① We use the expansion

$$|SMs_1s_2\rangle = \sum_{m_1+m_2=M} \underbrace{\langle s_1m_1 s_2m_2|SMs_1s_2\rangle}_{C_{m_1m_2} \text{ - Clebsch-Gordan coeff.}} |s_1m_1\rangle|s_2m_2\rangle$$

$s_1 = 1 \qquad s_2 = \frac{1}{2}$

$$|\tfrac{3}{2}\tfrac{3}{2}1\tfrac{1}{2}\rangle = C_{1\frac{1}{2}} |11\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle$$

$$|\tfrac{3}{2}\tfrac{1}{2}1\tfrac{1}{2}\rangle = C_{1-\frac{1}{2}} |11\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle + C_{0\frac{1}{2}}|10\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle \qquad (*)$$

$$|\tfrac{3}{2}-\tfrac{1}{2}1\tfrac{1}{2}\rangle = C_{0-\frac{1}{2}}|10\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle + C_{-1\frac{1}{2}}|1-1\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle \qquad (**)$$

$$|\tfrac{3}{2}-\tfrac{3}{2}1\tfrac{1}{2}\rangle = C_{-1-\frac{1}{2}}|1-1\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

It is obvious that $C_{1\frac{1}{2}} = 1$ and $C_{-1-\frac{1}{2}} = 1$ (both up to an arbitrary phase factor - subject to convention) due to the normalization condition.

To find other coefficients we can use the ladder operators $S_\pm = S_x \pm iS_y$. Their action on states $|sm\rangle$ is known:

$$S_\pm|sm\rangle = \hbar\sqrt{s(s+1)-m(m\pm1)}\,|s,m\pm1\rangle$$ ← here sm can be SM, s_1m_1, or s_2m_2

Now in our case $S_\pm = S_{1\pm} + S_{2\pm}$

By applying S_+ to the left-hand side of $(*)$ and $S_{1+}+S_{2+}$ to the right-hand side of $(*)$ we get:

$$S_+|\tfrac{3}{2}\tfrac{1}{2}1\tfrac{1}{2}\rangle = (S_{1+}+S_{2+})\left(C_{1-\frac{1}{2}}|11\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle + C_{0\frac{1}{2}}|10\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle\right)$$

$$\sqrt{\tfrac{3}{2}(\tfrac{3}{2}+1)-\tfrac{1}{2}(\tfrac{1}{2}+1)}\,|\tfrac{3}{2}\tfrac{3}{2}1\tfrac{1}{2}\rangle = C_{0\frac{1}{2}}\sqrt{1(1+1)-0}\,|11\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle + C_{1-\frac{1}{2}}\sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1)+\tfrac{1}{2}(-\tfrac{1}{2}+1)}\,\cdot$$
$$\cdot|11\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle$$

$$\sqrt{3} = \sqrt{2}\,C_{0\frac{1}{2}} + C_{1-\frac{1}{2}}$$

We also know that $|C_{0\frac{1}{2}}|^2 + |C_{1-\frac{1}{2}}|^2 = 1$. By solving the system of two algebraic equations we obtain:

$$C_{0\frac{1}{2}} = \sqrt{\frac{2}{3}} \qquad C_{1-\frac{1}{2}} = \sqrt{\frac{1}{3}}$$

The coefficients in equation (**) can be determined in a similar way:

$$S_-\left|\tfrac{3}{2}\,-\tfrac{1}{2}\,1\,\tfrac{1}{2}\right\rangle = (S_{1-} + S_{2-})\left(C_{0-\frac{1}{2}}|1\,0\rangle\left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle + C_{-1\frac{1}{2}}|1\,-1\rangle\left|\tfrac{1}{2}\,\tfrac{1}{2}\right\rangle\right)$$

