First midterm FYS4480 – Quantum mechanics for many-particle systems, deadline October 21 at midnight

FYS4480 – Quantum mechanics for many-particle systems

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Introduction

In this midterm we will develop two simple models for studying the helium atom (with two electrons) and the beryllium atom with four electrons.

After having introduced the Born-Oppenheimer approximation which effectively freezes out the nucleonic degrees of freedom, the Hamiltonian for N electrons takes the following form

$$\hat{H} = \sum_{i=1}^{N} t(x_i) - \sum_{i=1}^{N} k\frac{Ze^2}{r_i} + \sum_{i<j}^{N} \frac{ke^2}{r_{ij}},$$

with $k = 1.44$ eVnm. Througout this work we will use atomic units, this means that $\hbar = c = e = m_e = 1$. The constant k becomes also equal 1. The resulting energies have to be multiplied by 2×13.6 eV in order to obtain energies in eletronvolts.

We can rewrite our Hamiltonians as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{N} \hat{h}_0(x_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}, \tag{1}$$

where we have defined $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ and $\hat{h}_0(x_i) = \hat{t}(x_i) - \frac{Z}{r_i}$

The variable x contains both the spatial coordinates and the spin values. The first term of Eq. (**??**), H_0, is the sum of the N *one-body* Hamiltonians $\hat{h}_0$. Each individual Hamiltonian $\hat{h}_0$ contains the kinetic energy operator of an electron and its potential energy due to the attraction of the nucleus. The second term, H_I, is the sum of the $N(N-1)/2$ two-body interactions between each pair of electrons. Note that the double sum carries a restriction $i < j$.

As basis functions for our calculations we will use hydrogen-like single-particle functions. This means the onebody operator is diagonal in this basis for states i, j with quantum numbers nlm_lsm_s with energies

$$\langle i|\hat{h}_0|j\rangle = -Z^2/2n^2\delta_{i,j}.$$

The quantum number n refers to the number of nodes of the wave function. Observe that this expectation value is independent of spin.

We will in all calculations here restrict ourselves to only so-called s -waves, that is the orbital momentum l is zero. We will also limit the quantum number n to $n \leq 3$. It means that every ns state can accomodate two electrons due to the spin degeneracy.

In the calculations you will need the Coulomb interaction with matrix elements involving single-particle wave functions with $l = 0$ only, the so-called s-waves. We need only the radial part since the spherical harmonics for the s-waves are rather simple. We omit single-particle states with $l > 0$. The actual integrals we need, are tabulated at the end. Our radial wave functions are

$$R_{n0}(r) = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-1)!}{2n \times n!}} L_{n-1}^1 (\frac{2Zr}{n}) \exp\left(-\frac{Zr}{n}\right),$$

where $L_{n-1}^1(r)$ are the so-called Laguerre polynomials. These wave functions can then be used to compute the direct part of the Coulomb interaction

$$\langle \alpha\beta | V | \gamma\delta \rangle = \int r_1^2 dr_1 \int r_2^2 dr_2 R_{n_\alpha 0}^*(r_1) R_{n_\beta 0}^*(r_2) \frac{1}{r_{12}} R_{n_\gamma 0}(r_1) R_{n_\delta 0}(r_2)$$

Observe that this is only the radial integral and that the labels $\alpha\beta\gamma\delta$ refer only to the quantum numbers nlm_l, with m_l the projection of the orbital momentum l. A similar expression can be found for the exchange part. Since we have restricted ourselves to only s-waves, these integrals are straightforward but tedious to calculate. As an addendum to this midterm we list all closed-form expressions for the relevant matrix elements. Note well that these matrix elements do not include spin. When setting up the final antisymmetrized matrix elements you need to consider the spin degrees of freedom as well. Please pay in particular attention to the exchange part and the pertinent spin values of the single-particle states.

We will also, for both helium and beryllium assume that the many-particle states we construct have always the same total spin projection $M_S = 0$. This means that if we excite one or two particles from the ground state, the spins of the various single-particle states should always sum up to zero.

