QM3 workshop 3, Problem 1:
We have:

$$A\,u = \lambda\,u, \quad A\,v = \mu\,v$$

Consider the vector $\phi = B\,u$. Act on it with A:

$$A\,\phi = A\,B\,u = B\,A\,u = \lambda\,B\,u = \lambda\,\phi$$

Above we use $AB = BA$ because the operators commute. We conclude that ϕ is also an eigenvector of A with eigenvalue λ. Since this eigenvalue is not degenerate, there is only one eigenvector with this eigenvalue and that eigenvector is u. Therefore, ϕ must be a multiple of u (i.e. parallel to u).

$$\phi = a\,u, \quad \Rightarrow B\,u = a\,u$$

and we have shown that u is an eigenvector of B. Same for v.

When there is degeneracy, ϕ is still an eigenvector of A with the same eigenvalue $\lambda = \mu$ but we can no longer be certain that ϕ must be parallel to u as it can also have some projection along v.
To find the eigenvectors of B take a linear combination of u, v:

$$|\psi\rangle = \alpha|u\rangle + \beta|v\rangle \tag{1}$$

ψ is an eigenvector of A with eigenvalue λ. We want it to be also an eigenvector of B. Then, we have

$$B\,\psi = b\,\psi$$

So, we get:

$$B\big(\alpha|u\rangle + \beta|v\rangle\big) = b\,\big(\alpha|u\rangle + \beta|v\rangle\big)$$

Multiply with $\langle u|, \langle v|$:

$$\langle u|B|u\rangle\,\alpha + \langle u|B|v\rangle\,\beta = b\,\alpha$$

$$\langle v|B|u\rangle\,\alpha + \langle v|B|v\rangle\,\beta = b\,\beta$$

which is:

$$\begin{bmatrix} B_{uu} & B_{uv} \\ B_{vu} & B_{vv} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = b \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

So, we simply have to find the eigenvalues and eigenvectors of the 2×2 matrix B above.

Problem 2: (a) First we find the expectation value of the one-particle Hamiltonian $h(\boldsymbol{r}_1, \boldsymbol{p}_1)$:

$$\langle\Phi|h|\Phi\rangle = \frac{1}{2}\iint d^3r_1\,d^3r_2 \begin{vmatrix} \psi_1^*(\boldsymbol{r}_1)\,\chi_1^\dagger(1) & \psi_1^*(\boldsymbol{r}_2)\,\chi_1^\dagger(2) \\ \psi_2^*(\boldsymbol{r}_1)\,\chi_2^\dagger(1) & \psi_2^*(\boldsymbol{r}_2)\,\chi_2^\dagger(2) \end{vmatrix} h(\boldsymbol{r}_1, \boldsymbol{p}_1) \begin{vmatrix} \psi_1(\boldsymbol{r}_1)\,\chi_1(1) & \psi_1(\boldsymbol{r}_2)\,\chi_1(2) \\ \psi_2(\boldsymbol{r}_1)\,\chi_2(1) & \psi_2(\boldsymbol{r}_2)\,\chi_2(2) \end{vmatrix}$$

$$= \frac{1}{2}\iint d^3r_1\,d^3r_2 \Big[\psi_1^*(\boldsymbol{r}_1)\chi_1^\dagger(1)\;\psi_2^*(\boldsymbol{r}_2)\chi_2^\dagger(2) \pm \psi_2^*(\boldsymbol{r}_1)\chi_2^\dagger(1)\;\psi_1^*(\boldsymbol{r}_2)\chi_1^\dagger(2)\Big]\times$$

$$h(\boldsymbol{r}_1, \boldsymbol{p}_1)\Big[\psi_1(\boldsymbol{r}_1)\chi_1(1)\;\psi_2(\boldsymbol{r}_2)\chi_2(2) \pm \psi_2(\boldsymbol{r}_1)\chi_2(1)\;\psi_1(\boldsymbol{r}_2)\chi_1(2)\Big] =$$

$$= \int d^3r_1\ \psi_1^*(\boldsymbol{r}_1) h(\boldsymbol{r}_1, \boldsymbol{p}_1) \psi_1(\boldsymbol{r}_1) \underbrace{\int d^3r_2\, |\psi_2(\boldsymbol{r}_2)|^2}_{1}\ \underbrace{\chi_1^\dagger(1)\ \chi_1(1)}_{1}\ \underbrace{\chi_2^\dagger(2)\, \chi_2(2)}_{1}$$

