SOLUTIONS for Homework #3

1. In the potential of given form there is no unbound states. Bound states have positive energies E_n labeled by an integer n. For each energy level E, two symmetrically located classical turning points $x_{\pm} = \pm x_0(E)$ are the points where the classical momentum for motion with given E,

$$p(x; E) = \sqrt{2m[E - U(x)]}, \tag{1}$$

vanishes,

$$p(x_{\pm}; E) = 0 \quad \rightsquigarrow \quad U(x_{\pm}) = E. \tag{2}$$

The approximate quantization rule reads

$$\oint dx\, p(x; E) = 2\pi n\hbar, \tag{3}$$

where the integral runs over the classical period of motion, or, in our case of an even potential, $U(x) = U(-x)$, four times from $x = 0$ to the turning point $x = x_0$,

$$4\sqrt{2m} \int_0^{x_0} dx\, \sqrt{E - U(x)} = 2\pi n\hbar. \tag{4}$$

This equation determines energy levels E_n for large $n \gg 1$, in the validity region of the semiclassical quantization.

For our potential $U(x)$ it is convenient to change the coordinate variable introducing $x = [(E/\alpha)\eta]^{1/s}$. Then the upper limit $x_0 \to 1$, and the quantization condition (4) takes the form

$$\frac{4}{s}\sqrt{2mE}\left(\frac{E}{\alpha}\right)^{1/s} I_s = 2\pi n\hbar, \quad I_s = \int_0^1 d\eta\, \eta^{(1-s)/s}\sqrt{1-\eta}. \tag{5}$$

The integral here is a number of the order of 1 which depends on the potential power s. Therefore the energy spectrum is given by

$$E_n = (C_s n)^{2s/(s+2)}, \tag{6}$$

where the energy scaling is determined by the constant parameter

$$C_s = \frac{\pi\hbar s \alpha^{1/s}}{2\sqrt{2m} I_s}, \tag{7}$$

The integral I_s is the Euler integral of the first order, or the Beta-function, and can be expressed via the Gamma-functions,

$$I_s = \frac{\Gamma(1/s)\Gamma(3/2)}{\Gamma[(3/2) + (1/s)]}. \tag{8}$$

For the harmonic oscillator potential $U(x) = (1/2)m\omega^2 x^2$, we have

$$s = 2, \quad \alpha = (1/2)m\omega^2, \quad \Gamma(1/2) = \sqrt{\pi}, \quad \Gamma(3/2) = \frac{1}{2}\Gamma(1/2), \quad \Gamma(2) = 1, \tag{9}$$

so that

$$I_2 = \frac{\pi}{2} \quad \rightsquigarrow \quad E_n = C_2 n = \hbar\omega n. \tag{10}$$

The more precise quantization rule would contain $(n + 1/2)$ instead of n in the right hand side of eq. (3); this would lead to the exact result for the harmonic oscillator $E_n = \hbar\omega(n + 1/2)$ and to better approximations for other values of s.

2. Let the typical radii for the two electrons be r_1 and r_2. In the ground state their typical momenta are, according to the uncertainty relation, $p_1 \sim \hbar/r_1$ and $p_2 \sim \hbar/r_2$. The minimum repulsion energy for the two electrons can be roughly estimated as $e^2/|\mathbf{r}_1 - \mathbf{r}_2|_{\rm max} = e^2/(r_1 + r_2)$. Then the energy of the ground state can be written as

$$E(r_1, r_2) = \frac{\hbar^2}{2m}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_1 + r_2}. \tag{11}$$

Obviously, the electrons are equivalent (they should have opposite spin projections but the same orbital wave functions). Therefore, in the ground state it should be $r_1 = r_2 \equiv r$. The energy becomes a function of r,

$$E(r, r) = \frac{\hbar^2}{mr^2} - 2e^2\frac{Z - (1/4)}{r}. \tag{12}$$

The minimum of this function is reached at

$$r = a_B \frac{1}{Z - (1/4)}, \quad a_B = \frac{\hbar^2}{me^2}, \tag{13}$$

as if each electron would feel the Coulomb field of the effective charge

$$Z_{\rm eff} = Z - \frac{1}{4}. \tag{14}$$

The total two-electron energy (12) for this radius is equal to doubled energy of a single-electron orbit in a hydrogen-like field of the effective charge (13),

$$E = -\frac{me^4}{\hbar^2} Z_{\rm eff}^2 = -2Z_{\rm eff}^2 \,{\rm Ry}; \tag{15}$$

recall that 1 Ry (Rydberg)=$me^4/2\hbar^2$=13.6 eV. Now we predict binding energies (in Ry) 1.12 (H^-), 6.12 (He), 15.12 (Li^+), 28.12 (Be^{++}), 45.12 (B^{+++}), and 66.12 (C^{++++}), in agreement with data much better than one would expect for such a simple estimate.

