Quantum Physics, Course KFY/7KVAF
WS 2022/2023
Theme 7: Variational method

1. Find stationary points of the function $f(x, y, z) = 2x^2 + y^2 + 2z - xy - xz$.

2. Find constrained local extrema of the function $f(x, y) = x^2 + y^2$ with the constrain $g(x, y) = 3x - y + 1 = 0$. [Hint: find local extrema of Lagrangian function $L(x, y, \lambda) = f(x, y) + \lambda \cdot g(x, y)$.]

3. Proof the validity for the functional $E(\psi) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$ (for the non-degenerate discrete spectrum), where $|\psi\rangle$ is eigenfunction of Hamiltonian $\hat{H}$ and E_0 is lowest eigenvalue. [Hint: for non-degenerate discrete energy spectrum is $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$, $n = 0, 1, 2, ...$ and wavefunction is therefore possible to write $|\psi\rangle = \sum_{n=0}^{\infty} c_n|\psi_n\rangle$.]

4. Show using the variational method that at least one bound state is available for the particle in a one-dimensional potential well $V(x) = -V_0$ for $-a \leq x \leq a$ and $V(x) = 0$ pro $a \geq |x|$. [Hint: Use trial wavefunction containing one parameter α, $\psi(x) = \frac{1}{\sqrt{2\alpha}} \exp(-\frac{|x|}{2\alpha})$, and show the average total energy (Hamiltonian) $\langle\hat{H}\rangle = \langle\hat{T}\rangle + \langle\hat{V}\rangle$ is negative.]

5. Calculate the ground state of a hydrogen atom using a trial function of the form $\psi(r) = e^{-\alpha r}$.

6. Suppose a one-parameter (Z_e) trial wavefunction to represent the electronic structure of a two-electron ion of nuclear charge Z of the form $\psi(r_1, r_2) = \frac{Z_e^3}{\pi a_0^3} \exp(\frac{-Z_e r_1}{a_0}) \exp(\frac{-Z_e r_2}{a_0})$. Suppose that you were also lucky enough to be given the variational integral W (instead of asking you to derive it) as $W(Z_e) = (Z_e^2 - 2ZZ_e + \frac{5}{8}Z_e)\frac{e^2}{a_0}$. a) Find the optimum value of the variational parameter Z_e and the corresponding W (for an arbitrary nuclear charge Z). b) Using your optimized expression for W, calculate the estimated total energy of each of two-electron atoms/ions for $Z = 1 - 8$ and compare to experimental values (e.g., using relative error):

$Z = 1$	H^-	-14.35 eV
$Z = 2$	He	-78.98 eV
$Z = 3$	Li^+	-198.02 eV
$Z = 4$	Be^{2+}	-371.5 eV
$Z = 5$	B^{3+}	-599.3 eV
$Z = 6$	C^{4+}	-881.6 eV
$Z = 7$	N^{5+}	-1218.3 eV
$Z = 8$	O^{6+}	-1609.5 eV