

QUANTUM MECHANICS – PROBLEMS 4

1. Spin wave functions for a 2-electron system have the form

$$\alpha\alpha, \frac{1}{\sqrt{2}}(\alpha\beta \pm \beta\alpha) \text{ and } \beta\beta,$$

in the usual notation. By application of the operator $\mathbf{S}^2 = (\mathbf{s}_1 + \mathbf{s}_2)^2$, show that three of them form the triplet set with $S = 1$ and the fourth is a singlet function ($S = 0$).

You may use the result

$$2(S_{1x}S_{2x} + S_{1y}S_{2y})(\alpha\beta \pm \beta\alpha) = \pm(\alpha\beta \pm \beta\alpha).$$

2. The two angular momenta \mathbf{j}_1 and \mathbf{j}_2 are coupled together to form a resultant $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2$ which is also an angular momentum. By investigating the commutation relations between its components, show that the difference vector $\mathbf{j}_1 - \mathbf{j}_2$ is **not** an angular momentum.

3. The Hamiltonian for a He-like atom with nuclear charge Z can be written in atomic units as

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}.$$

In the atomic unit (a.u.) system, the quantities m , e and \hbar are all set equal to 1 and length is measured as a multiple of the Bohr radius a_0 . As a result, the Hamiltonian operator and Schrödinger's equation become much simpler. The a.u. of energy, known as the Hartree, is equivalent to $2R_H$.

Assuming the normalized trial wavefunction

$$\Psi(r_1, r_2) = \psi(r_1)\psi(r_2) = \frac{\zeta^3}{\pi} e^{-\zeta(r_1+r_2)},$$

use the variational method to determine the optimum value of ζ for He, Li^+ , and Be^{++} , and hence variational upper bounds on the true ground state energies of these atoms. The basic integrals required are

$$\left\langle \Psi \left| -\frac{1}{2}\nabla_i^2 \right| \Psi \right\rangle = \frac{1}{2}\zeta^2, \quad \left\langle \Psi \left| -\frac{Z}{r_i} \right| \Psi \right\rangle = -Z\zeta \quad \text{and} \quad \left\langle \Psi \left| \frac{1}{r_{12}} \right| \Psi \right\rangle = \frac{5}{8}\zeta,$$

and the experimental ground state energies are -2.85, -7.22 and -13.60 a.u.

4. For two electrons (ignoring spin-orbit coupling) a full wavefunction can be constructed as a product of an orbital function and a spin function

$$\Psi(1,2) = \Psi_{orb}(r_1, r_2) |S, M_s\rangle$$

which is antisymmetric under interchange of electronic coordinates and spin states. Show that

$$\Psi_{\pm}(1,2) = \frac{1}{\sqrt{2}} [1s(r_1)2s(r_2) \pm 1s(r_2)2s(r_1)] \\ \times \frac{1}{\sqrt{2}} (\alpha_1\beta_2 \mp \alpha_2\beta_1)$$

are such functions for the 1s2s configuration of helium. What are the values of S and M_s ? Can this function be an eigenstate of the Hamiltonian for helium? Show that the expectation value of $1/4\pi\epsilon_0 r_{12}$ (the electron repulsion energy) is $J \pm K$ where the upper sign refers to the singlet state and

$$J = \iint dr_1 dr_2 1s(r_1)2s(r_2)(1/4\pi\epsilon_0 r_{12})1s(r_1)2s(r_2) \\ K = \iint dr_1 dr_2 1s(r_1)2s(r_2)(1/4\pi\epsilon_0 r_{12})1s(r_2)2s(r_1).$$

(Note that, since r_{12} does not operate on the spin degrees of freedom, the spin function may be integrated out immediately, i.e. you may ignore the spin part of the wavefunction).

5. The first few S terms of helium lie at the following wavenumbers: $1s^2(^1S)0.0$, $1s2s(^1S)166\,272\text{ cm}^{-1}$, $1s2s(^3S)159\,850\text{ cm}^{-1}$, $1s3s(^1S)184\,859\text{ cm}^{-1}$, $1s3s(^3S)183\,231\text{ cm}^{-1}$. What are the values of K (the exchange integral) in the 1s2s and 1s3s configurations?

Would you expect the values of J and K in Li^+ to be larger or smaller than those in He?

6. Calculate the magnetic field required to produce a splitting of 1 cm^{-1} between adjacent M_J states of an atom in a singlet state. Consider an atom in a ^{2S+1}L term. Calculate the Landé g -factor for the level J which has (i) a maximum value for a given L, S and (ii) a minimum value.

$$(\mu_B = 9.274 \times 10^{-24} \text{ JT}^{-1}).$$