Quantum Chemistry NWI-MOL406

HG00.108, 8.30h-11.30h, 17 January 2017

For each question you can get the same number of points (so **1a** has the same number of points as **1b** and as **2a** and as **3c**, etc.). There is one exception: for **4b** you can get three times more.

Question 1: Wave functions and charge densities

A three-electron, normalized Slater determinant is given by

$$\Phi_a = \frac{1}{\sqrt{3!}} \left| \psi_1 \psi_2 \psi_3 \right| ,$$

where $\{\psi_1, \psi_2, \psi_3, \psi_4, \psi_5\}$ is an orthonormal set of spin-orbitals.

1a. Write out the complete wave function, i.e., complete the following:

$$\Phi_a = \frac{1}{\sqrt{3!}} \left[\psi_1(1)\psi_2(2)\psi_3(3) + \ldots \right] .$$

1b. Show that your result for Φ_a is properly normalized, i.e. that $\langle \Phi_a | \Phi_a \rangle = 1$.

We now turn our attention to another Slater determinant:

$$\Phi_b = \frac{1}{\sqrt{6!}} \left| \phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \phi_3 \bar{\phi}_3 \right| .$$

Here $\{\phi_1, \phi_2, \phi_3\}$ are orthonormal spatial orbitals.

1c. Give an expression for the charge density $n(\mathbf{r})$ in terms of the orbitals $\phi_1(\mathbf{r})$, $\phi_2(\mathbf{r})$ and $\phi_3(\mathbf{r})$. Briefly motivate your answer.

Question 2: From Hartree-Fock and Roothaan to DFT

In (restricted closed-shell) Hartree-Fock, one has to minimize the energy expression:

$$E = 2\sum_{k}^{N/2} h_{kk} + \sum_{k}^{N/2}\sum_{l}^{N/2}(2J_{kl} - K_{kl}). \tag{1}$$

There h_{kk}, J_{kl} and K_{kl} are one- and two-electron matrix elements involving the spatial molecular orbitals ϕ_1, ϕ_2, …, $\phi_{N/2}$.

2a. Give expressions for the integrals J_{kk} and K_{kl} in terms of the orbitals ϕ_k and ϕ_l.

2b. Why is there no factor 2 in front of K_{kl}? Explain briefly.

The above expression (formula 1) needs to be minimized with the constraints that the molecular orbitals are orthonormal. In practice this is achieved by introducing Lagrange multipliers Λ_{kl} and minimizing a modified energy expression:

$$E' = 2\sum_{k}^{N/2} h_{kk} + \sum_{k}^{N/2}\sum_{l}^{N/2}(2J_{kl} - K_{kl}) + \ldots \tag{2}$$

2c. What is the modified energy expression, i.e. what is on the "…" in formula (2)?

On a computer, the molecular orbitals are expanded in atomic orbitals χ_λ:

$$\phi_k(\mathbf{r}) = \sum_{\lambda}^{M} C_{\lambda k}\chi_\lambda(\mathbf{r}) = \sum_{\lambda}^{M} \chi_\lambda(\mathbf{r}) C_{\lambda k}. \tag{3}$$

So $\mathbf{C}$ is an $M \times N/2$ matrix.

2d. Suppose were are doing a calculation on the fluorine dimer, i.e., on F_2, and we use a minimal STO (Slater type orbital) basis. How large are M and $N/2$? Explain briefly. In case you forgot: fluorine has atomic number 9.

Inserting equation (3) into equation (2) and demanding that $\partial E'/\partial C^*_{\rho m} = 0$ yields the Roothaan equations. After diagonalization these are

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon}, \tag{4}$$

which can also be written as

$$\mathbf{F}\mathbf{c}_k = \epsilon_k \mathbf{S}\mathbf{c}_k. \tag{5}$$

Here $\mathbf{F}$ and $\mathbf{S}$ are the Fock and overlap matrix, respectively [$\boldsymbol{\epsilon}$ is the matrix with the ϵ_k on the diagonal, and 0 elsewhere].