$$- \int d^3r_1\, \psi_1^*(\boldsymbol{r}_1) h(\boldsymbol{r}_1, \boldsymbol{p}_1) \psi_2(\boldsymbol{r}_1) \underbrace{\int d^3r_2\, \psi_2^*(\boldsymbol{r}_2)\, \psi_1(\boldsymbol{r}_2)}_{0}\ \chi_1^\dagger(1)\, \chi_2(1)\ \chi_2^\dagger(2)\, \chi_1(2)$$

$$- \underbrace{\int d^3r_2\, \psi_1^*(\boldsymbol{r}_2)\, \psi_2(\boldsymbol{r}_2)}_{0} \int d^3r_1\, \psi_2^*(\boldsymbol{r}_1) h(\boldsymbol{r}_1, \boldsymbol{p}_1) \psi_1(\boldsymbol{r}_1)\ \chi_1^\dagger(2)\, \chi_2(2)\ \chi_2^\dagger(1)\, \chi_1(1)$$

$$+ \underbrace{\int d^3r_2\ |\psi_1(\boldsymbol{r}_2)|^2}_{1} \int d^3r_1\, \psi_2^*(\boldsymbol{r}_1) h(\boldsymbol{r}_1, \boldsymbol{p}_1) \psi_2(\boldsymbol{r}_1)\ \underbrace{\chi_1^\dagger(2)\ \chi_1(2)}_{1}\ \underbrace{\chi_2^\dagger(1)\, \chi_2(1)}_{1}$$

$$= \frac{1}{2} \sum_{i=1}^{2} \int d^3r_1\, \psi_i^*(\boldsymbol{r}_1) \Big(-\frac{\hbar^2 \nabla_1^2}{2m} + v(\boldsymbol{r}_1) \Big) \psi_i(\boldsymbol{r}_1) = \frac{1}{2} \sum_{i=1}^{2} \int d^3r_1\, \psi_i^*(\boldsymbol{r}_1) \Big(-\frac{\hbar^2 \nabla_1^2}{2m} \Big) \psi_i(\boldsymbol{r}_1) + \frac{1}{2} \int d^3r_1\, \rho(\boldsymbol{r}_1)\, v(\boldsymbol{r}_1)$$

Finally, we realise that $\boldsymbol{r}_1$ is just a dummy variable for integration and we can use $\boldsymbol{r}$. So, we have:

$$\langle \Phi | h | \Phi \rangle = \frac{1}{2} \sum_{i=1}^{2} \int d^3r\, \psi_i^*(\boldsymbol{r}) \Big(-\frac{\hbar^2 \nabla^2}{2m} \Big) \psi_i(\boldsymbol{r}) + \frac{1}{2} \int d^3r\, \rho(\boldsymbol{r})\, v(\boldsymbol{r})$$

Therefore:

$$\langle \Phi | H_0 | \Phi \rangle = 2\, \langle \Phi | h | \Phi \rangle = \sum_{i=1}^{2} \int d^3r\, \psi_i^*(\boldsymbol{r}) \Big(-\frac{\hbar^2 \nabla^2}{2m} \Big) \psi_i(\boldsymbol{r}) + \int d^3r\, \rho(\boldsymbol{r})\, v(\boldsymbol{r})$$

This can also be written:

$$\langle \Phi | H_0 | \Phi \rangle = \sum_{i=1}^{2} \int d^3r\, \psi_i^*(\boldsymbol{r}) \Big(-\frac{\hbar^2 \nabla^2}{2m} + v(\boldsymbol{r}) \Big) \psi_i(\boldsymbol{r}) \tag{2}$$

