Quantum Chemistry: week 5

Question 1

Consider a single electron, having the ground state density $n(x) = Ce^{-\gamma x^2}$. For our convenience this electron lives only in one dimension. Find the external potential V_{ext} that yields this density.

For a one electron system, the real *hamiltonian is very simple:*

$$H = T + V_{\text{ext}} \ .$$

We are going the guess the ground state wave function $|\Psi\rangle$*, and then demand that* V_{ext} *is such that* $|\Psi\rangle$ *is an eigenfunction:*

$$H|\Psi\rangle = E|\Psi\rangle \ .$$

Let's start:

$$n(x) = Ce^{-\gamma x^2} \rightarrow \Psi(x) = \sqrt{Ce^{-\gamma x^2}}$$

Of course we could multiply $\Psi(x)$ *with any phase factor* $e^{i\phi}$*, but why make life difficult? The same holds for the spin. We'd have to give* Ψ *either an* α *spin or a* β *spin or some mixture. But it doesn't mater...*

Now have the kinetic energy operator T *work on* $|\Psi\rangle$*:*

$$-\frac{\hbar^2}{2m_e}\frac{d}{dx}\left[\frac{d}{dx}\sqrt{Ce^{-\gamma x^2}}\right] = -\frac{\hbar^2}{2m_e}\frac{d}{dx}\left[\frac{1}{2}\frac{1}{\sqrt{Ce^{-\gamma x^2}}} \times (Ce^{-\gamma x^2}) \times (-2\gamma x)\right] = -\frac{\hbar^2}{2m_e}\frac{d}{dx}\left[-\gamma x\sqrt{Ce^{-\gamma x^2}}\right]$$
$$= -\frac{\hbar^2}{2m_e}\left(\gamma^2 x^2 - \gamma\right)\sqrt{Ce^{-\gamma x^2}}$$

Here we could easily factorize out the wave function. So the eigenvalue equation yields:

$$-\frac{\hbar^2}{2m_e}\left(\gamma^2 x^2 - \gamma\right) + V_{\text{ext}} = E$$

This determines V_{ext} *besides the "trivial additive constant" that defines the ground state energy.*

Question 2

We consider the DFT expression for the total energy and the Kohn-Sham (KS) eigenvalue equations.

(a) The total energy can be written as a sum of the eigenvalues (for the occupied states) plus so-called "double counting" corrections. Give the expression for these double counting corrections.

Let's first summarize the expressions. The energy:

$$E[n] = \sum_i^{\text{occ}} \langle\phi_i|\frac{p^2}{2m}|\phi_i\rangle + \frac{e^2}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})\,d\mathbf{r} + E^{\text{XC}}[n]$$

The eigenvalue equation with the Kohn-Sham Hamiltonian:

$$\left\{\frac{p^2}{2m} + e^2\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + V_{\text{ext}}(\mathbf{r}) + V^{\text{XC}}[n]\right\}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \tag{1}$$

$$\text{where} \quad V^{\text{XC}}(\mathbf{r}) = \frac{\delta E^{\text{XC}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Now we'll construct the eigenvalue sum applying on the right and left hand side of the eigenvalue equation the following operation:

$$\int \sum_i^{\text{occ}} \phi_i^*(\mathbf{r})\ldots\, d\mathbf{r} \tag{2}$$

We obtain:

$$\int \sum_i \phi_i^*(\mathbf{r}) \left\{ \frac{p^2}{2m} + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\text{ext}}(\mathbf{r}) + V^{\text{XC}}[n] \right\} \phi_i(\mathbf{r})\, d\mathbf{r} = \int \sum_i \phi_i^*(\mathbf{r}) \epsilon_i \phi_i(\mathbf{r})\, d\mathbf{r} = \sum_i \epsilon_i$$