2e. Solving equations (4) and (5) requires so-called *self-consistent* calculations. Explain what this means. Also explain, in words, what this is done.

Naively one would expect that the total ground state energy E can be written as a sum of all eigenvalues ϵ_k. However that is not true. You still need to add a correction.

2f. Provide this correction, i.e., what is on the "…" below. No proof needed.

$$E = 2\sum_{k}^{N/2} \epsilon_k + \ldots$$

The Fock matrix is, in principle, straightforwardly calculated by inserting expansion (3) into the expression for E of equation (1) and using:

$$\frac{\partial E}{\partial C^*_{\rho m}} = 2\sum_{\nu}^{M} F_{\rho\nu} C_{\nu m}.$$

There are single electron contributions and two-electron contributions deriving from J_{kl} and K_{kl}. In DFT the term $-K_{kl}$ in (1) is replaced by a density dependent exchange-correlation functional $E_{\mathrm{XC}}[n(\mathbf{r})]$ of the electron density $n(\mathbf{r})$. In this Question we choose:

$$E_{\mathrm{XC}} = A\int n(\mathbf{r})\, d\mathbf{r}.$$

This is not a realistic functional. We choose it for computational convenience. A is a known constant. We obtain a modified energy expression:

$$E = 2\sum_{k}^{N/2} h_{kk} + \sum_{k}^{N/2}\sum_{l}^{N/2} 2J_{kl} + E_{\mathrm{XC}} \tag{6}$$

Assume we have a working Hartree-Fock program. We want to convert this to DFT. So in the following we want to find an expression for the contribution of E_{X} to the "Fock" matrix that replaces the contribution due to K_{ij}. Of course the resulting matrix is not a true Fock matrix anymore, hence the quotes.

2g. Provide an expression for the density $n(\mathbf{r})$ in terms of the elements of the matrix $\mathbf{C}$. Use this result to obtain an expression for E_{XC} in terms of elements of the matrices $\mathbf{C}$ and $\mathbf{S}$.

2h. Use the result of **2g** to obtain the exchange contribution to the modified $F_{\rho\nu}$.

Question 3: Gaussian basis sets

Atomic basis sets are available online in the “EMSL basis set exchange” database. Ariane has downloaded a basis set for fluorine (F) from the EMSL web site. It is listed below:

```
#BASIS SET: (11s,5p,1d) -> [4s,3p,1d]
F    S
  11427.1000000              0.00180093
   1722.3500000              0.0137419
    395.7460000              0.0681334
    115.1390000              0.2333250
     33.6026000              0.5890860
      4.9190100              0.2995050
F    SP
     55.4441000              0.1145360             0.0354609
     12.6323000              0.9205120             0.2374510
      3.7175600             -0.00337804            0.8204580
F    SP
      1.1654500              1.0000000             1.0000000
F    SP
      0.3218920              1.0000000             1.0000000
F    D
      1.7500000              1.0000000
```

Unfortunately, Ariane forgot what type of Gaussian basis set this actually is.

3a. You have to help Ariane, and say what type of split valence basis set this is. It is 3-21+G, or is it 9-631G*, or - if it is neither of these - what else? Motivate your answer!

Ariane does two calculations on F_2 with this basis set. One calculation uses a basis set with the real spherical harmonics s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. The other uses so-called Cartesian spherical harmonics which can be written as

$$x^l y^m z^n \times \text{“some radial function with an exponent”}.$$

She is surprised that the calculations yield slightly different ground state energies.

3b. Explain what happened here, i.e. why the energies are different and which is lowest.

3c. Give an expression for the “radial function with an exponent” for the d-channel. This function not only features some kind of exponent (obviously) but has an other r-dependent factor.

Question 4: Basics of Density Functional Theory

The formal basis of Density Functional Theory (DFT) is provided by the Hohenberg-Kohn (HK) theorems. The 1th HK theorem is about the electronic ground state density $n(\mathbf{r})$ and the so-called “external potential” $V_{\text{ext}}(\mathbf{r})$. It says that $V_{\text{ext}}(\mathbf{r})$ is unique (besides an additive constant) given $n(\mathbf{r})$.

