Part IB Physics A: Lent 2022

QUANTUM PHYSICS EXAMPLES III MODEL ANSWERS

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1. For a free particle, $\hat{H} = \hat{p}^2/(2m)$. Using Ehrenfest's theorem, we can compute

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

where we used the commutation relation $[\hat{x}, \hat{p}^2] = 2i\hbar\hat{p}$.

We can then use this result to compute

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

The final result follows straightforwardly upon integrating the second order differential equation:

$$\langle \hat{x}^2 \rangle_t = \langle \hat{x}^2 \rangle_{t=0} + \left. \frac{d\langle \hat{x}^2 \rangle}{dt} \right|_{t=0} t + \frac{1}{2} \left. \frac{d^2 \langle \hat{x}^2 \rangle}{dt^2} \right|_{t=0} t^2 = \langle \hat{x}^2 \rangle_{t=0} + \langle \hat{p}^2 \rangle_{t=0} \frac{t^2}{m^2}.$$

2. Following a measurement of A yielding the eigenvalue a_1 , the system is in state ψ_1 , which is expressed in terms of energy eigenstates in the question. The state of the system evolves thereafter in time as

$$|\psi_1(t)\rangle = \frac{e^{-iE_1t/\hbar}}{\sqrt{2}}|u_1\rangle + \frac{e^{-iE_2t/\hbar}}{\sqrt{2}}|u_2\rangle.$$

We can then compute

$$\langle A \rangle(t) = \langle \psi_1(t) | \hat{A} | \psi_1(t) \rangle = \sum_{i,j=1}^2 \exp \left[i \frac{E_i - E_j}{\hbar} t \right] \langle u_i | \hat{A} | u_j \rangle,$$

where, upon inverting the equations given in the question,

$$u_1 = (\psi_1 + \psi_2)/\sqrt{2}$$
 and $u_2 = (\psi_1 - \psi_2)/\sqrt{2}$.

After some algebra, we finally obtain

$$\begin{split} \langle A \rangle(t) &= \frac{1}{2} \langle u_1 | \hat{A} | u_1 \rangle + \frac{1}{2} e^{i(E_1 - E_2)/\hbar t} \langle u_1 | \hat{A} | u_2 \rangle + \frac{1}{2} e^{i(E_2 - E_1)/\hbar t} \langle u_2 | \hat{A} | u_1 \rangle + \frac{1}{2} \langle u_2 | \hat{A} | u_2 \rangle \\ &= \frac{1}{2} \left(a_1 + a_2 \right) + \frac{1}{2} \cos \left[\frac{(E_1 - E_2)t}{\hbar} \right] \left(a_1 - a_2 \right) \\ &= \cos^2 \left[\frac{(E_1 - E_2)t}{2\hbar} \right] a_1 + \sin^2 \left[\frac{(E_1 - E_2)t}{2\hbar} \right] a_2 \,. \end{split}$$

3. Using the energy eigenstates $|n\rangle$, of eigenvalues ε_n , as a basis to represent the operators, we can write

$$\hat{H} = \sum_{n} \varepsilon_n |n\rangle \langle n|$$
 and $\hat{U} = \exp\left(i\hat{H}t\right) = \sum_{n} e^{i\varepsilon_n t} |n\rangle \langle n|$.

Then one can straightforwardly show that $\hat{U} \exp\left(i\hat{H}t\right) = \exp\left(i\hat{H}t\right)\hat{U}$ by explicit calculation, using the orthonormality of the eigenstates.

Alternatively, one can use the definition of function of an operator,

$$\hat{U} = \exp\left(i\hat{H}t\right) = \sum_{\ell=0}^{\infty} \frac{1}{\ell!} \left(i\hat{H}t\right)^n,$$

to show that the commutator $[\hat{H}, \hat{U}]$ reduces to

$$\sum_{\ell=0}^{\infty} \frac{1}{\ell!} (it)^n [\hat{H}, \hat{H}^n] = 0,$$

since an operators trivially commutes with itself (and any power thereof).

4. Given that the shift operator in question 6 acted on momentum-space eigenfunctions as multiplication by $\exp(-ipx_0/\hbar)$, it can be written as

$$\sum_{p} \exp\left(-ipx_0/\hbar\right) |p\rangle\langle p|,$$

which defines the operator $\exp(-i\hat{p}x_0/\hbar)$.

