Quantum Mechanics PHYS2B22
Solutions to problem sheet 4
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1) Since $\hat{O}$ is a Hermitian operator we have $I = \int_{-\infty}^{\infty} dx\ \psi^*(\hat{O}\psi) = \int_{-\infty}^{\infty} dx\ (\hat{O}^*\psi^*)\psi = I^*$. Hence I is real.

2)
$$\left[\hat{p}, \hat{V}(x)\right]\psi = -i\hbar\frac{d}{dx}[V(x)\psi(x)] - V(x)[-i\hbar\frac{d}{dx}\psi] = -i\hbar\frac{dV}{dx}\psi.$$
As this is true for all ψ we get the required result.

From the notes:
$$\frac{d\langle\hat{p}\rangle}{dt} = \frac{i}{\hbar}\left\langle[\hat{H}, \hat{p}]\right\rangle + \left\langle\frac{\partial\hat{p}}{\partial t}\right\rangle.$$

Since $\frac{\partial\hat{p}}{\partial t} = 0$, $[\frac{\hat{p}^2}{2m}, \hat{p}] = 0$ and $[A, B] = -[B, A]$ we get
$$\frac{d\langle\hat{p}\rangle}{dt} = \frac{i}{\hbar}\langle[V(x), \hat{p}]\rangle = -\left\langle\frac{dV}{dx}\right\rangle.$$

The classical result from Newton's second law would be
$$\frac{d\langle\hat{p}\rangle}{dt} = -\left.\frac{dV}{dx}\right|_{\langle x\rangle}.$$

These are similar for a localized wavefunction in a slowly varying potential when
$$\left\langle\frac{dV}{dx}\right\rangle \approx \left.\frac{dV}{dx}\right|_{\langle x\rangle}.$$

3) Atomic unit of time is
$$T = \left(\frac{4\pi\epsilon_0}{e^2}\right)^2\frac{\hbar^3}{m_e} = 2.419\times 10^{-17}\text{s}.$$

4) Using the formulae in the notes with $n = 2$ and $l = 1$ gives
$$R_{21}(r) = \frac{F_{21}(r)}{r}\exp(-r/2), \quad F_{21}(r) = r^2\sum_{p=0}^{\infty} a_p r^p, \quad \frac{a_{p+1}}{a_p} = \frac{p}{(p+3)(p+2)-2}.$$

So series terminates at first term ($p = 0$) and $F_{21} = a_0 r^2$. Setting $c = a_0$ gives the result in the question. Normalization condition is

$$\int_0^\infty dr\, r^2 |R_{21}|^2 = 1 \Rightarrow \int_0^\infty dr\, |c|^2 r^4 \exp(-r) = |c|^2 \times 4! = 1,$$

using the integral given on the question sheet. Hence $|c|^2 = 1/24$.

Probability per unit length is

$$P(r) = r^2 |R_{21}|^2 = \frac{1}{24} r^4 \exp(-r).$$

Most probable distance is when $dP(r)/dr = 0$. This gives $r = 4$ for the maximum (there is a minimum at $r = 0$). Mean value of r is

$$\langle r \rangle = \int_0^\infty dr\, r P(r) = \int_0^\infty dr\, \frac{1}{24} r^5 \exp(-r) = \frac{5!}{4!} = 5.$$

The Bohr model gives the radius of the orbits as $r_{\mathrm{Bohr}} = n^2 = 4$ in this case. So this is the same as the most likely value of r for this energy level (this is true in general for states with $l = n - 1$) and less than the mean value (this is true for all states).

5) The minimum potential is when $dV_{\mathrm{eff}}/dr = 0$, so

$$V_{min}(r) = -\frac{Z^2}{2l(l+1)}, \quad \text{and} \quad r_{min} = \frac{l(l+1)}{Z}.$$

$E_n = -Z^2/2n^2$ and $n > l$ so the lowest energy eigenfunction with angular momentum quantum number l has $n = l + 1$ and $E = -Z^2/2(l+1)^2$. This is a little bigger than V_{min}. We expect this because the mean KE must be positive and the uncertainty principle does not allow the electron to be stationary at V_{min}. The condition $E_n > V_{min}$ gives $n > l$.