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 \(E\),
\[
p(x; E) = \sqrt{2m[E - U(x)]},
\] (1)
vanishes,
\[
p(x_{\pm}; E) = 0 \quad \Rightarrow \quad U(x_{\pm}) = E.
\] (2)
The approximate quantization rule reads
\[
\oint dx p(x; E) = 2\pi n\bar{h},
\] (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 \(x = x_0\),
\[
4\sqrt{2m} \int_0^{x_0} dx \sqrt{E - U(x)} = 2\pi n\bar{h}.
\] (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 \(x_0 \rightarrow 1\), and the
quantization condition (4) takes the form
\[
\frac{4}{s} \sqrt{2mE} \left(\frac{E}{\alpha}\right)^{1/s} I_s = 2\pi n\bar{h}, \quad I_s = \int_0^1 d\eta \eta^{(1-s)/s} \sqrt{1-\eta}.
\] (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
\[
E_n = (C_s n)^{2s/(s+2)},
\] (6)
where the energy scaling is determined by the constant parameter
\[
C_s = \frac{\pi \hbar s\alpha^{1/s}}{2\sqrt{2m}I_s},
\] (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,
\[
I_s = \frac{\Gamma(1/s)\Gamma(3/2)}{\Gamma[(3/2) + (1/s)]},
\] (8)
For the harmonic oscillator potential $U(x) = (1/2)m\omega^2x^2$, we have

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

so that

$$I_2 = \frac{\pi}{2} \sim E_n = C_2n = \hbar\omega n. \tag{9}$$

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 $e^2/|r_1 - r_2|_{\text{max}} = e^2/(r_1 + r_2)$. 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 $r$,

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

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

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

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),

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

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 $\hat{H}$,

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

and taking the difference of these equations, we obtain

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

(17)

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

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

(18)

is real as well. Introducing the transition density

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

(19)

and the transition current

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

we come to the continuity equation

$$\frac{\partial \rho_{12}}{\partial t} + \text{div} j_{12} = 0.$$  

(21)

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

b. Two stationary wave functions $\Psi_1$ and $\Psi_2$ describe the states with certain energies $E_1$ and $E_2$, respectively. Their time dependence is given by

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

(22)

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

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

(23)

The continuity equation of point a can be written as

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

(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 $\rho_{12}$ oscillates in time with the transition frequency $\omega_{21} = (E_2 - E_1)/\hbar$; the expectation value of the density $\rho_{11}$ is simply constant in time for a stationary state $\Psi_1$. 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
\[ i\hbar \int d^3r \frac{\partial \rho_{12}}{\partial t} = -i\hbar \int d^3r \text{div} j_{12}. \] (25)
The volume integral in eq. (25) can be converted into the surface integral
\[ \oint dA \cdot j_{12}, \] the flux of the transition current through the surface area $A$.
Now we make the second assumption that this flux vanishes. This happens in particular if the wave functions $\psi_1$ and $\psi_2$, 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
\[ (E_1 - E_2) \int d^3r \psi_1^* \psi_2 = 0. \] (26)
If the energies $E_1$ and $E_2$ do not coincide, the corresponding coordinate eigenfunctions are orthogonal,
\[ \int d^3r \psi_1^* \psi_2 = 0. \] (27)
For coinciding energies we only extract that the integral of $\rho_{12}$ does not change in time,
\[ \int d^3r \psi_1^* \psi_2 = \text{const}. \] (28)
If there is no degeneracy so that there exists only one function $\psi$ corresponding to given energy, its normalization is time-independent,
\[ \int d^3r |\psi|^2 = \text{const}. \] (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
\[ i\hbar \frac{d}{dt} \langle \hat{O} \rangle = \langle [\hat{O}, \hat{H}] \rangle. \] (30)
For a free particle in one dimension
\[ \hat{H} = \frac{\hat{p}^2}{2m} \quad (\hat{p} = \hat{p}_x, \ [\hat{x}, \hat{p}_x] = i\hbar). \] (31)
We need the commutators
\[ [\hat{x}, \hat{p}_x^2] = 2i\hbar \hat{p}_x \] (32)
\[ [\hat{x}^2, \hat{p}^2] = \hat{x} [\hat{x}, \hat{p}^2] + [\hat{x}, \hat{p}^2] \hat{x} = 2i\hbar (\hat{x} \hat{p}_x + \hat{p}_x \hat{x}). \] (33)
Using these rules, we obtain the equations of motion for the mean values:

