s^2)}\right)$$
$$A=0.031091,\alpha_1=0.2137,\beta_1=7.5957,$$
$$\beta_2=3.5876,\beta_3=1.6382,\beta_4=0.49294$$
$$E_c=-0.044$$

```
import numpy as np
from scipy.integrate import quad

def rho(r):
    return (1/np.pi) * np.exp(-2 * r)

def r_s(r):
    # 限制r的值以避免溢出
    r = np.minimum(r, 20)  # 你可以根据需要调整这个值
    return (3/4) ** (1/3) * np.exp(2*r/3)

def epsilon_c(r):
    rs = r_s(r)
    x = np.sqrt(rs)

    A = 0.031091
    alpha1 = 0.2137
    beta1 = 7.5957
    beta2 = 3.5876
```

```python
    beta3 = 1.6382
    beta4 = 0.49294

    # 确保对数函数的参数为正且不会太小
    term = 1 + 1/(2*A * (beta1*x + beta2*x**2 + beta3*x**3 + beta4*x**4))
    if term <= 1:
        term = 1 + 1e-12 # 添加一个小的正数以避免对数为负或零

    ep = -2*A * (1 + alpha1*x**2) * np.log(term)
    return ep

def integrand(r):
    ep = epsilon_c(r)
    rho_val = rho(r)
    if np.isfinite(ep) and np.isfinite(rho_val):
        return ep * rho_val * 4 * np.pi * r**2
    else:
        return 0  # 如果epsilon_c或rho不是有限值，则返回0

E_c, error = quad(integrand, 0, np.inf, epsabs=1e-12, epsrel=1e-12)

print(f'关联能 E_c = {E_c}')
```

## 库伦能

$$
\begin{aligned}
&E_{cl} = \frac{1}{2}\iint \frac{\rho(r')\rho(r)}{|r-r'|}drdr' \\
&|r-r'| = \sqrt{r^2+r'^2-2rr'\cos\theta} \\
&E_{cl} = \frac{1}{2}\int dr\rho(r)\int \frac{p(r')dr'}{|r-r'|}
\end{aligned}
$$

$$
\begin{aligned}
&\int \frac{\rho(r')dr'}{|r-r'|} \\
&= \int \frac{1}{\pi}\frac{e^{-2r'}}{\sqrt{r^2+r'^2-2rr'\cos\theta}} r'^2 \sin\theta dr' d\theta d\varphi \\
&= \int \frac{2dr'}{\sqrt{2rr'}} e^{-2r'} r'^2 2\sqrt{\frac{r^2+r'^2}{2rr'}-\cos\theta}\Big|_0^\pi \\
&= 4\int \frac{e^{-2r'}dr'}{2rr'} r'^2(r+r'-|r-r'|) \\
&= \frac{2}{r}\left(\int_0^r e^{-2r'}dr'r'2r' + \int_r^\infty e^{-2r'}dr'r'2r\right) \\
&= -e^{-2r} - \frac{1}{r}e^{-2r} + \frac{1}{r}
\end{aligned}
$$

$$
\begin{aligned}
E_c \quad &= \frac{1}{2}\int \frac{1}{\pi}e^{-2r}r^2 dr(4\pi)\left(-e^{-2r}-\frac{1}{r}e^{-2r}+\frac{1}{r}\right) \\
&= 2\int dre^{-2r}(-r^2e^{-2r} - re^{-2r} + r) \\
&= 2\int_0^\infty dr\left(-r^2e^{-4r} - re^{-4r} + re^{-2r}\right) \\
&= 2(-\frac{2}{4^3} - \frac{1}{4^2} + \frac{1}{2^2}) \\
&= \frac{5}{16}
\end{aligned}
$$