Problem 3: Localised identical particles can be considered as distinguishable

First we find the square modulus of the two wave functions (probability one particle to be at r and the other at r'):

$$|\Psi_{AB}^{\text{ind}}(r, r')|^2 = \frac{1}{2} \left[\phi_A(r)\, \phi_B(r') \pm \phi_B(r)\, \phi_A(r') \right]^* \left[\phi_A(r)\, \phi_B(r') \pm \phi_B(r)\, \phi_A(r') \right] =$$

$$= \frac{1}{2} \Big[|\phi_A(r)|^2\, |\phi_B(r')|^2 + |\phi_B(r)|^2\, |\phi_A(r')|^2 \pm \underbrace{\phi_A^*(r)\, \phi_B(r)\, \phi_B^*(r')\, \phi_A(r')}_{0} \pm \underbrace{\phi_B^*(r)\, \phi_A(r)\, \phi_A^*(r')\, \phi_B(r')}_{0} \Big]$$

$$|\Psi_{AB}^{\text{ind}}(r, r')|^2 = \frac{1}{2} \Big[|\phi_A(r)|^2\, |\phi_B(r')|^2 + |\phi_B(r)|^2\, |\phi_A(r')|^2 \Big] \tag{3}$$

$$|\Psi_{AB}^{\text{dis}}(r, r')|^2 = |\phi_A(r)|^2\, |\phi_B(r')|^2 \tag{4}$$

The wave functions ϕ_A, ϕ_B are normalised:

$$\int dr\, |\phi_A(r)|^2 = 1, \quad \int dr\, |\phi_B(r)|^2 = 1$$

The two wave functions Ψ_{AB} are then normalised because:

$$\langle\Psi_{AB}^{\rm ind}|\Psi_{AB}^{\rm ind}\rangle = \iint dr dr'\, |\Psi_{AB}^{\rm ind}(r,r')|^2$$

$$= \frac{1}{2}\iint dr dr'\, \left[|\phi_A(r)|^2\, |\phi_B(r')|^2 + |\phi_B(r)|^2\, |\phi_A(r')|^2\right] = 1$$

$$\langle\Psi_{AB}^{\rm dis}|\Psi_{AB}^{\rm dis}\rangle = \iint dr dr'\, |\Psi_{AB}^{\rm dis}(r,r')|^2 = \iint dr dr'\, |\phi_A(r)|^2\, |\phi_B(r')|^2 = 1$$

The expectation values are given by:

$$\langle\Psi_{AB}^{\rm ind}|\hat{O}_1|\Psi_{AB}^{\rm ind}\rangle = \frac{1}{2}\iint dr dr'\ \left[\phi_A(r)\,\phi_B(r') \pm \phi_B(r)\,\phi_A(r')\right]^*\left[O_1(r,p)+O_1(r',p')\right]\left[\phi_A(r)\,\phi_B(r') \pm \phi_B(r)\,\phi_A(r')\right]$$

We can use the result (2) in previous problem: (the same cancellations take place with a symmetric or antisymmetric wf)

$$\langle\Psi_{AB}^{\rm ind}|\hat{O}_1|\Psi_{AB}^{\rm ind}\rangle = \int dr\, \phi_A^*(r)\, O_1(r,p)\phi_A(r) + \int dr\, \phi_B^*(r)\, O_1(r,p)\phi_B(r)$$

We must compare with the result for distinguishable particles. The expectation value is:

$$\langle\Psi_{AB}^{\rm dis}|\hat{O}_1|\Psi_{AB}^{\rm dis}\rangle = \iint dr dr'\, \phi_A^*(r)\,\phi_B^*(r')\left[O_1(r,p) + O_1(r',p')\right]\phi_A(r)\,\phi_B(r')$$

$$= \iint dr dr'\, \phi_A^*(r)\,\phi_B^*(r')\ O_1(r,p)\ \phi_A(r)\,\phi_B(r') + \iint dr dr'\, \phi_A^*(r)\,\phi_B^*(r')\ O_1(r',p')\ \phi_A(r)\,\phi_B(r')$$

$$= \int dr\, \phi_A^*(r)\ O_1(r,p)\ \phi_A(r) + \int dr'\, \phi_B^*(r')\ O_1(r',p')\ \phi_B(r') \quad (5)$$

We conclude that the two expectation values for a general one-body operator $\hat{O}_1$ are the same:

$$\langle\Psi_{AB}^{\rm ind}|\hat{O}_1|\Psi_{AB}^{\rm ind}\rangle = \langle\Psi_{AB}^{\rm dis}|\hat{O}_1|\Psi_{AB}^{\rm dis}\rangle$$