$$\sqrt{\tfrac{3}{2}\left(\tfrac{3}{2}+1\right)+\tfrac{1}{2}\left(-\tfrac{1}{2}-1\right)}\left|\tfrac{3}{2}\,-\tfrac{3}{2}\,1\,\tfrac{1}{2}\right\rangle = C_{0-\frac{1}{2}}\sqrt{1(1+1)-0}\,|1\,-1\rangle\left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle +$$

$$+\, C_{-1\frac{1}{2}}\sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right)-\tfrac{1}{2}\left(\tfrac{1}{2}-1\right)}\,|1\,-1\rangle\left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle$$

$$\sqrt{3} = \sqrt{2}\,C_{0-\frac{1}{2}} + C_{-1\frac{1}{2}} \qquad |C_{0-\frac{1}{2}}|^2 + |C_{-1\frac{1}{2}}|^2 = 1$$

so $C_{0-\frac{1}{2}} = \sqrt{\frac{2}{3}}$ and $C_{-1\frac{1}{2}} = \sqrt{\frac{1}{3}}$

(2) The Hamiltonian of the system is:

$$H = -\vec{\mu}\cdot\vec{B} = -gBS_y \qquad S_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$H = -\frac{gB\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

The eigenvalues and the corresponding eigenstates of this Hamiltonian are:

$$E_1 = -gB\hbar \qquad E_2 = 0 \qquad E_3 = gB\hbar$$

$$\psi_1 = \begin{pmatrix} -1/2 \\ -i/\sqrt{2} \\ 1/2 \end{pmatrix} \qquad \psi_2 = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{pmatrix} \qquad \psi_3 = \begin{pmatrix} -1/2 \\ i/\sqrt{2} \\ 1/2 \end{pmatrix}$$

The Hamiltonian does not have any time dependence. Therefore we can write the general solution of the time-dependent Schrödinger equation as

$$\psi(t) = C_1\psi_1 e^{-\frac{iE_1t}{\hbar}} + C_2\psi_2 e^{-\frac{iE_2t}{\hbar}} + C_3\psi_3 e^{-\frac{iE_3t}{\hbar}} =$$

$$= C_1\begin{pmatrix} -1/2 \\ -i/\sqrt{2} \\ 1/2 \end{pmatrix} e^{i\omega t} + C_2\begin{pmatrix} 1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{pmatrix} + C_3\begin{pmatrix} -1/2 \\ i/\sqrt{2} \\ 1/2 \end{pmatrix} e^{-i\omega t} \qquad \text{where} \quad \omega \equiv gB$$

From the initial condition we have:

$$\psi(t=0) = \underbrace{\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}}_{\text{state with zero projection on the Z-axis}} = \frac{1}{2}\begin{pmatrix} -C_1 + \sqrt{2}C_2 - C_3 \\ -\sqrt{2}iC_1 + \sqrt{2}iC_3 \\ C_1 + \sqrt{2}C_2 + C_3 \end{pmatrix}$$

Solving for C_i's yields the following

$$C_1 = \frac{i}{\sqrt{2}} \qquad C_2 = 0 \qquad C_3 = -\frac{i}{\sqrt{2}}$$

With that we can write $\psi(t)$ as:

$$\psi(t) = \begin{pmatrix} \frac{1}{\sqrt{2}} \frac{e^{i\omega t} - e^{-i\omega t}}{2i} \\ \frac{e^{i\omega t} + e^{-i\omega t}}{2} \\ -\frac{1}{\sqrt{2}} \frac{e^{i\omega t} - e^{-i\omega t}}{2i} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \sin \omega t \\ \cos \omega t \\ -\frac{1}{\sqrt{2}} \sin \omega t \end{pmatrix}$$

The probability of the particle to remain in state $\psi(0)$ at time t is

$$\underline{P} = |\langle \psi(0) | \psi(t) \rangle|^2 = \left| \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \sin \omega t \\ \cos \omega t \\ -\frac{1}{\sqrt{2}} \sin \omega t \end{pmatrix} \right|^2 = \cos^2 \omega t$$