Part a), setting up the basis. We start with the helium atom and define our single-particle Hilbert space to consist of the single-particle orbits $1s$, $2s$ and $3s$, with their corresponding spin degeneracies.

Set up the ansatz for the ground state $|c\rangle = |\Phi_0\rangle$ in second quantization and define a table of single-particle states. Construct thereafter all possible one-particle-one-hole excitations $|\Phi_i^a\rangle$ where i refer to levels below the Fermi level (define this level) and a refers to particle states. Define particles and holes. The Slater determinants have to be written in terms of the respective creation and annihilation operators. The states you construct should all have total spin projection $M_S = 0$. Construct also all possible two-particle-two-hole states $|\Phi_{ij}^{ab}\rangle$ in a second quantization representation.

Part b) Second quantized Hamiltonian.   Define the Hamiltonian in a second-quantized form and use this to compute the expectation value of the ground state (defining the so-called reference energy and later our Hartree-Fock functional) of the helium atom. Show that it is given by

$$E[\Phi_0] = \langle c|\hat{H}|c\rangle = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\left[\langle ij|\frac{1}{r}|ij\rangle - \langle ij|\frac{1}{r}|ji\rangle\right].$$

Define properly the sums keeping in mind that the states ij refer to all quantum numbers nlm_lsm_s. Use the values for the various matrix elements listed at the end of the midterm to find the value of E as function of Z and compute E as function of Z.

Part c) Limiting ourselves to one-particle-one excitations.   Hereafter we will limit ourselves to a system which now contains only one-particle-one-hole excitations beyond the chosen state $|c\rangle$. Using the possible Slater determinants from exercise a) for the helium atom, find the expressions (without inserting the explicit values for the matrix elements first) for

$$\langle c|\hat{H}|\Phi_i^a\rangle,$$

and

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle.$$

Represent these expressions in a diagrammatic form, both for the onebody part and the two-body part of the Hamiltonian.

Insert then the explicit values for the various matrix elements and set up the final Hamiltonian matrix and diagonalize it using for example Python as programming language.

Compare your results from those of exercise b) and comment your results.

The exact energy with our Hamiltonian is -2.9037 atomic units for helium. This value is also close to the experimental energy.

Part d) Moving to the Beryllium atom.   We repeat parts b) and c) but now for the beryllium atom.

Define the ansatz for $|c\rangle$ and limit yourself again to one-particle-one-hole excitations. Compute the reference energy $\langle c|\hat{H}|c\rangle$ as function of Z. Thereafter you will need to set up the appropriate Hamiltonian matrix which involves also one-particle-one-hole excitations. Diagonalize this matrix and compare your eigenvalues with $\langle c|\hat{H}|c\rangle$ as function of Z and comment your results. The exact energy with our Hamiltonian is -14.6674 atomic units for beryllium. This value is again close to the experimental energy.

With a given energy functional, we can perform at least two types of variational strategies. These are:

1. Vary the Slater determinant by changing the spatial part of the single-particle wave functions themselves, or

2. Expand the single-particle functions in a known basis and vary the coefficients, that is, the new function single-particle wave function $|p\rangle$ is written as a linear expansion in terms of a fixed basis ϕ (harmonic oscillator, Laguerre polynomials etc)

$$\psi_p = \sum_\lambda C_{p\lambda}\phi_\lambda,$$

Both cases lead to a new Slater determinant which is related to the previous via a unitary transformation. Below we will set up the Hartree-Fock equations using the second option. We assume that our basis is still formed by the hydrogen-like wave functions. We consider a Slater determinant built up of single-particle orbitals ϕ_λ where the indices λ refer to specific single-particle states. As an example, you could think of the ground state ansatz for the beryllium atom.

The unitary transformation

$$\psi_p = \sum_\lambda C_{p\lambda}\phi_\lambda,$$

brings us into the new basis ψ. The new basis is orthonormal and C is a unitary matrix.

