Homework4

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1 The exchange energy of a uniform electron gas

For the uniform gas of the electrons, the plane wave function is:

$$\phi_i(\vec{r},\sigma) = \frac{e^{i\vec{k_i}\cdot\vec{r}}}{\sqrt{V}}\psi(\sigma) \tag{1}$$

where V is the volume. We set: $\psi(\sigma)^*\psi(\sigma) = 1$

Using $\rho = \sum_i^N |\phi_i(\vec{r})|^2$, so we can get:

$$\rho = \frac{N}{V} \tag{2}$$

is same as in the classical concept. And $N_{up} = N_{down} = \frac{N}{2}$, $\rho_{up} = \rho_{down} = \frac{\rho}{2}$.

From the Hartree-Fock approximation, the exchange energy for i and j electron is:

$$\begin{aligned} K_{ij} &= \iint d\vec{r_i}d\vec{r_j}\phi_i^*(\vec{r_i},\sigma_i)\phi_j^*(\vec{r_j},\sigma_j)\frac{e^2}{|\vec{r_i}-\vec{r_j}|}\phi_i(\vec{r_j}.\sigma_j)\phi_j(\vec{r_i},\sigma_i) \\ &= \iint d\vec{r_i}d\vec{r_j}\frac{1}{V^2}e^{i(\vec{k_i}-\vec{k_j})\cdot(\vec{r_j}-\vec{r_i})}\frac{e^2}{|\vec{r_i}-\vec{r_j}|} \end{aligned} \tag{3}$$

And the exchange energy should be like:

$$\begin{aligned} E_x^\sigma &= -\frac{1}{2}\sum_{i,j}K_{ij} = -\frac{e^2}{2V^2}\sum_{i,j}\iint d\vec{r_i}d\vec{r_j}e^{i(\vec{k_i}-\vec{k_j})\cdot(\vec{r_j}-\vec{r_i})}\frac{1}{|\vec{r_i}-\vec{r_j}|} \\ &= -\frac{e^2}{2V^2}\sum_{i,j}\int d\vec{r_i}\int d(\vec{r_j}-\vec{r_i})e^{i(\vec{k_i}-\vec{k_j})\cdot(\vec{r_j}-\vec{r_i})}\frac{1}{|\vec{r_i}-\vec{r_j}|} \\ &= -\frac{e^2}{2V^2}\sum_{i,j}\delta_{i,j}\frac{4\pi}{|\vec{k_i}-\vec{k_j}|^2}\int d\vec{r_i} = -\frac{e^2}{2V}\sum_{i,j}\delta_{i,j}\frac{4\pi}{|\vec{k_i}-\vec{k_j}|^2} \\ = -\frac{e^2}{2V}\frac{4\pi V^2}{(2\pi)^6}\iint_{\vec{0}}^{k_F^\sigma} d\vec{k_i}d\vec{k_j}\frac{1}{(\vec{k_i}-\vec{k_j})^2} &= -\frac{e^2V}{(2\pi)^5}\iint_{\vec{0}}^{k_F^\sigma} d\vec{k_i}d\vec{k_j}\frac{1}{(\vec{k_i}-\vec{k_j})^2} \end{aligned} \tag{4}$$

The electron gas has a limit wave vector k_F^σ, due to Pauli exclusion, we could get:

$$\frac{4}{3}\pi(k_F^\sigma)^3 = \frac{(2\pi)^3}{V}N^\sigma \tag{5}$$

this is also the reason we could use integral to take the place of the Sum. Then

$$k_F = (6\pi^2)^{\frac{1}{3}}\rho^{\sigma\frac{1}{3}} \tag{6}$$

we could just focus on the calculation of the integral, we use the sphere coordinate system, so the integral should be:

$$\begin{aligned}
&\iiint\iiint \frac{k_i^2 k_j^2 \sin\theta_i \sin\theta_j dk_i dk_j d\theta_i d\theta_j d\varphi_i d\varphi_j}{k_i^2+k_j^2-2k_ik_j\cos\theta_i\cos\theta_j-2k_ik_j\sin\theta_i\sin\theta_j\cos(\varphi_i-\varphi_j)} \\
&= \iiint\iint \frac{2\pi k_i^2 k_j^2 \sin\theta_i \sin\theta_j dk_i dk_j d\theta_i d\theta_j d\varphi_i}{\sqrt{k_i^2+k_j^2-2k_ik_j\cos(\theta_i+\theta_j)}\sqrt{k_i^2+k_j^2-2k_ik_j\cos(\theta_i-\theta_j)}} \\
&= \iiint\int \frac{4\pi^2 k_i^2 k_j^2 \sin\theta_i \sin\theta_j dk_i dk_j d\theta_i d\theta_j}{\sqrt{k_i^2+k_j^2-2k_ik_j\cos(\theta_i+\theta_j)}\sqrt{k_i^2+k_j^2-2k_ik_j\cos(\theta_i-\theta_j)}} \\
&= \iiint 2\pi^2 k_i k_j dk_i dk_j d\cos\theta_i \ln\frac{k_i^2+k_j^2-2k_ik_j}{k_i^2+k_j^2+2k_ik_j} \\
&= \iint 4\pi^2 k_i k_j dk_i dk_j \ln\frac{k_i^2+k_j^2+2k_ik_j}{k_i^2+k_j^2-2k_ik_j} \\
&= 4\pi^2 k_F^4 \int 2x^2(1+\frac{1-x^2}{2x}\ln(\frac{1+x}{1-x}))dx = 4\pi^2 k_F^4
\end{aligned} \tag{7}$$