3. *a.* Using the Schrödinger equations for two wave functions with the same Hamiltonian $\hat{H}$,

$$-i\hbar\frac{\partial\Psi_1^*}{\partial t} = \hat{H}^*\Psi_1^*, \quad i\hbar\frac{\partial\Psi_2}{\partial t} = \hat{H}\Psi_2, \tag{16}$$

and taking the difference of these equations, we obtain

$$i\hbar\frac{\partial}{\partial t}(\Psi_1^*\Psi_2) = \Psi_1^*(\hat{H}\Psi_2) - (\hat{H}^*\Psi_1^*)\Psi_2. \tag{17}$$

In the coordinate representation the potential terms in the Hamiltonian $\hat{H} = \hat{K} + U$ cancel if the potential $U(\mathbf{r})$ is real, $U = U^*$. The remaining kinetic term

$$\hat{K} = \frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 = \hat{K}^* \tag{18}$$

is real as well. Introducing the *transition density*

$$\rho_{12} \equiv \Psi_1^*\Psi_2 \tag{19}$$

and the *transition current*

$$\mathbf{j}_{12} = \frac{\hbar}{2mi}[\Psi_1^*\nabla\Psi_2 - (\nabla\Psi_1^*)\Psi_2], \tag{20}$$

we come to the *continuity equation*

$$\frac{\partial\rho_{12}}{\partial t} + \operatorname{div}\mathbf{j}_{12} = 0. \tag{21}$$

The standard equation corresponds to the *diagonal* case, $\Psi_1 = \Psi_2$.

b. Two *stationary* wave functions Ψ_1 and Ψ_2 describe the states with certain energies E_1 and E_2, respectively. Their time dependence is given by

$$\Psi_{1,2}(\mathbf{r}, t) = \psi_{1,2}(\mathbf{r})e^{-(i/\hbar)E_{1.2}t}. \tag{22}$$

The coordinate amplitudes $\psi_{1,2}$ are the *eigenfunctions* of the same Hamiltonian,

$$\hat{H}\psi_{1,2} = E_{1,2}\psi_{1,2}. \tag{23}$$

The continuity equation of point *a* can be written as

$$i\hbar\frac{\partial\rho_{12}}{\partial t} = (E_2 - E_1^*)\psi_1^*\psi_2 e^{-(i/\hbar)(E_2-E_1^*)t}. \tag{24}$$

Our *first* assumption should be that the energy values E_1 and E_2 are *real*. Then eq. (24) means that the transition density ρ_{12} oscillates in time with the *transition frequency* $\omega_{21} = (E_2 - E_1)/\hbar$; the expectation value of the density ρ_{11} is simply constant in time for a stationary state Ψ_1. Now let us integrate both parts of eq. (24) over the entire available volume V. The left hand side, according to the continuity equation, reduces to

$$i\hbar \int d^3r \, \frac{\partial \rho_{12}}{\partial t} = -i\hbar \int d^3r \, \mathrm{div}\mathbf{j}_{12}. \tag{25}$$

The volume integral in eq. (25) can be converted into the surface integral $\oint d\mathcal{A} \cdot \mathbf{j}_{12}$, the flux of the transition current through the surface area $\mathcal{A}$. Now we make the *second* assumption that this flux vanishes. This happens in particular if the wave functions ψ_1 and ψ_2, along with their gradients, fall off at the remote boundaries of the volume sufficiently fast. If this is the case, eqs. (25) and (24) lead to the conclusion that

$$(E_1 - E_2) \int d^3r \, \psi_1^* \psi_2 = 0. \tag{26}$$

If the energies E_1 and E_2 do not coincide, the corresponding coordinate eigenfunctions are *orthogonal*,

$$\int d^3r \, \psi_1^* \psi_2 = 0. \tag{27}$$

For coinciding energies we only extract that the integral of ρ_{12} does not change in time,

$$\int d^3r \, \psi_1^* \psi_2 = \text{ const.} \tag{28}$$

If there is no degeneracy so that there exists only one function ψ corresponding to given energy, its *normalization* is time-independent,

$$\int d^3r \, |\psi|^2 = \text{ const.} \tag{29}$$

4. The Ehrenfest equations of motion for the expectation value of a time independent operator $\hat{O}$ in the system with hamiltonian $\hat{H}$ are

$$\imath\hbar \frac{d}{dt} \langle \hat{O} \rangle = \langle [\hat{O}, \hat{H}] \rangle. \tag{30}$$

For a free particle in one dimension

$$\hat{H} = \frac{\hat{p}^2}{2m} \quad (\hat{p} = \hat{p}_x, \; [\hat{x}, \hat{p}] = i\hbar). \tag{31}$$