Part e) Hartree-Fock. Minimizing with respect to $C_{p\alpha}^*$, remembering that $C_{p\alpha}^*$ and $C_{p\alpha}$ (and that the indices contain all single-particle quantum numbers including spin) are independent and defining

$$h_{\alpha\gamma}^{HF} = \langle\alpha|h|\gamma\rangle + \sum_p \sum_{\beta\delta} C_{p\beta}^* C_{p\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS},$$

show that you can write the Hartree-Fock equations as

$$\sum_\gamma h_{\alpha\gamma}^{HF} C_{p\gamma} = \epsilon_p^{\mathrm{HF}} C_{p\alpha}.$$

Explain the meaning of the different terms and define the Hartree-Fock operator in second quantization. Write down its diagrammatic representation as well. The greek letters refer to the wave functions in the original basis (in our case the hydrogen-like wave functions) while roman letters refer to the new basis.

Part f) The Hartree-Fock matrices. The Hartree-Fock equations with a variation of the coefficients $C_{p\alpha}$ lead to an eigenvalue problem whose eigenvectors are the coefficients $C_{p\alpha}$ and eigenvalues are the new single-particle energies. Use the single-particle orbits $1s - 3s$ and set up the Hartree-Fock matrix for both the helium atom and the beryllium atom. Find after the first diagonalization the new single-particle energies and the new ground state energy. Compare these results with those you obtained under the minimization of the ground states as functions of Z and the full diagonalization. When setting up the Hartree-Fock matrix in the first iteration, our guess for the coefficients $C_{p\beta}$ etc. is $C_{p\beta} = 1$ for $p = \beta$ and zero else.

Part g) Writing a Hartree-Fock code. The final stage is to set up an iterative scheme where you use the new wave functions determined via the coefficients $C_{p\alpha}$ to solve iteratively the Hartree-Fock equations till a given self-consistency is reached. A typical way of doing this is to compare the single-particle energies from the previous iteration with those obtained from the new diagonalization. If the total difference is smaller than a prefixed value, the iterative process is stopped. Feel free to use the code presented in the lecture notes of week 40. Compare these results with the those you obtained under the minimization of the ground states as functions of Z and the full diagonalization. Discuss your results.