So the total exchange energy should be:

$$E_x = E_x^{up} + E_x^{down} = -\frac{3e^2N^{up}}{4}(\frac{6\rho^{up}}{\pi})^{\frac{1}{3}} - \frac{3e^2N^{down}}{4}(\frac{6\rho^{down}}{\pi})^{\frac{1}{3}} = -\frac{3e^2N}{4}(\frac{3\rho}{\pi})^{\frac{1}{3}} \tag{8}$$

2 A mini Gaussian program

2.1 overlap matrix S

Just use the parameter given, and print the S and the SVAL, you can see that:

$$S = \begin{pmatrix} 1 & 0.5017 \\ 0.5017 & 1 \end{pmatrix} \tag{9}$$

and the eigenvalue of it should be 0.4983 and 1.5017.They are all real numbers and more than 0. If there is a vector like [x, y],

$$g(x,y) = [x,y]S[x,y]^T = x^2 + 1.0034xy + y^2 \tag{10}$$

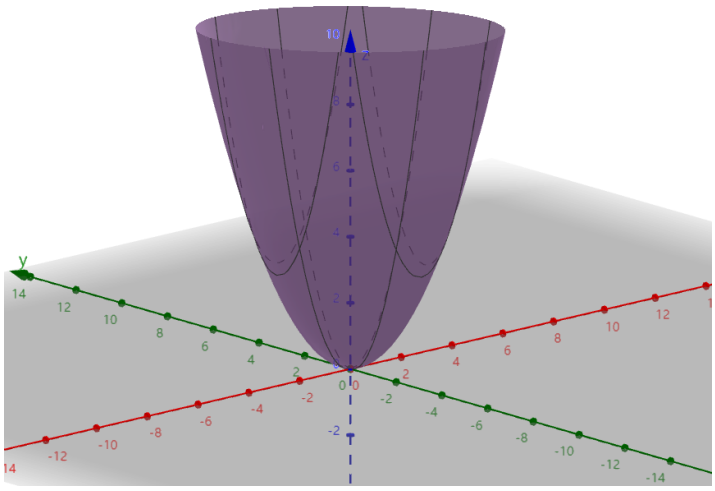

Figure 1: plot for the 3D function

You can see it in the figure, it is easy to prove that $g(x, y) >= 0$. Use the polarization coordinate, the function turn to be:

$$g(x, y) = g(r, \theta) = r^2(1 + 0.5017 \sin 2\theta) \tag{11}$$

Where $(1 + 0.5017 \sin 2\theta) > 0$. You can see that only when $r = 0$ which is $x = y = 0$, this function should be 0 and in the other situations, $g(x, y) > 0$. So the overlap matrix is positive definite.

2.2 HOMO, LUMO energies. HOMO, LUMO wavefunctions. Two orbitals using 3D isosurfaces. (label the hydrogen and helium nuclei clearly)

From the lecture we know that

$$E_{LUMO} = \epsilon_{N+1} = E_{HF}(N + 1) - E_{HF}(N) = -A \tag{12}$$

$$E_{HOMO} = \epsilon_N = E_{HF}(N) - E_{HF}(N - 1) = -I \tag{13}$$

in which N is the number of the electrons.

I modified the codes to plot the orbitals and the result is:

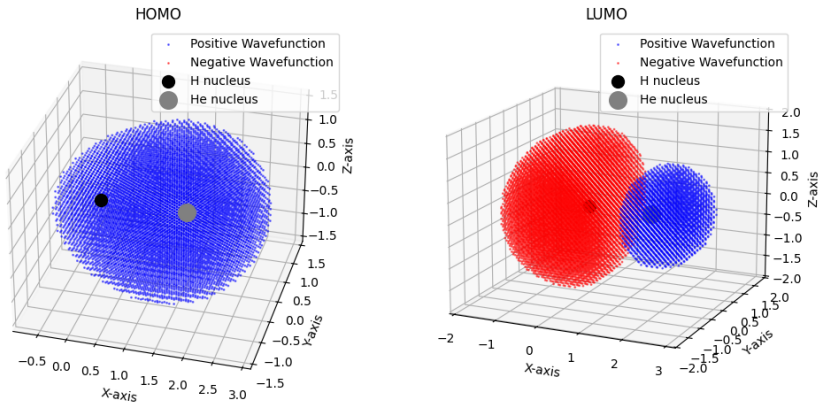

Figure 2: plot for the 3D function

The bigger and gray one is the nucleai of He, and the nucleai of H is located at (0,0,0). And I could get the energies and wavefunctions from the codes:

