Physics 685 – Electronic Structure

Homework 16-17-18-N

Please read Martin, Electronic Structure, Chapter 8, especially Chap 8.2, 8.3, 8.9. Read also R. O. Jones on Introduction to Density Functional Theory and Exchange and Correlation Functionals. Come prepared to answer questions based on reading.

1. Problems 7.11 if time.

2. **Equivalence of gradient and Laplacian in GEA**. So(ooooooo) the idea is that to second order in a density gradient expansion of the exchange (or exchange-correlation) energy, one can get a correction $\sim s_1^2$ or one $\sim s_2$ or both, with s_n defined as in Martin 8.2. Show that for exchange, these two lead to *identical* corrections to the gradient expansion:

$$E_x^{GEA}[n] = \int d^3r n(\mathbf{r})\epsilon_x^{heg}(n(\mathbf{r}))(1+\mu_1 s_1^2) \quad (1)$$

$$= \int d^3r n(\mathbf{r})\epsilon_x^{heg}(n(\mathbf{r}))(1+\mu_2 s_2) \quad (2)$$

   for $\mu_1/\mu_2 = 3$.

3. **Thomas-Fermi region of an atom**. Find the values for s_1^2 and s_2 for a two electron atom with approximate density:

$$n(r) = \frac{2\zeta^3}{\pi a_0^3}\exp\left(-2\zeta r/a_0\right). \quad (3)$$

   Plot these versus r for an appropriate value of ζ/a_0. When is the system "reasonably" slowly varying, i.e., both parameters are less than or equal to one? When does the system experience extreme variation – one or both parameters blow up to infinity? The former region is known as the Thomas-Fermi region of the atom, and is where in fact, Thomas-Fermi theory can be successfully applied. One finds that the total energy of all atoms for $Z > 2$ can actually be obtained by the appropriate Thomas-Fermi theory (with Weiszacker correction).

4. Show explicitly, if you have not already above, that s_n is unitless. Show that it is invariant under the following coordinate transformation:

$$r \rightarrow \lambda r \quad (4)$$

$$n(r) \rightarrow \lambda^3 n(\lambda r) \quad (5)$$

5. **Potential of a Laplacian-based model**. Consider the following alternate candidate for the first order correction to the LDA:

$$E_{xc}[n, \nabla n] = \int d^3r n(\mathbf{r}) \epsilon_{xc} \left[n(\mathbf{r}), \nabla^2 n(\mathbf{r}) \right]. \tag{6}$$

Here one could and perhaps should extend the theory to spin-densities, but let us keep it simple to start with. Use the basic theory of the calculus of variations to show that the contribution of such a term to the Kohn-Sham potential is:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \left[\epsilon_{xc} + n \frac{\partial \epsilon_{xc}}{\partial n} + \nabla^2 \left(n \frac{\partial \epsilon_{xc}}{\partial \nabla^2 n} \right) \right]_{n=n(\mathbf{r})} \tag{7}$$

The most general expression for an exchange-correlation potential for a "meta-GGA" functional, one that dependes on $n(\mathbf{r})$, $\nabla n(\mathbf{r})$ and $\nabla^2 n(\mathbf{r})$ simultaneously can thus be written as:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \left[\epsilon_{xc} + n \frac{\partial \epsilon_{xc}}{\partial n} - \nabla \cdot \left(n \frac{\partial \epsilon_{xc}}{\partial \nabla n} \right) + \nabla^2 \left(n \frac{\partial \epsilon_{xc}}{\partial \nabla^2 n} \right) \right]_{n=n(\mathbf{r})} \tag{8}$$

6. **Model of nuclear cusp**. Read in Jones about the cusp in the density at the nucleus of any atom. This comes about because of the divergence of the external Coulomb potential felt at the position of the nucleus.

   (a) Show, using a density of the form of Equation 3, that a GGA exchange model using gradients of the density (e.g., that of Equation 1) will produce an exchange potential $v_{xc} = \delta E_x / \delta n$ that diverges at the nucleus ($r \to 0$). This is not correct – it basically changes the charge at the nucleus!

   (b) Show, using a density of the form of Equation 3, that a GGA exchange model using $\nabla^2 n$ of the form

$$E_x^{GGA}[n] = \int d^3r n(\mathbf{r}) \epsilon_x^{heg}(n(\mathbf{r})) \left(1 + \frac{M_2}{s_2^\alpha} \right) \tag{9}$$

   does not go to infinity at the nucleus, provided $\alpha \geq 1$. (Refer to problem 5.) A goal for producing a working candidate for a Laplacian-based functional is to merge successfully from a small s_2 form such as Eq. 2 to a large s_2 form such as Eq. 9 in a smooth way.