Using, for example, the definition of function of an operator, one can straightforwardly verify the proposed commutation relation:

$$[\exp(-i\hat{p}x_{01}/\hbar), \exp(-i\hat{p}x_{02}/\hbar)] = \sum_{n,m=0}^{\infty} \frac{(-ix_{01}/\hbar)^n (-ix_{02}/\hbar)^m}{n!m!} [\hat{p}^n, \hat{p}^m] = 0.$$

5. From the commutation relations $[\hat{\alpha}, \hat{p}_{\beta}] = i\hbar \delta_{\alpha,\beta}$ and $[\hat{\alpha}, \hat{\beta}] = [\hat{p}_{\alpha}, \hat{p}_{\beta}] = 0$, for $\alpha, \beta = x, y, z$, and from the definition $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$, we obtain:

$$\begin{aligned} & [\hat{L}_{x}, \hat{x}] &= 0 \\ & [\hat{L}_{x}, \hat{y}] &= -\hat{z}[\hat{p}_{y}, \hat{y}] = i\hbar \hat{z} \\ & [\hat{L}_{x}, \hat{p}_{x}] &= 0 \\ & [\hat{L}_{x}, \hat{p}_{y}] &= [\hat{y}, \hat{p}_{y}]\hat{p}_{z} = i\hbar \hat{p}_{z} \,. \end{aligned}$$

One can also derive, as in the lecture notes, $[\hat{L}_{\alpha}, \hat{L}_{\beta}] = i\hbar\epsilon^{\alpha,\beta\gamma}\hat{L}_{\gamma}$, where $\alpha, \beta, \gamma = x, y, z$ and $\epsilon^{\alpha,\beta\gamma}$ is the antisymmetric symbol.

From the definitions $\hat{r}^2 = \hat{x}^2 + \hat{y}^2 + \hat{z}^2$, $\hat{p}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$ and $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ we obtain

$$\begin{split} &[\hat{L}_x,\hat{r}^2] &= -\hat{z}[\hat{p}_y,\hat{y}^2] + \hat{y}[\hat{p}_z,\hat{z}^2] = 2i\hbar \, (\hat{z}\hat{y} - \hat{y}\hat{z}) = 0 \\ &[\hat{L}_x,\hat{p}^2] &= [\hat{y},\hat{p}_y^2]\hat{p}_z - [\hat{z},\hat{p}_z^2]\hat{p}_y = 2i\hbar \, (\hat{p}_y\hat{p}_z - \hat{p}_z\hat{p}_y) = 0 \\ &[\hat{L}_x,\hat{L}^2] &= [\hat{L}_x,\hat{L}_y^2] + [\hat{L}_x,\hat{L}_z^2] = 2\hat{L}_y\hat{L}_z - 2\hat{L}_y\hat{L}_z = 0 \,, \end{split}$$

where we omitted steps of the type $[\hat{y}^2, \hat{p}_y] = \hat{y}[\hat{y}, \hat{p}_y] + [\hat{y}, \hat{p}_y]\hat{y} = 2i\hbar\hat{y}$ and $[\hat{L}_x, \hat{L}_y^2] = \hat{L}_y[\hat{L}_x, \hat{L}_y] + [\hat{L}_x, \hat{L}_y]\hat{L}_y = 2\hat{L}_y\hat{L}_z$.

We conclude that there cannot be simultaneous eigenstates of any two components of the angular momentum operator. However, it is possible to find simultaneous eigenstates, for example, of \hat{r}^2 , \hat{L}_x and \hat{L}^2 .

6. From the definition $\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$ we can compute

$$[\hat{L}_+, \hat{L}_-] = -i[\hat{L}_x, \hat{L}_y] + i[\hat{L}_y, \hat{L}_x] = 2\hbar \hat{L}_z$$
.

