Homework Sheet No. 2

Issued 2 Oct. 2017 and **due 16 October 2017**

1. In the Hartree-Fock method, derive the Koopmans theorem, namely,

$$-\Delta E = \int \varphi_k^*(q_1)\hat{h}_k\varphi_k(q_1)d\tau_1 + \sum_{k(\neq i)}\iint \frac{|\varphi_i(q_1)|^2|\varphi_k(q_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|}d\tau_1 d\tau_2$$

$$-\sum_{k(\neq i)}\iint \frac{\varphi_i^*(q_1)\varphi_i(q_2)\varphi_k^*(q_2)\varphi_k(q_1)}{|\mathbf{r}_1-\mathbf{r}_2|}d\tau_1 d\tau_2 = \varepsilon_i, \quad \text{or} -\Delta E = \varepsilon_i.$$

(see also Martin, p. 72, excise 3.18.)

2. In the extremely low density limit, a system of electrons will form a regular lattice, with each electron occupying a unit cell; this is known as the Wigner crystal. The energy of this crystal has been calculated to be $E^{Wig} = \left[-\frac{3}{(r_s/a_0)} + \frac{3}{(r_s/a_0)^{3/2}}\right]$Ry where $\frac{4\pi}{3}r_s^3 = n^{-1}$ and a_0 is Bohr radius. This can be compared with the energy of the electron gas in the Hartree-Fock approximation $\frac{E^{HF}}{N} = \left[\frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)}\right]$Ry, to which we must add the electrostatic energy (this term is canceled by the uniform positive background of the ions, but here we are considering the electron gas by itself). The electrostatic energy turns out to be $E^{es} = -\frac{6}{5}\frac{1}{(r_s/a_0)}$Ry. Taking the difference between the two energies, E^{Wig} and $E^{HF} + E^{es}$, we obtain the correlation energy, which is by definition the interaction energy after we have taken into account all the other contributions, kinetic, electrostatic and exchange. Show that the result is compatible with the Wigner correlation energy given in Table 2.1 in the next page, in the low density (high (r_s/a_0)) limit. (see also Efthimios Kaxiras, p. 80, problem 7.)

3. The bulk modulus B of a solid is defined as $B = -\Omega\frac{\partial P}{\partial \Omega} = \Omega\frac{\partial^2 E}{\partial \Omega^2}$ where Ω is the volume, P is the pressure, and E is the total energy; this quantity describes how the solid responds to external pressure by changes in its volume. Show that for the uniform electron gas with the exchange energy and kinetic energy terms only, $E^X = -N\frac{0.916}{(r_s/a_0)}$Ry and $E^{kin} = N\frac{3}{5}\varepsilon_F$ where $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m_e}$ and $n = \frac{k_F^3}{3\pi^2}$, respectively, the bulk modulus is given by

$B = \left[\frac{5}{6\pi} \frac{2.21}{(r_s/a_0)^5} - \frac{2}{6\pi} \frac{0.916}{(r_s/a_0)^4} \right] (Ry/a_0^3)$ or equivalently, in terms of the kinetic and exchange energies, $B = \frac{1}{6\pi (r_s/a_0)^3} \left[5\frac{E^{kin}}{N} + 2\frac{E^X}{N} \right] (1/a_0^3)$. Discuss the physical implications of this result for a real solid that might be reasonably described in terms of the uniform electron gas, and in which the value of (r_s/a_0) is relatively small ($(r_s/a_0) < 1$). (see also Efthimios Kaxiras, p. 79, problem 4.)

4. Derive the Thomas-Fermi equation $(1/2)(3\pi^2)^{2/3} n(\mathbf{r})^{2/3} + V(\mathbf{r}) - \mu = 0$ from the variational of the functional. Use the method of Lagrange multipliers as given in $\delta\left[\langle \Psi | H | \Psi \rangle - E(\langle \Psi | \Psi \rangle - 1)\right] = 0$ and used in $\Omega_{TF}[n] = E_{TF}[n] - \mu\left\{\int d^3 r n(\mathbf{r}) - N\right\}$. (see also Martin, p. 133, excise 6.1.)

Table 2.1. *Correlation energy functionals* $\epsilon^{cor}[n(\mathbf{r})]$ *and exchange-correlation potentials* $V^{XC}[n(\mathbf{r})]$ *in various models.*

H–L = Hedin–Lundqvist [24], P–Z = Perdew–Zunger [25]. ϵ^X is the pure exchange energy from Eq. (2.91). r_s is measured in units of a_0 and the energy is in rydbergs. The numerical constants have units which depend on the factor of r_s involved with each.

Model	$\epsilon^{cor}[n(\mathbf{r})]$	$V^{XC}[n(\mathbf{r})]$
Exchange	0	$\frac{4}{3}\epsilon^X$
Slater	$(\frac{3}{2}\alpha - 1)\epsilon^X$	$2\alpha\epsilon^X$
Wigner	$A(B + r_s)^{-1}$	
	$A = 0.884, \quad B = 7.8$	
H–L		$\frac{4}{3}\epsilon^X \left[1 + Br_s \ln\left(1 + Ar_s^{-1}\right)\right]$
		$A = 21, \quad B = 0.0368$
P–Z: $r_s < 1$	$A_1 + A_2 r_s + [A_3 + A_4 r_s] \ln(r_s)$	
	$A_1 = -0.096, \quad A_2 = -0.0232$	
	$A_3 = 0.0622, \quad A_4 = 0.004$	
$r_s \geq 1$	$B_1 \left[1 + B_2\sqrt{r_s} + B_3 r_s\right]^{-1}$	
	$B_1 = -0.2846, \quad B_2 = 1.0529$	
	$B_3 = 0.3334$	