

Further Quantum Mechanics TT 2014 Problems 3 (TT)

Exchange Symmetry

3.1 Show that when the state of a pair of photons is expanded as

$$|\psi\rangle = \sum_{nn'} b_{nn'} |n\rangle |n'\rangle, \quad (3.1)$$

where $\{|n\rangle\}$ is a complete set of single-photon states, the expansion coefficients satisfy $b_{nn'} = b_{n'n}$.

3.2 Explain the physical content of writing the wavefunction of a pair of electrons in the form

$$\langle \mathbf{x}, \mathbf{x}' | \psi \rangle = \begin{pmatrix} \psi_{++}(\mathbf{x}, \mathbf{x}') \\ \psi_{-+}(\mathbf{x}, \mathbf{x}') \\ \psi_{+-}(\mathbf{x}, \mathbf{x}') \\ \psi_{--}(\mathbf{x}, \mathbf{x}') \end{pmatrix}. \quad (3.2)$$

Which of these functions vanishes when the pair is a spin singlet? What relation holds between the non-zero functions? Suppose $|\psi\rangle$ for a spin singlet can be expanded in terms of products of the single-particle states $|u, \pm\rangle$ and $|v, \pm\rangle$ in which the individual electrons are in the states associated with spatial amplitudes $u(\mathbf{x})$ and $v(\mathbf{x})$ with S_z returning $\pm\frac{1}{2}$. Show that

$$|\psi\rangle = \frac{1}{2}(|u, +\rangle |v, -\rangle - |v, -\rangle |u, +\rangle + |v, +\rangle |u, -\rangle - |u, -\rangle |v, +\rangle)$$

and explain why this expansion is consistent with exchange symmetry.

Given the four single-particle states $|u, \pm\rangle$ and $|v, \pm\rangle$, how many linearly independent entangled states of a pair of particles can be constructed if the particles are not identical? How many linearly independent states are possible if the particles are identical fermions? Why are only four of these states accounted for by the states in the first excited level of helium?

3.3 A state of a composite system can be expanded $|\psi\rangle = \sum_{ij} c_{ij} |A; i\rangle |B; j\rangle$ in terms of products of states $|A; i\rangle$ and $|B; j\rangle$ of the individual systems. What property does the matrix c_{ij} have if the systems are not entangled in the sense that $|\psi\rangle$ can be written as a product $|A\rangle |B\rangle$ of states of each subsystem? Show that this condition is always violated in the case that A and B are both electrons, so any two electrons are always entangled.

Helium

3.4 Show that the exchange integral

$$\int d^3\mathbf{x} d^3\mathbf{x}' \frac{\Psi_1^*(\mathbf{x}) \Psi_2(\mathbf{x}) \Psi_2^*(\mathbf{x}') \Psi_1(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}$$

is real for any single-particle wavefunctions Ψ_1 and Ψ_2 .

3.5 The H^- ion consists of two electrons bound to a proton. Estimate its ground-state energy by adapting the calculation of helium's ground-state energy that uses the variational principle. Show that using single-particle wavefunctions $u(\mathbf{x}) \propto e^{-r/a}$ the expectation of the Hamiltonian is

$$\langle H \rangle_a = \mathcal{R}(2x^2 - \frac{11}{4}x) \quad \text{where} \quad x \equiv \frac{a_0}{a}. \quad (3.3)$$

Hence find that the binding energy of H^- is $\sim 0.945\mathcal{R}$. Will H^- be a stable ion? [A more accurate calculation shows that the binding energy of H^- is $1.056\mathcal{R}$ (C. L. Pekeris, *Phys. Rev.*, **125**, 1470 (1962)).]

3.6* In terms of the position vectors \mathbf{x}_α , \mathbf{x}_1 and \mathbf{x}_2 of the α particle and two electrons, the centre of mass and relative coordinates of a helium atom are

$$\mathbf{X} \equiv \frac{m_\alpha \mathbf{x}_\alpha + m_e (\mathbf{x}_1 + \mathbf{x}_2)}{m_t}, \quad \mathbf{r}_1 \equiv \mathbf{x}_1 - \mathbf{X}, \quad \mathbf{r}_2 \equiv \mathbf{x}_2 - \mathbf{X}, \quad (3.4)$$

where $m_t \equiv m_\alpha + 2m_e$. Write the atom's potential energy operator in terms of the \mathbf{r}_i .

