Exercise 10

Hand in your solutions before next Friday at 8.00 am or send an email to luca.donati@fu-berlin.de

1 Variational method applied to Helium atom (15 points)

The Hamiltonian operator of the helium atom is

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where the terms in the above expression represent the kinetic energy of the first electron, the electrostatic attraction between the nucleus and the first electron; the kinetic energy of the second electron, the electrostatic attraction between the nucleus and the second electron; and the electrostatic repulsion between the two electrons, respectively. Last week (exercise09), we saw how it is possible to approach this Hamiltonian using the perturbation theory.

Another way to study this problem is to use the variational method. To take into account the effect of the repulsive term of the Hamiltonian, we now consider each elecron interacting with the nuclear charge as if it was shielded by the other electron. This means that the "effective" nuclear charge is $Z_e < 2$. The effective charge will be our variational parameter, then our trial function is:

$$\phi_0(\mathbf{r_1}, \mathbf{r_2}, \mathbf{Z_e}) = \phi(\mathbf{r_1})\phi(\mathbf{r_2}) = \frac{Z_e^3}{a_0^3\pi} e^{-Z_e(r_1+r_2)/a_0}$$

To find the optimal value of Z_e, it is necessary to minimize the total energy:

$$E(Z_e) = \langle \phi_0(\mathbf{r_1}, \mathbf{r_2}, \mathbf{Z_e}) | \hat{H} | \phi_0(\mathbf{r_1}, \mathbf{r_2}, \mathbf{Z_e}) \rangle$$

where $\hat{H}$ is the Hamiltonian operator of the Helium atom.

1. Show that
$$E(Z_e) = Z_e^2 - \frac{27}{8} Z_e$$

2. What is the value of Z_e that minimizes $E(Z_e)$? What is the energy of the ground state with this approximation?

2 Linearized variational principle applied to Stark effect (10 points)

The Schrödinger equation (in atomic units) for a hydrogen atom in a uniform electric field F in the z direction is

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r} + Fr\cos\theta\right)|\phi\rangle = (H_0 + Fr\cos\theta)|\phi\rangle = E_0(F)|\phi\rangle$$

Use the trial function

$$|\phi\rangle = c_1|1s\rangle + c_2|2p_z\rangle$$

where $|1s\rangle$ and $|2p_z\rangle$ are

$$|1s\rangle = \sqrt{\frac{1}{\pi}} e^{-r}$$

$$|2p_z\rangle = \sqrt{\frac{1}{32\pi}} r e^{-r/2} \cos\theta$$

to find an upper bound to $E_0(F)$. In constructing the matrix representation of H, you can avoid a lot of work by noting that

$$H_0|1s\rangle = -\frac{1}{2}|1s\rangle$$

$$H_0|2p_z\rangle = -\frac{1}{8}|2p_z\rangle$$

Using $(1+x)^{1/2} \simeq 1 + x/2$, expand your answer in a Taylor series in F

$$E(F) = E(0) - \frac{1}{2}\alpha F^2$$

What is the value of α?