\[ i\hbar \frac{d}{dt}\langle \hat{x} \rangle = [\hat{x}, \hat{H}] = \frac{\hbar}{m} \frac{d\langle \hat{p} \rangle}{dt} = \frac{\langle \hat{p} \rangle}{m} \]  \hspace{1cm} (34)

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

\[ \frac{d}{dt}\langle \hat{x}^2 \rangle = \frac{1}{m} \langle (\hat{x}\hat{p} + \hat{p}\hat{x}) \rangle; \]  \hspace{1cm} (35)

\[ \frac{d}{dt}\langle \hat{p} \rangle = \frac{d}{dt}\langle \hat{p}^2 \rangle = 0. \]  \hspace{1cm} (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,

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

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

\[ \langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle = 2\frac{\langle \hat{p}^2 \rangle}{m} t + \langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0, \]  \hspace{1cm} (38)

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

\[ \langle \hat{x}^2 \rangle = \frac{\langle \hat{p}^2 \rangle}{m^2} t^2 + \frac{\langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle_0}{m} t + \langle \hat{x}^2 \rangle_0; \]  \hspace{1cm} (39)

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

\[ \langle \hat{x} \rangle = \frac{\langle \hat{p} \rangle}{m} t + \langle \hat{x} \rangle_0. \]  \hspace{1cm} (40)

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

\[ (\Delta x)^2 = \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2 \]  \hspace{1cm} (41)

as a function of time:

\[ (\Delta x)^2 = (\Delta x)_0^2 + \frac{1}{m} \langle (\hat{x}\hat{p} + \hat{p}\hat{x})_0 - 2\langle \hat{x} \rangle_0 \langle \hat{p} \rangle_0 \rangle t + \frac{(\Delta p)^2}{m^2} t^2. \]  \hspace{1cm} (42)

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

\[ (\Delta x)^2 \approx \frac{(\Delta p)^2}{m^2} t^2, \]  \hspace{1cm} (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:

\[ \frac{d}{dt} \langle \hat{x} \rangle = \frac{\langle \hat{p} \rangle}{m}, \]

(44)\[ \frac{d}{dt} \langle \hat{p} \rangle = -m\omega^2 \langle \hat{x} \rangle. \]

(45)

The general solution describes oscillations with frequency \( \omega \),

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

(46)

From equations of motion we obtain

\[ C = m\omega B, \quad D = -m\omega A, \]

(47)

and from the initial conditions

\[ \langle \hat{x} \rangle_0 = A, \quad \langle \hat{p} \rangle_0 = C. \]

(48)

Thus, the solution is

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

(49)\[ \langle \hat{p} \rangle = \langle \hat{p} \rangle_0 \cos(\omega t) - m\omega \langle \hat{x} \rangle_0 \sin(\omega t). \]

(50)

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

\[ K = \frac{\hat{p}^2}{2m}, \quad \dot{U} = \frac{1}{2} m\omega^2 \dot{x}^2, \]

(51)

can be easily derived with the help of the commutators,

\[ \frac{d}{dt} \langle K \rangle = -\frac{\omega^2}{2} \langle \dot{x} \hat{p} + \hat{p} \dot{x} \rangle, \]

(52)\[ \frac{d}{dt} \langle \dot{U} \rangle = \frac{\omega^2}{2} \langle \dot{x} \dot{\hat{p}} + \dot{\hat{p}} \dot{x} \rangle. \]

(53)

Of course, energy is conserved,

\[ \frac{d}{dt} \langle K + \dot{U} \rangle = \frac{d}{dt} \langle \dot{H} \rangle = 0. \]

