Theoretical Physics V – Quantum Mechanics II

Winter Semester 2019/20

Carsten Henkel / Timo Felbinger

Problem Set #4

Hand Out: 18 November 2019

Hand In: 03 December 2019

Problem 4.1 – Hartree-Fock theory for the Helium ground state (20 points)

In the Book "Quantum Mechanics of One- and Two-Electron Atoms" by H. A. Bethe and E. E. Salpeter (Dover 2008), we find the following formulation of Hartree-Fock theory for the Helium atom.

The ground state has the two electrons in the same Hartree-Fock wave function $u(\mathbf{x})$ that solves the equation (atomic units are used, $Z = 2$ is the charge of the Helium nucleus)

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W(r)\right] u = E_1 u \tag{4.1}$$

where the electron-electron interaction is described by the mean field

$$W(r_1) = \int \mathrm{d}V(\mathbf{x}_2) |u(\mathbf{x}_2)|^2 \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \tag{4.2}$$

A convenient parametrisation of this interaction is the function $Z_p(r)$ defined by

$$\frac{Z_p(r)}{r} = \frac{Z}{r} - W(r) \tag{4.3}$$

This set of equations was solved numerically by W. S. Wilson and R. B. Lindsay [*Phys. Rev.* **47** (1935) 681]. The following results have been found:

H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Dover 2008), p145

Table 5. *The ground state of the neutral helium atom; self-consistent field, potential and charge distribution.*

r	$P(r)$	$Z_p(r)$	$Z_{\mathrm{eff}}(r)$	r	$P(r)$	$Z_p(r)$	$Z_{\mathrm{eff}}(r)$
0	0.000	2.000	2.000	1.6	0.489	1.024	0.239
0.05	0.215	1.916	1.998	1.8	0.405	1.014	0.158
0.1	0.390	1.834	1.989	2.0	0.333	1.009	0.105
0.2	0.643	1.683	1.932	2.2	0.272	1.005	0.068
0.3	0.798	1.552	1.826	2.4	0.221	1.003	0.044
0.4	0.885	1.442	1.683	2.6	0.178	1.0018	0.028
0.5	0.924	1.352	1.518	2.8	0.143	1.0011	0.018
0.6	0.930	1.279	1.345	3.0	0.115	1.0006	0.012
				3.2	0.092	1.0004	0.007
0.8	0.880	1.173	1.014				
1.0	0.789	1.106	0.734	3.6	0.058	1.0001	0.0028
1.2	0.686	1.065	0.516	4.0	0.036	1.0000	0.0012
1.4	0.584	1.039	0.355	4.8	0.014	1.0000	0.0002

Here is $P(r) = r u(\mathbf{x})\sqrt{4\pi}$ and $Z_{\text{eff}}(r)$ is the total charge including the nucleus inside the radius r.

(1) Justify using the concepts of the lecture that this formulation corresponds to the ground state of the Helium atom in Hartree-Fock theory. (Think about the spin states first.) Bethe and Salpeter write that the ground state energy is given by $E(\text{He}) = 2E_1 - \langle W \rangle$ where $\langle W \rangle$ is the mean value of $W(r)$ in the HF state $u(\mathbf{x})$. Show that the same answer can be found from the expression in the lecture $E(\text{He}) = \frac{1}{2}\sum_{k<k_F} [\epsilon_k + \langle u_k|(K_0 + V_1(|u_k\rangle]$ where $u_k = u_k(\mathbf{x})$ is the Hartree-Fock wave function (to the eigenvalue ϵ_k) and $K_0 + V_1$ the single-particle Hamiltonian (without interactions). The "$k < k_F$" sum runs over all occupied levels.

(2) The solutions of Eq.(4.1) with $l, m = 0, 0$ symmetry (1s-like states) are of the form $u(\mathbf{x}) = R(r)/\sqrt{4\pi}$ where R solves the radial Schrödinger equation

$$-\frac{1}{2r}\frac{\mathrm{d}^2}{\mathrm{d}r^2} rR + \left(-\frac{Z}{r} + W(r)\right) R = E_1 R \tag{4.4}$$

The mean-field potential $W(r)$ only depends on the radial coordinate. In the lecture, we found the integral representation

$$W(r) = \int_0^\infty \mathrm{d}r'\, r'^2 \frac{R^2(r)}{\max(r, r')} \tag{4.5}$$

Compute this integral analytically for the hydrogen-like ground state $R_{1s}(r) = 2Z^{3/2}\,\mathrm{e}^{-Zr}$ and show that it has a "one-electron Coulomb tail", i.e.: $r \to \infty : W(r) \approx 1/r$. Justify in words why this is to be expected. Make a plot of this potential and of the total potential $W(r) - Z/r$.

(3) Write a few sentences to interpret the numerical data computed by Wilson and Lindsay.

(4) On the web site, you find a *Python* script that solves Eq.(4.4) numerically on a finite interval $0 \le r \le r_{\max}$. Describe in words how you can use this script to solve by iteration the Hartree-Fock theory. At the end of the file, there is a list of tasks to do: generate the corresponding plots and give the correction of the Helium atom ground state energy relative to the value $E_{\text{n.i.}} = -2Z^2/(2(n = 1)^2) = -4\,\text{a.u.}$ for non-interacting electrons. Find experimental data for this energy (the "Spectroscopy Database" of the US American NIST may be too helpful here) and compare.