Therefore,

$$\hat{L}^{2} = \frac{(\hat{L}_{+} + \hat{L}_{-})^{2}}{4} - \frac{(\hat{L}_{+} - \hat{L}_{-})^{2}}{4} + \hat{L}_{z}^{2} = \frac{\hat{L}_{+}\hat{L}_{-} + \hat{L}_{-}\hat{L}_{+}}{2} + \hat{L}_{z}^{2} = \frac{2\hat{L}_{+}\hat{L}_{-} - [\hat{L}_{+}, \hat{L}_{-}]}{2} + \hat{L}_{z}^{2} \\
= \hat{L}_{+}\hat{L}_{-} + \hat{L}_{z}^{2} - \hbar\hat{L}_{z}.$$
(1)

From the definition

$$\hat{L}_{\pm} = \hbar \ e^{\pm i\phi} \left(\pm \partial_{\theta} + i \cot \theta \partial_{\phi} \right) \,.$$

we can then compute

$$\hat{L}_{z} = \frac{1}{2\hbar} \left(\hat{L}_{+} \hat{L}_{-} - \hat{L}_{-} \hat{L}_{+} \right)
= \frac{\hbar}{2} \left[e^{i\phi} \left(\partial_{\theta} + i \cot \theta \partial_{\phi} \right) \right] \left[e^{-i\phi} \left(-\partial_{\theta} + i \cot \theta \partial_{\phi} \right) \right]
- \frac{\hbar}{2} \left[e^{-i\phi} \left(-\partial_{\theta} + i \cot \theta \partial_{\phi} \right) \right] \left[e^{i\phi} \left(\partial_{\theta} + i \cot \theta \partial_{\phi} \right) \right]
= \frac{\hbar}{2} \partial_{\theta} \left(-\partial_{\theta} + i \cot \theta \partial_{\phi} \right) + \frac{\hbar}{2} i e^{i\phi} \cot \theta \partial_{\phi} \left[e^{-i\phi} \left(-\partial_{\theta} + i \cot \theta \partial_{\phi} \right) \right]
+ \frac{\hbar}{2} \partial_{\theta} \left(\partial_{\theta} + i \cot \theta \partial_{\phi} \right) - \frac{\hbar}{2} i e^{-i\phi} \cot \theta \partial_{\phi} \left[e^{i\phi} \left(\partial_{\theta} + i \cot \theta \partial_{\phi} \right) \right]
= i\hbar \partial_{\theta} (\cot \theta \partial_{\phi}) - i\hbar \cot \theta \partial_{\phi} \partial_{\theta} + \hbar \cot^{2} \theta \partial_{\phi}
= -i\hbar \frac{\partial}{\partial \phi}$$

and

$$\begin{split} \hat{L}^2 &= \hat{L}_+ \hat{L}_- + \hat{L}_z^2 - \hbar \hat{L}_z \\ &= \hbar^2 \left[e^{i\phi} \left(\partial_\theta + i \cot \theta \partial_\phi \right) \right] \left[e^{-i\phi} \left(-\partial_\theta + i \cot \theta \partial_\phi \right) \right] - \hbar^2 \partial_\phi^2 + i\hbar^2 \partial_\phi \\ &= \hbar^2 \partial_\theta \left(-\partial_\theta + i \cot \theta \partial_\phi \right) + \hbar^2 e^{i\phi} \left(i \cot \theta \partial_\phi \right) \left[e^{-i\phi} \left(-\partial_\theta + i \cot \theta \partial_\phi \right) \right] - \hbar^2 \partial_\phi^2 + i\hbar^2 \partial_\phi \\ &= -\hbar^2 \partial_\theta^2 - \frac{i\hbar^2}{\sin^2 \theta} \partial_\phi + i\hbar^2 \cot \theta \partial_\theta \partial_\phi + \hbar^2 \cot \theta \left(-\partial_\theta + i \cot \theta \partial_\phi \right) + i\hbar^2 \cot \theta \partial_\phi \left(-\partial_\theta + i \cot \theta \partial_\phi \right) \\ &- \hbar^2 \partial_\phi^2 + i\hbar^2 \partial_\phi \\ &= -\hbar^2 \left(\partial_\theta^2 + \cot \theta \partial_\theta + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right) \,. \end{split}$$

