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http://www.itp.tu-berlin.de/menue/lehre/lv/ss08/wpfv/tfkp/

Theoretical Material Science: exercise sheet 3

Return: Wednesday, May 14, 4 pm in the exercise

Exercise 7 (4 points): *Koopmans' theorem*
Inspect the chapter in the lecture notes, where the relation between Ionization energy I_k and Lagrange parameters ϵ_{oi} is shown, i.e. at the equation

$$I_k := \langle \Phi^{N-1} | H^{e,N-1} | \Phi^{N-1} \rangle - \langle \Phi^N | H^{e,N} | \Phi^N \rangle \approx -\epsilon_{o_k s_k}.$$

Write down and explain the calculation leading to this result. Which assumptions are needed?

Exercise 8 (4 points): *Thomas-Fermi atom*
We start from the effective potential in the Thomas Fermi formalism

$$V(\mathbf{r}) = \int d^3\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}') - \frac{ze^2}{|\mathbf{r}|}. \tag{1}$$

a) For the Fermi energy ϵ_F and the corresponding momentum p_F we have $|p_F(\mathbf{r})| = \sqrt{2m(\epsilon_F - V(\mathbf{r}))}$. The average electron density is $n(\mathbf{r}) = \frac{(p_F(\mathbf{r})/\hbar)^3}{3\pi^2}$. Outside the atom the electric potential should vanish, i.e. $V(r) = 0$ if $r > R$, where R is the atom radius. Use that to show

$$n(\mathbf{r}) = \frac{1}{3\pi^2\hbar^3}(-2mV(\mathbf{r}))^{3/2}.$$

b) Show that the equation

$$\Delta V(\mathbf{r}) = -4\pi e^2 n(\mathbf{r}) + 4\pi Z e^2 \delta^{(3)}(\mathbf{r}) \tag{2}$$

is equivalent to equation 1.

c) Transform equation 2 to spherical coordinates. Use that the problem has spherical symmetry.

d) For small distances to the nucleus the potential $V(\mathbf{r})$ should become the potential of the pure nucleus. Therefore we write it in the form

$$V(r) = -\frac{Ze^2}{r}\chi(r).$$

Determine that the differential equation for χ is

$$\frac{d^2\chi}{dr^2} = \frac{\chi^{3/2}(r)}{\sqrt{r}}. \tag{3}$$

e) Plot the numerical solution of equation 3, which is given by

$$\chi(r) = \begin{cases} 1 - 1.59r & r \to 0 \\ \frac{144}{r^3} & r \to \infty \end{cases}. \tag{4}$$

Do you think this is an adequate approximation for any atom (H-U)? Why or why not?

Please turn over!⟶

Exercise 9 (4 points): *Exchange and correlation in Jellium*

a) Use Mathematica to plot the exchange energy per particle, ϵ^x, of Jellium according to Slater's $X\alpha$ method as a function of the density n, for $\alpha = 2/3$ and 1. Plot also the exchange potential v^x, defined as

$$v^x(n) = \frac{\partial}{\partial n} n\epsilon^x(n).$$

b) The exchange and correlation energy of Jellium are centrally important in many density-functional calculations for real systems, and therefore accurately known in numerical form. One of the most popular parametrizations is that of Perdew and Wang [Phys. Ref. B **45**, 13244], which is based on a fit of Quantum Monte Carlo calculations by Ceperley and Alder [Phys. Rev. Lett. **45**, 566]. For the unpolarized Jellium, the parameterizations for exchange and correlation take the following separate forms:

$$\epsilon^x(n) = -0.738558766382022406 n^{1/3}$$

$$\epsilon^c(n) = -2A(1-\alpha_1 r_s)\ln\left[1 + \frac{1}{2A(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)}\right].$$

Both are given in Hartree units, with $r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$, and with the following parameters:

$$\begin{array}{lll} A = 0.031091 & \alpha_1 = 0.21370 & \beta_1 = 7.5957 \\ \beta_2 = 3.5876 & \beta_3 = 1.6382 & \beta_4 = 0.49294 \end{array}$$

Plot the Perdew-Wang exchange and correlation energies per particle, and the corresponding exchange-correlation potentials, defined as above. Which similarities and differences to Slater's approximation do you see?

- **Webpage of the lecture:** http://www.itp.tu-berlin.de/menue/lehre/lv/ss08/wpfv/tfkp/
- **Lecture:** Tue. & Fri., 10:00 a.m.-12:00 p.m. in room EW 203, TU Berlin
- **Exercise:** Mon., 14:00 a.m. in room H 1029
- **Literature:** See webpage.
- **"Übungsschein"-criteria:**
  - Regular and active participation in the exercises
  - Presentation of homework tasks and
  - 50% of the homework points.
- **Consultation hours:**
  - Prof. Dr. Matthias Scheffler: on appointment
  - Dr. Volker Blum: on appointment
  - Philipp Zedler: Wed, 11:00 - 12:00 a.m. in room EW 711