Physics 685 – Electronic Structure

Homework 5

Please read Martin, Electronic Structure, Chapter 2, sections 1-2, 5-6, 8-9. Come prepared to answer questions based on reading.

1. **Project: Exchange hole of an atom**

   Consider the exchange hole formed by two electrons in the valence shell of boron. The valence shell configuration is $2s^2 2p$ and has a $2s$ and $2p_0$ electron pair in one spin and a single $2s$ electron in the other spin. To gain some insight into this case, let's just look at the $2s, 2p_0$ pair and ignore the other spin. Assume these can be described by the (simplified) orbitals:

$$\psi_{2s}(\mathbf{r}) = \frac{1}{\sqrt{4\pi}} r \exp\left(-r/2a\right) \tag{1}$$

$$\psi_{2p_0}(\mathbf{r}) = \sqrt{\frac{3}{4\pi}} z \exp\left(-r/2a\right) \tag{2}$$

   where a is the effective Bohr radius for the boron valence shell, roughly 1.6 bohr radii. Note that the angular state for the $2p_0$ electron is included in the above definition with the $l = 1, m = 0$ spherical harmonic being

$$Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}. \tag{3}$$

   (a) First, use equation (3.54) in Martin to write out the exchange pair density $\Delta n_x(\mathbf{r}, \sigma, \mathbf{r}', \sigma)$ for the pair in question. As we are only considering one spin species, you can drop the spin index.

   (b) The true definition of "hole", as in exchange or exchange-correlation hole that is in 99% of the literature is in terms of the conditional expectation to find a particle at $\mathbf{r}$ given you know one is at $\mathbf{r}'$. This conditional expectation is

$$n(\mathbf{r}, \sigma|\mathbf{r}', \sigma') = n(\mathbf{r}, \sigma) - \Delta n(\mathbf{r}, \sigma|\mathbf{r}', \sigma') \tag{4}$$

   where Δn is the conditional density hole and defines how the expectation of finding the particle at $\mathbf{r}$ has changed from the average density at $\mathbf{r}$ by the knowledge that the other electron is at $\mathbf{r}'$.

   The hole is related to the pair density (Eq. 3.49) by the rule

$$n(\mathbf{r}, \sigma; \mathbf{r}', \sigma') = n(\mathbf{r}', \sigma') n(\mathbf{r}, \sigma|\mathbf{r}', \sigma') \tag{5}$$

   which can be read as "the expectation of finding simultaneously a particle at $\mathbf{r}$ and one at $\mathbf{r}'$ is equal to the expectation of finding one at $\mathbf{r}'$ times the *conditional* expectation of finding another at $\mathbf{r}$ *given* one is already at $\mathbf{r}'$. So comparing this equation to the definition of Δn given in (3.51) we see that the hole is the change in pair density Δn at $\mathbf{r}$ divided by the density at $\mathbf{r}'$:

$$\Delta n(\mathbf{r},\sigma|\mathbf{r}',\sigma') = \frac{\Delta n(\mathbf{r},\sigma;\mathbf{r}',\sigma')}{n(\mathbf{r}',\sigma')}. \tag{6}$$

In the literature, one usually encounters the following special cases for the conditional density hole: The *exchange* hole $n_x(\mathbf{r},\sigma;\mathbf{r}',\sigma')$ is the expectation of Δn for a *Slater determinant wavefunction.* The true ground-state wavefunction is much more complicated than that, and has correlation effects due not only to Fermi statistics but also Coulomb repulsion between electrons. This is the *exchange-correlation* hole n_{xc}. The difference between the two is the *correlation* hole, $n_c = n_{xc} - n_x$.

Using this definition and the formula (3.54) for the Δn as used by book (";", not "|"), find the exchange hole as a function of $\mathbf{r}$ about a particle fixed at $\mathbf{r}'$ for the following cases:

i. $\mathbf{r}' = a\hat{x}$

ii. $\mathbf{r}' = a\hat{z}$

(c) Make a surface plot (try gnuplot) of the exchange hole in each case and interpret.

2. Show the following sum rules:

$$\sum_{\sigma}\int d^3r n(\mathbf{r},\sigma) = N \tag{7}$$

$$\sum_{\sigma,\sigma'}\int d^3r\int d^3r' n(\mathbf{r},\sigma;\mathbf{r},\sigma) = N(N-1) \tag{8}$$

It is easiest to start from the definition given in equation (3.49) and the equivalent for the single-particle density:

$$n(\mathbf{r},\sigma) = \langle\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\delta(\sigma-\sigma_i)\rangle \tag{9}$$