(54)

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

\[ \frac{d}{dt} \langle \dot{x} \hat{p} + \dot{\hat{p}} \dot{x} \rangle = 4 \langle \dot{K} + \dot{U} \rangle. \]

(55)
Taking the second time derivative we come to
\[
\left( \frac{d^2}{dt^2} + 4\omega^2 \right) \langle \hat{K} - \hat{U} \rangle = 0. \tag{56}
\]

The general solution corresponds to the oscillation with a double frequency,
\[
\langle \hat{K} - \hat{U} \rangle = A \cos(2\omega t) + B \sin(2\omega t). \tag{57}
\]

Remembering that
\[
\langle \hat{H} \rangle = \langle \hat{K} + \hat{U} \rangle = \langle \hat{K} + \hat{U} \rangle_0, \tag{58}
\]
we find separately the expectation values of kinetic and potential energy,
\[
\langle \hat{K} \rangle = \frac{1}{2} \left[ \langle \hat{K} + \hat{U} \rangle_0 + A \cos(2\omega t) + B \sin(2\omega t) \right], \tag{59}
\]
\[
\langle \hat{U} \rangle = \frac{1}{2} \left[ \langle \hat{K} + \hat{U} \rangle_0 - A \cos(2\omega t) - B \sin(2\omega t) \right]. \tag{60}
\]

To find the constant coefficients \(A\) and \(B\), we apply the initial conditions:
\[
A = \langle \hat{K} - \hat{U} \rangle_0, \quad B = -\frac{\omega}{2} (\hat{x}\hat{p} + \hat{p}\hat{x})_0, \tag{61}
\]
where the last equation follows from eqs. (52) and (59).

With all these results,
\[
\langle \hat{x}^2 \rangle = \frac{1}{m\omega^2} \left\{ \langle \hat{U} \rangle_0 [1 + \cos(2\omega t)] + \langle \hat{K} \rangle_0 [1 - \cos(2\omega t)] + \frac{\omega}{2} (\hat{x}\hat{p} + \hat{p}\hat{x})_0 \sin(2\omega t) \right\}. \tag{62}
\]

Similarly,
\[
\langle \hat{p}^2 \rangle = m \left\{ \langle \hat{U} \rangle_0 [1 - \cos(2\omega t)] + \langle \hat{K} \rangle_0 [1 + \cos(2\omega t)] - \frac{\omega}{2} (\hat{x}\hat{p} + \hat{p}\hat{x})_0 \sin(2\omega t) \right\}. \tag{63}
\]

c. Collecting our previous calculations we find the mean square deviation of the coordinate
\[
(\Delta x)^2 = (\Delta x)_0^2 \cos^2(\omega t) + \frac{(\Delta p)_0^2}{m^2\omega^2} \sin^2(\omega t) + \frac{\langle \dot{x}\hat{p} + \hat{p}\dot{x} \rangle_0 - 2 \langle \dot{x} \rangle_0 \langle \hat{p} \rangle_0}{2m} \sin(2\omega t), \tag{64}
\]
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
\[
(\Delta x)^2 = (\Delta x)_0^2 + \frac{(\Delta p)_0^2}{m^2} t^2 + \frac{\langle \dot{x}\hat{p} + \hat{p}\dot{x} \rangle_0 - 2 \langle \dot{x} \rangle_0 \langle \hat{p} \rangle_0}{m} \sin(2\omega t), \tag{65}
\]
d. With the use of eq. (50) we find the mean square deviation of the momentum
\[
(\Delta p)^2 = (\Delta p)_0^2 \cos^2(\omega t) + m^2 \omega^2 (\Delta x)_0^2 \sin^2(\omega t) - \frac{m\omega}{2} \left[ \langle \dot{x}\hat{p} + \hat{p}\dot{x} \rangle_0 - 2 \langle \dot{x} \rangle_0 \langle \hat{p} \rangle_0 \right] \sin(2\omega t). \tag{66}
\]