$$E_{HOMO} = -1.4472 hartrees = -39.38 eV \tag{14}$$

$$E_{LUMO} = -0.1052 hartrees = -2.86 eV \tag{15}$$

$$\phi_{HOMO} = 0.3178\psi_1 + 0.8020\psi_2 \tag{16}$$

$$\phi_{LUMO} = -1.1115\psi_1 + 0.8325\psi_2 \tag{17}$$

2.3 Total energy, Hartree and exchange energies

The Hartree Fock energy:

$$E_{HF} = 2\sum_{i}^{N/2} E_{ii} + \sum_{i,j}^{N/2} (2J_{ij} - K_{ij}) \tag{18}$$

$$E_{HF} = \frac{1}{2}\sum_{\mu=1}^{M}\sum_{\nu=1}^{M} P_{\mu\nu}(H_{\mu\nu}^{core} + F_{\mu\nu}) + V_{NN} \tag{19}$$

using

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{a}^{N/2} \int \phi_{\mu}^{*}[2J_a - K_a]\phi_{\nu} d\vec{r} \tag{20}$$

so

$$\frac{1}{2}\sum_{\mu=1}^{M}\sum_{\nu=1}^{M} P_{\mu\nu}(H_{\mu\nu}^{core} + F_{\mu\nu}) = \frac{1}{2}\sum_{\mu=1}^{M}\sum_{\nu=1}^{M} P_{\mu\nu}(2H_{\mu\nu}^{core} + \sum_{a}^{N/2} \int \phi_{\mu}^{*}[2J_a - K_a]\phi_{\nu} d\vec{r}) \tag{21}$$

and

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*} \tag{22}$$

so

$$\frac{1}{2}\sum_{\mu=1}^{M}\sum_{\nu=1}^{M} P_{\mu\nu}(H_{\mu\nu}^{core} + F_{\mu\nu}) = \sum_{\mu=1}^{M}\sum_{\nu=1}^{M}\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*}(2\int \phi_{\mu}^{*}\hat{h_1}\phi_{\nu}^{*} d\vec{r} + \sum_{a}^{N/2} \int \phi_{\mu}^{*}[2J_a - K_a]\phi_{\nu} d\vec{r}) \tag{23}$$

in which:

$$\sum_{\mu=1}^{M}\sum_{\nu=1}^{M}\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*} 2\int \phi_{\mu}^{*}\hat{h_1}\phi_{\nu}^{*} d\vec{r} = 2\sum_{a}^{N/2}\int \psi_{a}^{*}\hat{h_1}\psi_{a}^{*} d\vec{r} = 2\sum_{i}^{N/2} E_{ii} \tag{24}$$

using same way:

$$\sum_{\mu=1}^{M}\sum_{\nu=1}^{M}\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*} \sum_{a}^{N/2}\int \phi_{\mu}^{*}[2J_a - K_a]\phi_{\nu} d\vec{r}) = \sum_{i,j}^{N/2}(2J_{ii} - K_{ij}) \tag{25}$$

If you have set that the V_{NN} is constant, it is no problem that:

$$E_{HF} = \frac{1}{2}\sum_{\mu=1}^{M}\sum_{\nu=1}^{M} P_{\mu\nu}(H_{\mu\nu}^{core} + F_{\mu\nu}) + V_{NN} \tag{26}$$

proved.

$$HartreeEnergy((E_{Hartree})) : E_{Hartree} = \frac{1}{2}\sum_{\mu=1}^{M_X}\sum_{\nu=1}^{M_X} P_{\mu\nu}\sum_{\lambda=1}^{M_X}\sum_{\sigma=1}^{M_X} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) \tag{27}$$

$$ExchangeEnergy((E_{exchange})) : E_{exchange} = -\frac{1}{2}\sum_{\mu=1}^{M_X}\sum_{\nu=1}^{M_X} P_{\mu\nu}\sum_{\lambda=1}^{M_X}\sum_{\sigma=1}^{M_X} P_{\lambda\sigma}(\mu\lambda|\nu\sigma) \tag{28}$$

The hartree energy and exchange energy is:

$$E_{Hartree} = 1.7456 hartrees \tag{29}$$

$$E_{exhange} = -1.7456 hartrees \tag{30}$$