Finally, we can use the relations $\hat{L}_z\psi = \hbar m_\ell \psi$ and $\hat{L}^2\psi = \hbar^2 \ell(\ell+1)\psi$ to find the angular momentum quantum numbers of the Hydrogen eigenfunctions in the question:

$$(\text{trivially}) \rightarrow \ell = 0, \ m_{\ell} = 0$$

$$\hat{L}^{2}\psi = \hbar^{2} \left(1 - \frac{\cos^{2}\theta}{\sin^{2}\theta} + \frac{1}{\sin^{2}\theta} \right) \psi = 2\hbar^{2}\psi, \ \hat{L}_{z}\psi = \hbar\psi \rightarrow \ell = 1, \ m_{\ell} = 1$$

$$\hat{L}^{2}\psi = \hbar^{2} \left(24\cos^{2}\theta - 6\sin^{2}\theta \right) R_{3} = 6\hbar^{2}\psi, \ \hat{L}_{z}\psi = 0 \rightarrow \ell = 2, \ m_{\ell} = 0$$

7. Using the expression for the angular momentum in cartesian coordinates, e.g., $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar y\partial_z + i\hbar z\partial_y$, and the fact that e.g., $\partial_y f(r) = (y/r)\partial_r f$, we can readily obtain:

$$\hat{L}_x \psi_x = -i\hbar y x \frac{z}{r} \partial_r f + i\hbar z x \frac{y}{r} \partial_r f = 0$$

$$\hat{L}_x \psi_y = -i\hbar y^2 \frac{z}{r} \partial_r f + i\hbar z \left(f + \frac{y^2}{r} \partial_r f \right) = i\hbar \psi_z$$

$$\hat{L}_x \psi_z = -i\hbar y \left(f + \frac{z^2}{r} \partial_r f \right) + i\hbar z^2 \frac{y}{r} \partial_r f = -i\hbar \psi_y .$$

Trivially, $\langle \psi_x | \hat{L}_x | \psi_x \rangle = 0$, and

$$\langle \psi_y | \hat{L}_x | \psi_y \rangle = i\hbar \langle \psi_y | \psi_z \rangle = 0$$
$$\langle \psi_z | \hat{L}_x | \psi_z \rangle = -i\hbar \langle \psi_z | \psi_y \rangle = 0.$$

Similarly for the other components of the angular momentum. On the other hand,

$$\begin{split} \langle \psi_x | \hat{L}_x^2 | \psi_x \rangle &= 0 \\ \langle \psi_x | \hat{L}_y^2 | \psi_x \rangle &= -i\hbar \langle \psi_x | \hat{L}_y | \psi_z \rangle = \hbar^2 \langle \psi_x | \psi_x \rangle \\ \langle \psi_x | \hat{L}_z^2 | \psi_x \rangle &= i\hbar \langle \psi_x | \hat{L}_z | \psi_y \rangle = \hbar^2 \langle \psi_x | \psi_x \rangle \,, \end{split}$$

and similarly for $|\psi_y\rangle$ and $|\psi_z\rangle$. Therefore, they are all eigenstates of the orbital angular momentum squared operator, with eigenvalue $2\hbar^2 = \hbar^2 \ell(\ell+1)$, i.e., $\ell=1$.

Finally, we consider ψ_{\pm} (which are linear combinations of ψ_x and ψ_y , and therefore are also eigenstates of \hat{L}^2 with quantum number $\ell = 1$):

$$\hat{L}_z | \psi_{\pm} \rangle = \hat{L}_z | \psi_x \rangle \pm i \hat{L}_z | \psi_y \rangle
= i \hbar | \psi_y \rangle \pm i (-i \hbar) | \psi_x \rangle = \pm \hbar | \psi_{\pm} \rangle ,$$

and therefore $m_{\ell} = \pm 1$.

8. For $\ell = 1$:

$$\frac{3}{4\pi}\cos^2\theta + 2\frac{3}{8\pi}\sin^2\theta = \frac{3}{4\pi}.$$

For $\ell = 2$:

$$\frac{5}{16\pi} \left(2\cos^2\theta - \sin^2\theta \right)^2 + 2\frac{15}{8\pi} \sin^2\theta \cos^2\theta + 2\frac{15}{32\pi} \sin^4\theta$$
$$= \frac{1}{16\pi} \left(20\cos^4\theta + 40\sin^2\theta \cos^2\theta + 20\sin^4\theta \right)$$
$$= \frac{5}{4\pi} \left(\sin^2\theta + \cos^2\theta \right)^2 = \frac{5}{4\pi} .$$