③ a) $\psi(x_1,x_2) = \phi_n(x_1)\,\phi_e(x_2)$ ← distinguishable particles

$$\langle (x_1-x_2)^2\rangle = \iint (x_1-x_2)^2 |\psi|^2 dx_1 dx_2 = \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1 x_2\rangle$$

$$\langle x_1^2\rangle = \int x_1^2 |\phi_n(x_1)|^2 dx_1 \int |\phi_e(x_2)|^2 dx_2 \equiv \langle x^2\rangle_n$$

$$\langle x_2^2\rangle = \int |\phi_n(x_1)|^2 dx_1 \int x_2^2 |\phi_e(x_2)|^2 dx_2 \equiv \langle x^2\rangle_e$$

$$\langle x_1 x_2\rangle = \int x_1 |\phi_n(x_1)|^2 dx_1 \int x_2 |\phi_e(x_2)|^2 dx_2 \equiv \langle x\rangle_n \langle x\rangle_e$$

Now the value of $\langle x\rangle_n$ can be found in the formula sheet (or can be deduced from the symmetry :-) :

$$\langle x\rangle_n = \frac{a}{2}$$

For $\langle x_n^2\rangle$ we have

$$\langle x^2\rangle_n = \frac{2}{a}\int_0^a x^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a}\left(\frac{a}{n\pi}\right)^3 \int_0^{n\pi} y^2 \sin^2 y\, dy =$$

$$= \frac{2a^2}{(n\pi)^3}\left[\frac{y^3}{6} - \left(\frac{y^2}{4} - \frac{1}{8}\right)\sin 2y - \frac{y\cos 2y}{4}\right]\Bigg|_0^{n\pi} = \frac{2a^2}{(n\pi)^3}\left[\frac{(n\pi)^3}{6} - \frac{n\pi\cos(2n\pi)}{4}\right] =$$

$$= a^2\left[\frac{1}{3} - \frac{1}{2n^2\pi^2}\right]$$

Hence our result for $\langle (x_1-x_2)^2\rangle$ can be written as

$$\langle (x_1-x_2)^2\rangle = \langle x^2\rangle_n + \langle x^2\rangle_e - 2\langle x\rangle_n \langle x_e\rangle = a^2\left[\frac{2}{3} - \frac{1}{2\pi^2}\left(\frac{1}{n^2} + \frac{1}{e^2}\right) - \frac{1}{2}\right] =$$

$$= a^2\left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{n^2} + \frac{1}{e^2}\right)\right]$$

b) and c) Here our wave function should be

$$\psi(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\phi_n(x_1)\phi_e(x_2) \pm \phi_e(x_1)\phi_n(x_2)\right]$$

With such a wave function we get

$$\langle x_1^2\rangle = \frac{1}{2}\iint x_1^2 \left[\phi_n(x_1)\phi_e(x_2) \pm \phi_e(x_1)\phi_n(x_2)\right]^2 dx =$$

$$= \frac{1}{2}\int x_1^2 \phi_n^2(x_1)\,dx_1 \underbrace{\int \phi_e^2(x_2)\,dx_2}_{1} + \frac{1}{2}\int x_1^2 \phi_e^2(x_1)\,dx_1 \underbrace{\int \phi_n^2(x_2)\,dx_2}_{1} \pm$$

$$\pm \frac{1}{2}\int x_1^2 \phi_n(x_1)\phi_e(x_1)\,dx_1 \underbrace{\int \phi_n(x_2)\phi_e(x_2)\,dx_2}_{\delta_{ne}=0 \text{ if } n\neq e} \pm \frac{1}{2}\int x_1^2 \phi_n(x_1)\phi_e(x_1)\,dx_1 \underbrace{\int \phi_n(x_2)\phi_e(x_2)\,dx_2}_{\delta_{ne}=0}$$

$$= \frac{1}{2}\left(\langle x^2\rangle_n + \langle x^2\rangle_e\right)$$

Similarly we get

$$\langle x_2^2\rangle = \frac{1}{2}\left(\langle x^2\rangle_e + \langle x^2\rangle_n\right)$$