We need the commutators

$$[\hat{x}, \hat{p}^2] = 2i\hbar\hat{p}, \tag{32}$$

$$[\hat{x}^2, \hat{p}^2] = \hat{x}[\hat{x}, \hat{p}^2] + [\hat{x}, \hat{p}^2]\hat{x} = 2i\hbar(\hat{x}\hat{p} + \hat{p}\hat{x}). \tag{33}$$

Using these rules, we obtain the equations of motion for the mean values:

$$i\hbar\frac{d}{dt}\langle\hat{x}\rangle = [\hat{x},\hat{H}] = i\hbar\frac{\langle\hat{p}\rangle}{m} \quad \rightsquigarrow \frac{d\langle\hat{x}\rangle}{dt} = \frac{\langle\hat{p}\rangle}{m} \tag{34}$$

(an analog of the velocity definition $v = p/m$);

$$\frac{d}{dt}\langle\hat{x}^2\rangle = \frac{1}{m}\langle(\hat{x}\hat{p}+\hat{p}\hat{x}); \tag{35}$$

$$\frac{d}{dt}\langle\hat{p}\rangle = \frac{d}{dt}\langle\hat{p}^2\rangle = 0. \tag{36}$$

The last result, eq. (36), means that the momentum distribution does not change in free motion, in concordance with physical arguments. The conservation of $\langle\hat{p}^2\rangle$ is the same as the conservation of mean energy. Finally,

$$\frac{d}{dt}\langle\hat{x}\hat{p}+\hat{p}\hat{x}\rangle = \frac{1}{i\hbar}\langle[\hat{x}\hat{p}+\hat{p}\hat{x},\hat{H}] = \frac{2}{m}\langle\hat{p}^2\rangle. \tag{37}$$

Now we can solve the equations of motion for the expectation values. From eq. (37) we obtain

$$\langle\hat{x}\hat{p}+\hat{p}\hat{x}\rangle = 2\frac{\langle\hat{p}^2\rangle}{m}t + \langle\hat{x}\hat{p}+\hat{p}\hat{x}\rangle_0, \tag{38}$$

where the last item is determined by the initial conditions. Eq. (35) now gives

$$\langle\hat{x}^2\rangle = \frac{\langle\hat{p}^2\rangle}{m^2}t^2 + \frac{\langle\hat{x}\hat{p}+\hat{p}\hat{x}\rangle_0}{m}t + \langle\hat{x}^2\rangle_0, \tag{39}$$

whereas eq. (34) defines the analog of the uniform motion,

$$\langle\hat{x}\rangle = \frac{\langle\hat{p}\rangle}{m}t + \langle\hat{x}\rangle_0. \tag{40}$$

Combining those results, we can calculate the uncertainty of the position

$$(\Delta x)^2 = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2 \tag{41}$$

as a function of time:

$$(\Delta x)^2 = (\Delta x)_0^2 + \frac{1}{m}\left[\langle\hat{x}\hat{p}+\hat{p}\hat{x}\rangle_0 - 2\langle\hat{x}\rangle_0\langle\hat{p}\rangle_0\right]t + \frac{(\Delta p)^2}{m^2}t^2. \tag{42}$$

After a very long time interval, one will see only "ballistic" spreading,

$$(\Delta x)^2 \approx \frac{(\Delta p)^2}{m^2}t^2, \tag{43}$$

the packet is broadening because of the spread of velocities $\Delta v \sim \Delta p/m$ in the initial state.

5. *a.* The equations of motion for the expectation values of the position and momentum are *linear* and similar to classical Newton equations:

$$\frac{d}{dt}\langle\hat{x}\rangle = \frac{\langle\hat{p}\rangle}{m}, \tag{44}$$

$$\frac{d}{dt}\langle\hat{p}\rangle = -m\omega^2\langle\hat{x}\rangle. \tag{45}$$

The general solution describes oscillations with frequency ω,

$$\langle\hat{x}\rangle = A\cos(\omega t) + B\sin(\omega t), \quad \langle\hat{p}\rangle = C\cos(\omega t) + D\sin(\omega t). \tag{46}$$