Show that

$$\begin{aligned} \frac{\partial}{\partial \mathbf{X}} &= \frac{\partial}{\partial \mathbf{x}_\alpha} + \frac{\partial}{\partial \mathbf{x}_1} + \frac{\partial}{\partial \mathbf{x}_2} \\ \frac{\partial}{\partial \mathbf{r}_1} &= \frac{\partial}{\partial \mathbf{x}_1} - \frac{m_e}{m_\alpha} \frac{\partial}{\partial \mathbf{x}_\alpha} & \frac{\partial}{\partial \mathbf{r}_2} &= \frac{\partial}{\partial \mathbf{x}_2} - \frac{m_e}{m_\alpha} \frac{\partial}{\partial \mathbf{x}_\alpha} \end{aligned} \quad (3.5)$$

and hence that the kinetic energy operator of the helium atom can be written

$$K = -\frac{\hbar^2}{2m_t} \frac{\partial^2}{\partial \mathbf{X}^2} - \frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial \mathbf{r}_1^2} + \frac{\partial^2}{\partial \mathbf{r}_2^2} \right) - \frac{\hbar^2}{2m_t} \left(\frac{\partial}{\partial \mathbf{x}_1} - \frac{\partial}{\partial \mathbf{x}_2} \right)^2, \quad (3.6)$$

where $\mu \equiv m_e(1 + 2m_e/m_\alpha)$. What is the physical interpretation of the third term on the right? Explain why it is reasonable to neglect this term.

3.7* In this problem we use the variational principle to estimate the energies of the singlet and triplet states $1s2s$ of helium by refining the working of Appendix K.

The idea is to use as the trial wavefunction symmetrised products of the $1s$ and $2s$ hydrogenic wavefunctions (Table 8.1) with the scale length a_Z replaced by a_1 in the $1s$ wavefunction and by a different length a_2 in the $2s$ wavefunction. Explain physically why with this choice of wavefunction we expect $\langle H \rangle$ to be minimised with $a_1 \sim 0.5a_0$ but a_2 distinctly larger.

Using the scaling properties of the expectation values of the kinetic-energy and potential-energy operators, show that

$$\langle H \rangle = \left\{ \frac{a_0^2}{a_1^2} - \frac{4a_0}{a_1} + \frac{a_0^2}{4a_2^2} - \frac{a_0}{a_2} + 2a_0(D(a_1, a_2) \pm E(a_1, a_2)) \right\} \mathcal{R},$$

where D and E are the direct and exchange integrals.

Show that the direct integral can be written

$$D = \frac{2}{a_2} \int_0^\infty dx x^2 e^{-2x} \frac{1}{4y} \{8 - (8 + 6y + 2y^2 + y^3)e^{-y}\},$$

where $x \equiv r_1/a_1$ and $y = r_1/a_2$. Hence show that with $\alpha \equiv 1 + 2a_2/a_1$ we have

$$D = \frac{1}{a_1} \left\{ 1 - \frac{a_2^2}{a_1^2} \left(\frac{4}{\alpha^2} + \frac{6}{\alpha^3} + \frac{6}{\alpha^4} + \frac{12}{\alpha^5} \right) \right\}.$$

Show that with $y = r_1/a_2$ and $\rho = \alpha r_2/2a_2$ the exchange integral is

$$\begin{aligned} E &= \frac{\sqrt{2}}{(a_1 a_2)^{3/2}} \int d^3 \mathbf{x}_1 \Psi_{10}^{0*}(\mathbf{x}_1) \Psi_{20}^0(\mathbf{x}_1) \\ &\times \left\{ \frac{1}{r_1} \left(\frac{2a_2}{\alpha} \right)^3 \int_0^{\alpha y/2} d\rho (\rho^2 - \rho^3/\alpha) e^{-\rho} + \left(\frac{2a_2}{\alpha} \right)^2 \int_{\alpha y/2}^\infty d\rho (\rho - \rho^2/\alpha) e^{-\rho} \right\}. \end{aligned}$$

