1. **Magnetic susceptibility** (2 p.)

   Atomic diamagnetic susceptibility can be evaluated as

$$\chi = -\frac{n_{\text{at}}}{6m_e} e^2 \mu_0 \sum_i \langle \psi_i | r^2 | \psi_i \rangle. \tag{1}$$

   We have to evaluate the $\langle r^2 \rangle$ matrix elements. The wave function is defined as

$$\psi(r) = Ne^{-cr}. \tag{2}$$

   Let's normalize them (using the Γ-function identities):

$$1 = \int \psi^* \psi = \int_0^\infty N^2 e^{-2cr} 4\pi r^2 dr = 4\pi N^2 \frac{\Gamma(3)}{(2c)^3} \tag{3}$$

$$N^2 = \frac{c^3}{\pi} \tag{4}$$

   Expectation value of r^2 is then

$$\langle r^2 \rangle = \int_0^\infty r^2 N^2 e^{-2cr} 4\pi r^2 dr = 4\pi N^2 \int_0^\infty r^4 e^{-2cr} dr = 4\pi N^2 \frac{\Gamma(5)}{(2c)^5} = \frac{3}{c^2}$$

   Inserting this into Eq. 1, where the sum over electrons gives just an additional factor of 2 and $n_{\text{at}} = \rho/(4m_u)$, we obtain $\chi^{\text{volume}} = -9.23 \cdot 10^{-10}$ in pretty good agreement with the experiment. Molar diamagnetic susceptibility is obtained by using N_A instead of n_{at} and yields $\chi^{\text{molar}} = -2.0710^{-11}$ m^3/mole.

2. **Dipole-dipole interactions** (1 p.)

The vector potential of magnetic field produced by magnetic moment m is

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi}\frac{\mathbf{m}\times\mathbf{r}}{|\mathbf{r}|^3} = \frac{\mu_0}{4\pi}\frac{\mathbf{m}\times\hat{\mathbf{r}}}{|\mathbf{r}|^2} \tag{5}$$

and magnetic flux density is

$$\mathbf{B}(\mathbf{r}) = \nabla\times\mathbf{A} = \frac{\mu_0}{4\pi}\left(\frac{3\mathbf{r}(\mathbf{m}\cdot\mathbf{r})}{|\mathbf{r}|^5} - \frac{\mathbf{m}}{|\mathbf{r}|^3}\right) = \frac{\mu_0}{4\pi|\mathbf{r}|^3}\left(3\left(\mathbf{m}\cdot\hat{\mathbf{r}}\right)\hat{\mathbf{r}} - \mathbf{m}\right). \tag{6}$$

Thus the magnetic field in the plane perpendicular to the the magnetic moment ($\mathbf{m}\cdot\mathbf{r}$=0) is

$$B = -\mu_0\frac{\mu_B}{4\pi r^3} \tag{7}$$

(or $B = \mu_0 2\mu_B/4\pi r^3$ when $\mathbf{r}$ is parallel to $\mathbf{m}$), where $m = \mu_B$. The interaction energy $E = -\mu_B\cdot\mathbf{B}$ has maximum value $E^{\max} = \mu_B B \approx 2$ μeV, which should be less than $k_B T$ to be significant:

$$T < \mu_B B/k_B \approx 23\,\mathrm{mK}. \tag{8}$$

3. **Heisenberg Hamiltonian**

The electron spins are $S_1 = S_2 = 1/2$. Thus, the total spin is either $S = 0$ or $S = 1$. The spin wave function for the singlet state ($S = 0$) is

$$|\chi_s\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \text{ with } S_z = 0 \tag{9}$$

and for the triplet state ($S = 1$)

$$|\chi_t\rangle = \begin{cases} |\uparrow\uparrow\rangle & \text{with } S_z = +1 \\ \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) & \text{with } S_z = 0 \\ |\downarrow\downarrow\rangle & \text{with } S_z = -1 \end{cases} . \tag{10}$$

Consider $\boldsymbol{S}^2 = (\boldsymbol{S}_1 + \boldsymbol{S}_2)^2 = \boldsymbol{S}_1^2 + \boldsymbol{S}_2^2 + 2\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$. Thus the Hamiltonian can be rewritten

$$\hat{H} = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 \tag{11}$$

$$= \frac{1}{4}(E_S + 3E_T) - \frac{1}{2}(E_S - E_T)(\boldsymbol{S}^2 - \boldsymbol{S}_1^2 - \boldsymbol{S}_2^2). \tag{12}$$

In general, it holds that $\boldsymbol{L}^2 |L\rangle = L(L+1) |L\rangle$. In the present case,

$$\boldsymbol{S}_i^2 |\chi_j\rangle = \frac{1}{2}\left(\frac{1}{2} + 1\right) |\chi_j\rangle = \frac{3}{4} |\chi_j\rangle$$

for $i \in \{1, 2\}$ and $j \in \{s, t\}$. So,

$$(\boldsymbol{S}_1^2 + \boldsymbol{S}_2^2) |\chi_j\rangle = \frac{3}{2} |\chi_j\rangle .$$

For the total spin

$$\boldsymbol{S}^2 |\chi_s\rangle = 0(0+1) |\chi_s\rangle = 0$$

and

$$\boldsymbol{S}^2 |\chi_t\rangle = 1(1+1) |\chi_t\rangle = 2 |\chi_t\rangle .$$

Thus,

$$\hat{H} |\chi_s\rangle = \left[\frac{1}{4}(E_S + 3E_T) - \frac{1}{2}(E_S - E_T)\left(0 - \frac{3}{2}\right)\right] |\chi_s\rangle = E_S |\chi_s\rangle$$

and

$$\hat{H} |\chi_t\rangle = \left[\frac{1}{4}(E_S + 3E_T) - \frac{1}{2}(E_S - E_T)\left(2 - \frac{3}{2}\right)\right] |\chi_t\rangle = E_T |\chi_t\rangle .$$

Consider operator $-J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ (this is the Hamiltonian after neglecting the constant term). $J = E_S - E_T$ corresponds to exchange splitting. Like above, we get

$$\langle\chi_s| - J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |\chi_s\rangle = \langle\chi_s| - J\frac{1}{2}\left(0 - \frac{3}{2}\right) |\chi_s\rangle = \frac{3}{4}J$$

and

$$\langle\chi_t| - J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |\chi_t\rangle = \langle\chi_t| - J\frac{1}{2}\left(2 - \frac{3}{2}\right) |\chi_t\rangle = -\frac{1}{4}J.$$

If $J > 0$, then $\langle\chi_t| - J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |\chi_t\rangle < \langle\chi_s| - J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |\chi_s\rangle$, i.e., triplet state (e.g., $\uparrow\uparrow$, ferromagnet) is ground state.

If $J < 0$, then $\langle\chi_s| - J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |\chi_s\rangle < \langle\chi_t| - J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |\chi_t\rangle$, i.e., singlet state ($\uparrow\downarrow$, antiferromagnet) is ground state.