On the right hand side we thus have our sum of eigenvalues (using normalization of the $|\phi_i\rangle$). On the left hand side we get several terms. The first is exactly the kinetic energy of the energy functional. Also the interaction energy with the external potential is exactly retrieved (remember how $n(\mathbf{r})$ is obtained from the orbitals). So that's fine. The other terms yield differences. Let's be more specific:

$$\int \sum_i \phi_i^*(\mathbf{r}) \left\{ e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right\} \phi_i(\mathbf{r})\, d\mathbf{r} = e^2 \iint \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \left(\sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \right) d\mathbf{r} d\mathbf{r}' = e^2 \iint \frac{n(\mathbf{r}') n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

This is twice the Hartree energy of $E[n]$, so we have to correct for double counting *by subtracting half. We also have a correction in the XC part. The XC contribution to $E[n]$ is $E^{\text{XC}}[n]$ whereas applying (2) to the eigenvalue equation yields and XC contribution:*

$$\int \sum_i \phi_i^*(\mathbf{r}) \left\{ V^{\text{XC}}[n(\mathbf{r})] \right\} \phi_i(\mathbf{r})\, d\mathbf{r} = \int V^{\text{XC}}[n(\mathbf{r})] n(\mathbf{r})\, d\mathbf{r}$$

(note that after inserting $n(\mathbf{r})$ into the functional $V^{\text{XC}}[n]$ just a function of $\mathbf{r}$ results, i.e. not some weird operator, so it commutes with ϕ_i and you are able to join it with its complex conjugate and obtain the density $n(\mathbf{r})$.) Putting things together:

$$E = \sum_i^{\text{occ}} \epsilon_i - \frac{e^2}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E^{\text{XC}}[n] - \int V^{\text{XC}}[n(\mathbf{r})] n(\mathbf{r})\, d\mathbf{r}$$

So here you see that corrections only occur for those terms in the KS Hamiltonian that depend on the density, i.e. on the orbitals.

(b) The eigenvalues in the KS equations are Lagrange multipliers introduced to handle the orthornomality constraints on the KS orbitals. A physical interpretation of these eigenvalues is problematic. A well-defined meaning of the eigenvalues, however, exists *within the theory.* To derive this, write the density as

$$n(\mathbf{r}) = \sum_i^{\text{occ}} n_i |\phi_i(\mathbf{r})|^2$$

Here the n_i are the "filling factors", usually we just take them to be 1 and 0 for occupied and empty orbitals respectively. However, now we consider them as variables, and calculate the derivatives dE/dn_i where E is the DFT energy functional. Using the result, relate the derivatives dE/dn_i to the KS eigenvalues ϵ_i. The result is the "Janak" theorem.

Now consider the highest occupied state, and integrate. What is the physical interpretation of the highest occupied state?

Note: in Hartree-Fock you have Koopman's theorem, that relates the i-th eigenvalue to the removal energy of an electron in the i-th orbital:

$$\epsilon_i^{\text{HF}} = E(n_1, \ldots, n_i, \ldots, n_N) - E(n_1, \ldots, n_i - 1, \ldots, n_N)$$

(neglecting the change of orbitals when an electron is removed). This powerful theorem allows for an immediate connection with experiment: photo-emission measures the energy needed to remove an electron from a material. In DFT things are not that straightforward.

We follow the prescription, and obtain:

$$E[n] = \sum_i^{\text{occ}} n_i \langle \phi_i | \frac{p^2}{2m} | \phi_i \rangle + \frac{e^2}{2} \sum_{ij} \iint \frac{n_i |\phi_i(\mathbf{r})|^2\, n_j |\phi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$
$$+ \sum_i \int n_i |\phi_i(\mathbf{r})|^2 V_{\text{ext}}(\mathbf{r})\, d\mathbf{r} + E^{\text{XC}}[\sum_i n_i |\phi_i(\mathbf{r})|^2]$$