- **9.** The probability density as a function of the radial coordinate only, for an electron in the ground state of a hydrogen-like atom, is $P(r) = r^2 |R_{10}(r)|^2$.
- (a) The average distance from the nucleus can then be computed as

$$\langle r \rangle = \int_0^\infty r P(r) dr = 4 \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r^3 \exp\left(-\frac{2Zr}{a_0}\right) dr = \frac{3}{2} \frac{a_0}{Z}.$$

(b) Its most likely distance is given by the position of the maximum in the probability density:

$$\frac{d}{dr} \left(r^2 |R_{10}|^2 \right) = 2r |R_{10}|^2 + 2r^2 |R_{10}|^2 \left(-\frac{Z}{a_0} \right) = 2r \left(1 - r\frac{Z}{a_0} \right) |R_{10}|^2 = 0,$$

and therefore $r_{\text{max}} = a_0/Z$.

(c) The expectation value of the potential energy operator \hat{V} of the electron can be computed as

$$\langle V \rangle = \langle -\frac{Ze^2}{4\pi\epsilon_0 r} \rangle = -\frac{Ze^2}{4\pi\epsilon_0} \int_0^\infty \frac{1}{r} P(r) \ dr = -\frac{Z^2e^2}{4\pi\epsilon_0 a_0} \,.$$

(d) By the virial theorem for a Coulombic potential, $2\langle T \rangle = -\langle V \rangle$ and therefore $\langle T \rangle = Z^2 e^2/(8\pi\epsilon_0 a_0)$.

Alternatively, one can explicitly compute the expectation value of the kinetic energy operator

$$T = \frac{p^2}{2} = -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r,$$

$$\langle T \rangle = -\frac{\hbar^2}{2m} \int_0^\infty R_{10}^* \frac{1}{r} \left[\frac{\partial^2}{\partial r^2} (rR_{10}) \right] r^2 dr$$

$$= -\frac{2\hbar^2}{m} \left(\frac{Z}{a_0} \right)^4 \int_0^\infty r \left(-2 + \frac{rZ}{a_0} \right) e^{-2Zr/a_0} dr = \frac{\hbar^2}{2m} \frac{Z^2}{a_0^2} ,$$

and substitute the value $a_0 = 4\pi\epsilon_0 \hbar^2/(me^2)$ from the lecture notes, to obtain the desired result.

(e) Hence the expectation value of the Hamiltonian is $\langle T \rangle + \langle V \rangle = -Z^2 e^2/(8\pi\epsilon_0 a_0)$, which is in agreement with the ground state energy from the lecture notes:

$$E_1 = -\frac{\hbar^2}{2m} \frac{Z^2}{a_0^2} \quad \text{where} \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \,,$$

i.e., $E_1 = -Z^2 e^2/(8\pi\epsilon_0 a_0)$.

10. The Hamiltonian of the system can be conveniently written in cartesian coordinates as

$$H = -\frac{\hbar^2}{2m} \left(\partial_x^2 + \partial_y^2 + \partial_z^2 \right) + \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2).$$

By inspection, the eigenvalue problem allows for a separable solution of the form:

$$\psi_{n_1,n_2,n_3} = X_{n_1}(x)Y_{n_2}(y)Z_{n_3}(z),$$

where $X_{n_1}(x)$, $Y_{n_2}(y)$, $Z_{n_3}(z)$ are eigenstates of the 1D SHO with quantum numbers n_1, n_2, n_3 , respectively. The total energy of the system is $E = \hbar \omega (n_1 + n_2 + n_3 + 3/2)$.

- The lowest level has $n_1+n_2+n_3=0$ $(n_1=n_2=n_3=0), E=3\hbar\omega/2$ and degeneracy 1.
- The first level has $n_1 + n_2 + n_3 = 1$ ($n_1 = 1$, $n_2 = n_3 = 0$, and cyclic permutations), $E = 5\hbar\omega/2$ and degeneracy 3.
- The second level has $n_1 + n_2 + n_3 = 2$ ($n_1 = 2$, $n_2 = n_3 = 0$ or $n_1 = n_2 = 1$, $n_3 = 0$, and cyclic permutations), $E = 7\hbar\omega/2$ and degeneracy 6.