4a. Explain what is meant with the “external potential” V_{ext}, i.e. what does it represent in a DFT calculation on a molecule or a crystal?

4b. [**This question gives triple points**] Prove the 1th Hohenberg-Kohn theorem. The standard prove shows that a non-unique V_{ext} for a given (unique) density $n(\mathbf{r})$ results in an absurdity. It assumes the ground state to be non-degenerate. You may do the same.

Question 5: Practical aspects of DFT

This questions deals with several aspects of DFT.

5a. In DFT the energy functional is (in atomic units $m_e = 1$ and $e = 1$):

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

Write down the Kohn-Sham equation. Note that $V^{\text{XC}}(\mathbf{r}) = \dfrac{\delta E^{\text{XC}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$.

5b. In DFT the functional $E_{\text{XC}}[n(\mathbf{r})]$ has to account for several effects. One is exchange. What are the others?

5c. Explain what the acronym “LDA” stands for, and what this actually means.

5d. Given that the exchange energy density of the uniform electron gas is

$$\frac{E^X}{N} = -\frac{3}{4}e^2\sqrt[3]{\frac{3}{\pi}}\,n^{1/3} \quad ,$$

write the explicit LDA expression for the exchange energy.

5e. The LDA (and many density functionals), contrary to Hartree-Fock, is plagued with imperfect “self-interaction” cancellation. Explain what this is, i.e. why it happens.

5f. The "LDA" is one of the oldest, but also one of the least accurate DFT functionals. Later so-called GGAs and hybrid functionals have been developed. Briefly explain what are GGAs and hybrid functionals.

5g. The "LDA", GGAs and hybrid functionals all are unsuitable for calculations on molecular complexes that are held together by dispersion interactions (although the LDA sometimes gives good results, for bad reasons). Recently, so-called "vdW-DF" functionals have been developed, that do a reasonable job in describing dispersion. Briefly mention the key improvement that makes that vdW-DF functionals work for dispersion.

5h. Suppose you want to study a molecular crystal that is kept to together by inter-molecular hydrogen bonds. Do you use LDA or GGA? Why?

5i. Suppose are studying a semi-conducting crystal, like, e.g., zincblende GaAs. You want to study the optical properties, so you need to attain realistic values for excitation across the band gap from the valence to the conduction band. Would you use PBE or PBE0?

5j. The electron-electron interaction energy can be written as:[1]

$$E_{\mathrm{e-e}} = \frac{e^2}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + \frac{e^2}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\left\{g(\mathbf{r},\mathbf{r}')-1\right\}\,d\mathbf{r}\,d\mathbf{r}'.$$

Here $g(\mathbf{r},\mathbf{r}')$ is the electron-electron pair correlation function. Give an expression for the XC-hole and identify it in the above expression. LDA (and many post-LDA functionals) typically yield a very bad description of $g(\mathbf{r},\mathbf{r}')$. However, the energies calculated with the LDA are often reasonably accurate. This is related to an important observation on the behaviour of the LDA XC-hole. Briefly summarize that observation. Also use the above formula to explain why that observation makes that LDA energies are reasonable nevertheless.

Question 6: Post-Hartree Fock methods (not part of 2017 exam)

6a. Briefly describe how to do a full CI calculation, i.e., how do you obtain the functions to build your determinants, how do you build the determinants from these functions, and how do the determinants build the wave function? Also explain how CISD differs from full CI.

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[1] In DFT this is not quite true, but that subtlety is now neglected.

6b. In Møller-Plesset (MP) perturbation theory you do, obviously, a perturbation theory calculation. As a starting point you need an unperturbed system for which you know the exact Hamiltonian H_0 and its corresponding ground state eigenfunction $|\Phi_0\rangle$ (of course for MP3 and beyond you also need the excited states of H_0). Explain how MP chose H_0 and $|\Phi_0\rangle$.

6c. MCSCF methods deal with several SDs of which you independently optimize the orbitals that these SDs are made of. When is it advisable to use such methods?