Lastly,

$$\langle x_1 x_2\rangle = \frac{1}{2}\int x_1 \phi_n^2(x_1)\,dx_1 \int x_2 \phi_e^2(x_2)\,dx_2 + \frac{1}{2}\int x_1 \phi_e^2(x_1)\,dx_1 \int x_2 \phi_n^2(x_2)\,dx_2$$

$$\pm \frac{1}{2}\int x_1 \phi_n(x_1)\phi_e(x_1)\,dx_1 \int x_2 \phi_e(x_2)\phi_n(x_2)\,dx_2 \pm \frac{1}{2}\int x_1 \phi_e(x_1)\phi_n(x_1)\,dx_1 \int x_2 \phi_n(x_2)\phi_e(x_2)\,dx_2$$

$$= \frac{1}{2}\left(\langle x\rangle_n\langle x\rangle_e + \langle x\rangle_e\langle x\rangle_n \pm \langle x\rangle_{ne}\langle x\rangle_{en} \pm \langle x\rangle_{en}\langle x\rangle_{ne}\right)$$

After we combine everything, we obtain

$$\langle (x_1-x_2)\rangle^2 = \frac{1}{2}\left(\langle x^2\rangle_n + \langle x^2\rangle_e\right) + \frac{1}{2}\left(\langle x^2\rangle_e + \langle x^2\rangle_n\right) - 2\left(\langle x\rangle_n\langle x\rangle_e \pm \langle x\rangle_{ne}^2\right)$$

$\langle x\rangle_{ne}$ can be found in the formula sheet (we assume $n\neq e$)

$$\langle x\rangle_{ne} = \begin{cases} 0 & \text{if } n+e \text{ is even} \\ -\dfrac{8ne}{\pi^2(n^2-e^2)^2}\,a & \text{if } n+e \text{ is odd} \end{cases}$$

With that the final result becomes

$$\langle (x_1-x_2)\rangle^2 = a^2\left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{n^2}+\frac{1}{e^2}\right)\right] \mp \begin{cases} 0, & n+e \text{ is even} \\ \dfrac{128\,n^2e^2a^2}{\pi^4(n^2-e^2)^4}, & n+e \text{ is odd} \end{cases}$$

4 a) Here we have two electrons that move independently in the field of a nucleus with $Z=2$. The electrons are fermions. The grond state of this system is a product of the spatial part that is symmetric with respect to the interchange of particle positions and the spin part that is antisymmetric with respect to the interchange of particle spins:

$$\Psi(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)\,\frac{1}{\sqrt{2}}\left[\left|\tfrac{1}{2}\right\rangle_1\left|-\tfrac{1}{2}\right\rangle_2 - \left|-\tfrac{1}{2}\right\rangle_1\left|\tfrac{1}{2}\right\rangle_2\right]$$

here $\psi_{100}(\vec{r}) = R_{10}(r)\,Y_{00}(\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{3/2} e^{-\frac{2r}{a_0}}$

$$E_{tot} = -\frac{Z^2}{2n^2} - \frac{Z^2}{2n^2} = -\frac{2^2}{2\cdot1^2} - \frac{2^2}{2\cdot1^2} = -4 \text{ hartree} \approx -108.8 \text{ eV}$$

b) The electronic configuration of the boron atom is $1s^2 2s^2 2p$

So we have 5 independent electrons moving in the field of a nucleus with $Z=5$. For two of the electrons $n=1$, for the other three $n=2$.

For a hydrogen-like atom we have (in atomic units)

$$E_n = -\frac{Z^2}{2n^2}$$

So for our system we have

$$E_{total} = -5^2\left(\frac{2}{2\cdot1^2} + \frac{3}{2\cdot2^2}\right) = -25\cdot\left(1+\frac{3}{8}\right) = -\frac{275}{8} \text{ hartree}$$

$$= -34.375 \text{ hartree}$$

$$\approx -935.4 \text{ eV}$$