In general, the *n*-th level is given by all possible combinations of non-negative integers n_1, n_2, n_3 such that $n_1 + n_2 + n_3 = n$. This can be obtained, for example, by fixing $n_3 = n - n_1 - n_2$ and looking for all possible pairs n_1, n_2 such that $n_1 + n_2 = 0, 1, \ldots, n$. One can see that for each value $j = 0, 1, \ldots, n$ of the latter sum, there are j+1 possibilities for n_1, n_2 , and therefore the total degeneracy is given by

$$\sum_{j=0}^{n} (j+1) = \frac{(n+1)(n+2)}{2}.$$

11. This question addresses a simpler special case of the two-particle problem in the lecture notes. For equal masses and in 1D, it is convenient to re-write the Hamiltonian of the system:

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + \frac{1}{2}m\omega^2 \left(\hat{x}_1^2 + \hat{x}_2^2\right)^2 ,$$

in terms of $\hat{X} = (\hat{x}_1 + \hat{x}_2)/2$, $\hat{x} = \hat{x}_2 - \hat{x}_1$, $\hat{P} = \hat{p}_1 + \hat{p}_2$, and $\hat{p} = (\hat{p}_2 - \hat{p}_1)/2$:

$$\hat{H} = \frac{\hat{P}^2}{4m} + \frac{\hat{p}^2}{m} + \frac{1}{2}m\omega^2\hat{x}^2 = -\frac{\hbar^2}{4m}\frac{\partial^2}{\partial_X^2} - \frac{\hbar^2}{m}\frac{\partial^2}{\partial_x^2} + \frac{1}{2}m\omega^2\hat{x}^2.$$

The solution is separable in X and x, and the first term only contributes the energy of the centre of mass (free) motion, which the questions assumes to vanish.

[Notice that the step from $\hat{p}^2 = (\hat{p}_2 - \hat{p}_1)^2/4 = -\hbar^2(\partial_{x_2} - \partial_{x_1})^2/4$ to $-\hbar^2\partial_x^2 = -\hbar^2\partial_{x_2-x_1}^2$ follows from the Jacobian of the change of variables $x_1, x_2 \to x, X$. If this is not clear, it is worth doing the calculation explicitly at least once.]

Finally, we see that the relative motion part of the Hamiltonian is equivalent to a 1D SHO of (reduced) mass $\mu = m/2$ and characteristic frequency $\omega_0 = \sqrt{2} \omega$. The energy levels are $E_n = \hbar \omega \sqrt{2}(n+1/2)$.

12. Recall that position operators commute between themselves, and so do momentum operators. Moreover, position operators commute with momentum operators if they refer to different (independent) degrees of freedom (e.g., different particles a and b). Therefore, trivially, $[\hat{r}, \hat{R}] = [\hat{p}, \hat{P}] = 0$, and:

$$\begin{split} \left[\hat{r}, \hat{p} \right] &= \left[\hat{r}_a - \hat{r}_b, \frac{\hat{p}_a}{m_a} - \frac{\hat{p}_b}{m_b} \right] \frac{m_a m_b}{m_a + m_b} = i\hbar \left(\frac{m_b}{m_a + m_b} + \frac{m_a}{m_a + m_b} \right) = i\hbar \\ \left[\hat{r}, \hat{P} \right] &= \left[\hat{r}_a - \hat{r}_b, \hat{p}_a + \hat{p}_b \right] = i\hbar - i\hbar = 0 \\ \left[\hat{R}, \hat{p} \right] &= \left[m_a \hat{r}_a + m_b \hat{r}_b, \frac{\hat{p}_a}{m_a} - \frac{\hat{p}_b}{m_b} \right] \frac{m_a m_b}{(m_a + m_b)^2} = (i\hbar - i\hbar) \frac{m_a m_b}{(m_a + m_b)^2} = 0 \\ \left[\hat{R}, \hat{P} \right] &= \left[m_a \hat{r}_a + m_b \hat{r}_b, \hat{p}_a + \hat{p}_b \right] \frac{1}{m_a + m_b} = i\hbar \,. \end{split}$$

Therefore \hat{r}, \hat{p} and \hat{R}, \hat{P} are valid position and momentum operators associated with two *independent* degrees of freedom (describing the centre of mass motion and the relative motion).