We now single out one specific orbital, let's for clarity call it k, and differentiate this expression with respect to n_k. The result:

$$\frac{dE}{dn_k} = \langle\phi_k|\frac{p^2}{2m}|\phi_k\rangle + \frac{e^2}{2}\sum_i \iint \frac{n_i|\phi_i(\mathbf{r})|^2\,|\phi_k(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \frac{e^2}{2}\sum_j \iint \frac{|\phi_k(\mathbf{r})|^2\,n_j|\phi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' +$$
$$\int |\phi_k(\mathbf{r})|^2 V_{\text{ext}}(\mathbf{r})\,d\mathbf{r} + \int \frac{\delta E^{\text{XC}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\,|\phi_k(\mathbf{r})|^2\,d\mathbf{r}$$

The two Hartree terms are identical (just relabel $\mathbf{r} \leftrightarrow \mathbf{r}'$). Taken together they yield:

$$e^2 \iint \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}|\phi_k(\mathbf{r})|^2 d\mathbf{r}d\mathbf{r}'$$

For the XC part we had to be more creative. We don't have the tools to do it formally exact, but realize that (a) the n_k is in the argument of the functional, so we had to apply some kind of chain rule, moreover (b) we have to get a number out, hence the integration. Now compare to the eigenvalue equation (1) and observe that:

$$\frac{dE}{dn_k} = \langle\phi_k|H^{\text{KS}}|\phi_k\rangle = \epsilon_k$$

Now we remove an "electron" from a KS level:

$$E(n_1,\ldots,n_i,\ldots,n_N) - E(n_1,\ldots,n_i-1,\ldots,n_N) = \int_0^1 \frac{dE(n_1,\ldots,n_i-1+n,\ldots,n_N)}{dn_i}\,dn =$$
$$\int_0^1 \epsilon_i(n_1,\ldots,n_i-1+n,\ldots,n_N)\,dn$$

Doing this for the highest occupied orbital, yields (minus) the ionization potential (IP):

$$-\text{IP} \approx \epsilon_h$$

With ϵ_h the KS eigenvalue of the highest occupied orbital. Here we had to assume that the eigenvalue did not (or weakely) depend on n_i, for $0 < n_N < 1$ (see notes). We have a "Koopmans"-like expression, relating the HOMO eigenvalue and the IP. For the LUMO one might expect a similar result, however, it should be calculated with just a tiny amount of charge δN added, i.e. $N+\delta N$ (see notes of next week). Moreover, in practise one works with approximations to the real density functional, which makes for even more trouble.

Question 3

Show that in Hartree-Fock the exchange-correlation hole intergrates to -1:

$$\int \tilde{n}_{\text{X}}^{\text{HF}}(\mathbf{r},\mathbf{r}')\,d\mathbf{r}' = -1$$

As starting point you could take the energy expression in terms of spin-orbitals from the first week, which is the same at the X(C) energy expressed as the Coulomb interaction of the charge density and the XC hole:

$$E_{\text{XC}} = \frac{e^2}{2}\iint \frac{n(\mathbf{r})\tilde{n}_{\text{XC}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$$

In terms of spin-orbitals the X energy in HF is (atomic units):

$$-\frac{1}{2}\sum_i^N\sum_j^N \langle\psi_i(1)\psi_j(2)|\hat{g}(1,2)|\psi_j(1)\psi_i(2)\rangle = -\frac{1}{2}\iint \sum_i^N\sum_j^N \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$$
$$= \frac{1}{2}\iint \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\left(-\sum_i^N\sum_j^N \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{n(\mathbf{r})}\right)d\mathbf{r}\,d\mathbf{r}'$$

In the last step we took care to "split off" the exchange-correlation hole between the large brackets. Now let's integerate this expression over $\mathbf{r}'$*:*

$$\int -\sum_i^N \sum_j^N \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{n(\mathbf{r})}\, d\mathbf{r}' = -\sum_i^N \sum_j^N \delta_{ij} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})}{n(\mathbf{r})} = -\sum_i^N \frac{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})}{n(\mathbf{r})} = -\frac{n(\mathbf{r})}{n(\mathbf{r})} = -1$$