From equations of motion we obtain

$$C = m\omega B, \quad D = -m\omega A, \tag{47}$$

and from the initial conditions

$$\langle\hat{x}\rangle_0 = A, \quad \langle\hat{p}\rangle_0 = C. \tag{48}$$

Thus, the solution is

$$\langle\hat{x}\rangle = \langle\hat{x}\rangle_0\cos(\omega t) + \frac{\langle\hat{p}\rangle_0}{m\omega}\sin(\omega t), \tag{49}$$

$$\langle\hat{p}\rangle = \langle\hat{p}\rangle_0\cos(\omega t) - m\omega\langle\hat{x}\rangle_0\sin(\omega t). \tag{50}$$

b. The equations of motion for quadratic components of the Hamiltonian,

$$\hat{K} = \frac{\hat{p}^2}{2m}, \quad \hat{U} = \frac{1}{2}m\omega^2\hat{x}^2, \tag{51}$$

can be easily derived with the help of the commutators,

$$\frac{d}{dt}\langle\hat{K}\rangle = -\frac{\omega^2}{2}\langle\hat{x}\hat{p} + \hat{p}\hat{x}\rangle, \tag{52}$$

$$\frac{d}{dt}\langle\hat{U}\rangle = \frac{\omega^2}{2}\langle\hat{x}\hat{p} + \hat{p}\hat{x}\rangle. \tag{53}$$

Of course, energy is conserved,

$$\frac{d}{dt}\langle\hat{K} + \hat{U}\rangle = \frac{d}{dt}\langle\hat{H}\rangle = 0. \tag{54}$$

For the operator in the right hand side parts of eqs. (53) and (54) we find

$$\frac{d}{dt}\langle\hat{x}\hat{p} + \hat{p}\hat{x}\rangle = 4\langle\hat{K} - \hat{U}\rangle. \tag{55}$$

Taking the second time derivative we come to

$$\left(\frac{d^2}{dt^2} + 4\omega^2\right) \langle \hat{K} - \hat{U} \rangle = 0. \qquad (56)$$

The general solution corresponds to the oscillation with a double frequency,

$$\langle \hat{K} - \hat{U} \rangle = A \cos(2\omega t) + B \sin(2\omega t). \qquad (57)$$

Remembering that

$$\langle \hat{H} \rangle = \langle \hat{K} + \hat{U} \rangle = \langle \hat{K} + \hat{U} \rangle_0, \qquad (58)$$

we find separately the expectation values of kinetic and potential energy,

$$\langle \hat{K} \rangle = \frac{1}{2} \left[\langle \hat{K} + \hat{U} \rangle_0 + A \cos(2\omega t) + B \sin(2\omega t) \right], \qquad (59)$$

$$\langle \hat{U} \rangle = \frac{1}{2} \left[\langle \hat{K} + \hat{U} \rangle_0 - A \cos(2\omega t) - B \sin(2\omega t) \right], \qquad (60)$$

To find the constant coefficients A and B, we apply the initial conditions:

$$A = \langle \hat{K} - \hat{U} \rangle_0, \quad B = -\frac{\omega}{2} \langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0, \qquad (61)$$

where the last equation follows from eqs. (52) and (59). With all these results,

$$\langle \hat{x}^2 \rangle = \frac{1}{m\omega^2} \left\{ \langle \hat{U} \rangle_0 [1 + \cos(2\omega t)] + \langle \hat{K} \rangle_0 [1 - \cos(2\omega t)] + \frac{\omega}{2} \langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0 \sin(2\omega t) \right\}. \qquad (62)$$

Similarly,

$$\langle \hat{p}^2 \rangle = m \left\{ \langle \hat{U} \rangle_0 [1 - \cos(2\omega t)] + \langle \hat{K} \rangle_0 [1 + \cos(2\omega t)] - \frac{\omega}{2} \langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0 \sin(2\omega t) \right\}. \qquad (63)$$

c. Collecting our previous calculations we find the mean square deviation of the coordinate

$$(\Delta x)^2 = (\Delta x)_0^2 \cos^2(\omega t) + \frac{(\Delta p)_0^2}{m^2\omega^2} \sin^2(\omega t) + \frac{\langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0 - 2\langle \hat{x} \rangle_0 \langle \hat{p} \rangle_0}{2m\omega} \sin(2\omega t), \qquad (64)$$

as in the textbook. For $\omega \to 0$ we arrive at the limit of free motion; using $\sin x/x \to 1$ for $x \to 0$, eq. (64) becomes

$$(\Delta x)^2 = (\Delta x)_0^2 + \frac{(\Delta p)_0^2}{m^2} t^2 + \frac{\langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0 - 2\langle \hat{x} \rangle_0 \langle \hat{p} \rangle_0}{m} t. \qquad (65)$$

d. With the use of eq. (50) we find the mean square deviation of the momentum

$$(\Delta p)^2 = (\Delta p)_0^2 \cos^2(\omega t) + m^2\omega^2 (\Delta x)_0^2 \sin^2(\omega t) - \frac{m\omega}{2} [\langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0 - 2\langle \hat{x} \rangle_0 \langle \hat{p} \rangle_0] \sin(2\omega t). \qquad (66)$$