But note that we have not used so far that the particles are localised in different places; we have only used that their wfs are orthogonal. Localisation at different places is much stronger condition!
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What about the expectation value of a two-body operator? (e.g. such as the electron-electron interaction V_{ee}) There is no differential operator in O_2, so we just need the modulus square of the wavefunctions in (3), (4)

$$\begin{aligned}
\langle\Psi_{AB}^{\rm ind}|\hat{O}_2|\Psi_{AB}^{\rm ind}\rangle &= \iint dr dr'\, |\Psi_{AB}^{\rm ind}(r,r')|^2\, O_2(|r-r'|) \\
&= \frac{1}{2}\iint dr dr'\, \left[|\phi_A(r)|^2\, |\phi_B(r')|^2 + |\phi_B(r)|^2\, |\phi_A(r')|^2\right] O_2(|r-r'|) \\
&= \frac{1}{2}\Big[\iint dr dr'\, |\phi_A(r)|^2\, |\phi_B(r')|^2\, O_2(|r-r'|) + \iint dr dr'\, |\phi_B(r)|^2\, |\phi_A(r')|^2\big]\, O_2(|r-r'|)\Big] \\
&= \iint dr dr'\, |\phi_A(r)|^2\, |\phi_B(r')|^2\, O_2(|r-r'|)
\end{aligned}$$

$$\langle \Psi_{AB}^{\text{dis}} | \hat{O}_2 | \Psi_{AB}^{\text{dis}} \rangle \;=\; \iint dr dr' \, |\phi_A(r)|^2 \, |\phi_B(r')|^2 \, O_2(|r - r'|)$$

The expectation values of the two-body operators are the same. Here we had to use the stronger condition that the particles are localised in different places to show it. (When we found the modulus square of the wfs.)

Finally, we find that the expectation values of any one or two-body operator are the same between a wf for distinguishable particles and a wf for indistinguishable particles:

$$\langle \Psi_{AB}^{\text{ind}} | \hat{O}_1 | \Psi_{AB}^{\text{ind}} \rangle = \langle \Psi_{AB}^{\text{dis}} | \hat{O}_1 | \Psi_{AB}^{\text{dis}} \rangle \quad \text{and} \quad \langle \Psi_{AB}^{\text{ind}} | \hat{O}_2 | \Psi_{AB}^{\text{ind}} \rangle = \langle \Psi_{AB}^{\text{dis}} | \hat{O}_2 | \Psi_{AB}^{\text{dis}} \rangle$$

We conclude that although identical particles should strictly be described by wave functions that respect exchange symmetry, nevertheless, when they are localised, the symmetry of the wave function does not make a difference in the expectation values of any (one or two-body) operator and the particles can then be treated as distinguishable.

Problem 4:

(a) We must know the wf on 10 grid point for x times 10 grid point for y times 10 grid points for z, so in total we have a grid with 10^3 grid points and on each grid point we need the numerical value of the wf (a real number). We must store 10^3 real numbers which take 4×10^3 bytes, or 4kB (easy!).

(b) Li atom has 3 electrons, the wf is $\psi(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3)$. We need a much larger grid with

$$\left(10^3\right)^3 = 10^9 \text{ grid points} \Rightarrow \; 10^9 \text{ real numbers} \Rightarrow \; 4 \times 10^9 \text{ bytes}$$

The wf of one state of the Li atom requires 4GB capacity which fits in a DVD.

(c)

An atom with N electrons requires a grid with

$$\left(10^3\right)^N = 10^{3N} \text{ grid points} \Rightarrow \; 10^{3N} \text{ real numbers} \Rightarrow \; 4 \times 10^{3N} \text{ bytes}$$

A DVD can store up to 10^{10} bytes. So, the number of DVDs required for the N-electron atom is: $4 \times 10^{3N-10}$. These weigh $4 \times 10^{3N-10}\text{g} = 4 \times 10^{3N-13}\text{kg}$.

To exceed Earth mass:

$$4 \times 10^{3N-13} > 6 \times 10^{24} \;\Rightarrow\; N > \frac{24+13}{3} \;\Rightarrow N \geq 13 \;\; \text{Al atom}$$

To exceed solar mass:

$$4 \times 10^{3N-13} > 2 \times 10^{30} \;\Rightarrow\; N > \frac{30+13}{3} \;\Rightarrow N \geq 15 \;\; \text{P atom}$$

To exceed Milky Way mass (without dark matter!):

$$4 \times 10^{3N-13} > 5 \times 10^{11} \times 2 \times 10^{30} \;\Rightarrow\; N > \frac{42+13}{3} \;\Rightarrow N \geq 19 \;\; \text{K atom}$$