Using

$$\int_a^b d\rho (\rho^2 - \rho^3/\alpha) e^{-\rho} = -\left[\left\{ \left(1 - \frac{3}{\alpha}\right)(2 + 2\rho + \rho^2) - \frac{1}{\alpha} \rho^3 \right\} e^{-\rho} \right]_a^b$$

and

$$\int_a^b d\rho (\rho - \rho^2/\alpha) e^{-\rho} = -\left[\left\{ \left(1 - \frac{2}{\alpha}\right)(1 + \rho) - \frac{1}{\alpha} \rho^2 \right\} e^{-\rho} \right]_a^b$$

show that

$$\begin{aligned}
 E &= \frac{2}{(a_1 a_2)^3} \int_0^\infty dr_1 r_1^2 \left(1 - \frac{r_1}{2a_2}\right) e^{-\alpha r_1/2a_2} \\
 &\times \left\{ \frac{1}{r_1} \left(\frac{2a_2}{\alpha}\right)^3 \left[2\left(1 - \frac{3}{\alpha}\right) - \left\{ \left(1 - \frac{3}{\alpha}\right)(2 + \alpha y + \frac{1}{4}\alpha^2 y^2) - \frac{1}{8}\alpha^2 y^3 \right\} e^{-\alpha y/2} \right] \right. \\
 &\qquad \qquad \qquad \left. + \left(\frac{2a_2}{\alpha}\right)^2 \left\{ \left(1 - \frac{2}{\alpha}\right)(1 + \frac{1}{2}\alpha y) - \frac{1}{4}\alpha y^2 \right\} e^{-\alpha y/2} \right\} \\
 &= \frac{8a_2^2}{\alpha^5 a_1^3} \left(10 - \frac{50}{\alpha} + \frac{66}{\alpha^2}\right),
 \end{aligned}$$

Using the above results, show numerically that the minimum of $\langle H \rangle$ occurs near $a_1 = 0.5a_0$ and $a_2 = 0.8a_0$ in both the singlet and triplet cases. Show that for the triplet the minimum is -60.11 eV and for the singlet it is -57.0 eV. Compare these results with the experimental values and the values obtained in Appendix K.

Adiabatic Principle

3.8 We have derived approximate expressions for the change in the energies of stationary states when an electric or magnetic field is applied. Discuss whether the derivation of these results implicitly assumed the validity of the adiabatic principle.

3.9 Explain why E/ω is an adiabatic invariant of a simple harmonic oscillator, where ω is the oscillator's angular frequency. Einstein proved this result in classical physics when he was developing the "old quantum theory", which involved quantising adiabatic invariants such as E/ω and angular momentum. Derive the result for a classical oscillator by adapting the derivation of the WKB approximation to the oscillator's equation of motion $\ddot{x} = -\omega^2 x$.

3.10 Suppose the charge carried by a proton gradually decayed from its current value, e , being at a general time fe . Write down an expression for the binding energy of a hydrogen atom in terms of f . As $\alpha \rightarrow 0$ the binding energy vanishes. Explain physically where the energy required to free the electron has come from.

When the spring constant of an oscillator is adiabatically weakened by a factor f^4 , the oscillator's energy reduces by a factor f^2 . Where has the energy gone?

In Problems 3.14 and 3.15 we considered an oscillator in its ground state when the spring constant was suddenly weakened by a factor $f = 1/16$. We found that the energy decreased from $\frac{1}{2}\hbar\omega$ to $0.2656\hbar\omega$ not to $\hbar\omega/512$. Explain physically the difference between the sudden and adiabatic cases.

3.11 Photons are trapped inside a cavity that has perfectly reflecting walls which slowly recede, increasing the cavity's volume \mathcal{V} . Give a physical motivation for the assumption that each photon's frequency $\nu \propto \mathcal{V}^{-1/3}$. Using this assumption, show that the energy density of photons $u \propto \mathcal{V}^{-4/3}$ and hence determine (without quoting results from thermodynamics) the scaling with \mathcal{V} of the pressure exerted by the photons on the container's walls.

Black-body radiation comprises an infinite set of thermally excited harmonic oscillators – each normal mode of a large cavity corresponds to a new oscillator. Initially the cavity is filled with black-body radiation of temperature T_0 . Show that as the cavity expands, the radiation continues to be black-body radiation although its temperature falls as $\mathcal{V}^{-1/3}$.