We conclude by listing the matrix elements for the radial integrals to be used for the direct part and the exchange part. Note again that these integrals do not include spin. The nomenclature is $1 = 1s$, $2 = 2s$, and $3 = 3s$, with no spin degrees of freedom.

```
<11|V|11> = (5*Z)/8
<11|V|12> = (4096*Sqrt[2]*Z)/64827
<11|V|13> = (1269*Sqrt[3]*Z)/50000
<11|V|21> = (4096*Sqrt[2]*Z)/64827
<11|V|22> = (16*Z)/729
<11|V|23> = (110592*Sqrt[6]*Z)/24137569
<11|V|31> = (1269*Sqrt[3]*Z)/50000
<11|V|32> = (110592*Sqrt[6]*Z)/24137569
<11|V|33> = (189*Z)/32768
<12|V|11> = (4096*Sqrt[2]*Z)/64827
<12|V|12> = (17*Z)/81
<12|V|13> = (1555918848*Sqrt[6]*Z)/75429903125
<12|V|21> = (16*Z)/729
<12|V|22> = (512*Sqrt[2]*Z)/84375
<12|V|23> = (2160*Sqrt[3]*Z)/823543
<12|V|31> = (110592*Sqrt[6]*Z)/24137569
<12|V|32> = (29943*Sqrt[3]*Z)/13176688
<12|V|33> = (1216512*Sqrt[2]*Z)/815730721
<13|V|11> = (1269*Sqrt[3]*Z)/50000
<13|V|12> = (1555918848*Sqrt[6]*Z)/75429903125
<13|V|13> = (815*Z)/8192
<13|V|21> = (110592*Sqrt[6]*Z)/24137569
<13|V|22> = (2160*Sqrt[3]*Z)/823543
<13|V|23> = (37826560*Sqrt[2]*Z)/22024729467
<13|V|31> = (189*Z)/32768
<13|V|32> = (1216512*Sqrt[2]*Z)/815730721
<13|V|33> = (617*Z)/(314928*Sqrt[3])
<21|V|11> = (4096*Sqrt[2]*Z)/64827
<21|V|12> = (16*Z)/729
<21|V|13> = (110592*Sqrt[6]*Z)/24137569
<21|V|21> = (17*Z)/81
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```
<21|V|22> = (512*Sqrt[2]*Z)/84375
<21|V|23> = (29943*Sqrt[3]*Z)/13176688
<21|V|31> = (1555918848*Sqrt[6]*Z)/75429903125
<21|V|32> = (2160*Sqrt[3]*Z)/823543
<21|V|33> = (1216512*Sqrt[2]*Z)/815730721
<22|V|11> = (16*Z)/729
<22|V|12> = (512*Sqrt[2]*Z)/84375
<22|V|13> = (2160*Sqrt[3]*Z)/823543
<22|V|21> = (512*Sqrt[2]*Z)/84375
<22|V|22> = (77*Z)/512
<22|V|23> = (5870679552*Sqrt[6]*Z)/669871503125
<22|V|31> = (2160*Sqrt[3]*Z)/823543
<22|V|32> = (5870679552*Sqrt[6]*Z)/669871503125
<22|V|33> = (73008*Z)/9765625
<23|V|11> = (110592*Sqrt[6]*Z)/24137569
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<23|V|13> = (37826560*Sqrt[2]*Z)/22024729467
<23|V|21> = (29943*Sqrt[3]*Z)/13176688
<23|V|22> = (5870679552*Sqrt[6]*Z)/669871503125
<23|V|23> = (32857*Z)/390625
<23|V|31> = (1216512*Sqrt[2]*Z)/815730721
<23|V|32> = (73008*Z)/9765625
<23|V|33> = (6890942464*Sqrt[2/3]*Z)/1210689028125
<31|V|11> = (1269*Sqrt[3]*Z)/50000
<31|V|12> = (110592*Sqrt[6]*Z)/24137569
<31|V|13> = (189*Z)/32768
<31|V|21> = (1555918848*Sqrt[6]*Z)/75429903125
<31|V|22> = (2160*Sqrt[3]*Z)/823543
<31|V|23> = (1216512*Sqrt[2]*Z)/815730721
<31|V|31> = (815*Z)/8192
<31|V|32> = (37826560*Sqrt[2]*Z)/22024729467
<31|V|33> = (617*Z)/(314928*Sqrt[3])
<32|V|11> = (110592*Sqrt[6]*Z)/24137569
<32|V|12> = (29943*Sqrt[3]*Z)/13176688
<32|V|13> = (1216512*Sqrt[2]*Z)/815730721
<32|V|21> = (2160*Sqrt[3]*Z)/823543
<32|V|22> = (5870679552*Sqrt[6]*Z)/669871503125
<32|V|23> = (73008*Z)/9765625
<32|V|31> = (37826560*Sqrt[2]*Z)/22024729467
<32|V|32> = (32857*Z)/390625
<32|V|33> = (6890942464*Sqrt[2/3]*Z)/1210689028125
<33|V|11> = (189*Z)/32768
<33|V|12> = (1216512*Sqrt[2]*Z)/815730721
<33|V|13> = (617*Z)/(314928*Sqrt[3])
<33|V|21> = (1216512*Sqrt[2]*Z)/815730721
<33|V|22> = (73008*Z)/9765625
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```
<33|V|23> = (6890942464*Sqrt[2/3]*Z)/1210689028125
<33|V|31> = (617*Z)/(314928*Sqrt[3])
<33|V|32> = (6890942464*Sqrt[2/3]*Z)/1210689028125
<33|V|33> = (17*Z)/256
```