

Ay121 PS6 Solutions

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Based on the solutions from Rachel Theios in 2015.

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1 Electron Correlation Effect

(a) The normalized antisymmetric wavefunction is given by

$$\psi(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) = \frac{1}{\sqrt{2}}[u_a(1)u_b(2) - u_b(1)u_a(2)]. \quad (1)$$

The operator we want to take the expectation value of is

$$R^2 = (\mathbf{r}_1 - \mathbf{r}_2)^2 = r_1^2 - 2\mathbf{r}_1 \cdot \mathbf{r}_2 + r_2^2 \quad (2)$$

So using Dirac notation, we have

$$\langle R^2 \rangle = \int \psi^* R^2 \psi d^3r_1 d^3r_2 = \langle \psi | R^2 | \psi \rangle \quad (3)$$

$$= \langle \psi | r_1^2 | \psi \rangle + \langle \psi | r_2^2 | \psi \rangle - 2 \langle \psi | \mathbf{r}_1 \cdot \mathbf{r}_2 | \psi \rangle \quad (4)$$

Now, multiplying out the first term, and noting that \mathbf{r}_1 only operates on functions of \mathbf{r}_1 , we have

$$\begin{aligned} \langle \psi | r_1^2 | \psi \rangle &= \frac{1}{2} [\langle u_a(1) | r_1^2 | u_a(1) \rangle \langle u_b(2) | u_b(2) \rangle - \langle u_b(2) | u_a(2) \rangle \langle u_a(1) | r_1^2 | u_b(1) \rangle \\ &\quad - \langle u_a(2) | u_b(2) \rangle \langle u_b(1) | r_1^2 | u_a(1) \rangle + \langle u_a(2) | u_a(2) \rangle \langle u_b(1) | r_1^2 | u_b(1) \rangle]. \end{aligned}$$

Noting that $\langle a | a \rangle = 1$ and $\langle a | b \rangle = 0$ due to the orthogonality of states, this simplifies to

$$\langle \psi | r_1^2 | \psi \rangle = \frac{1}{2} [\langle a | r_1^2 | a \rangle + \langle b | r_1^2 | b \rangle] \quad (5)$$

where we've denoted $\langle u_a(1) | r_1^2 | u_a(1) \rangle \equiv \langle a | r_1^2 | a \rangle$. Similarly, we find that

$$\langle \psi | r_2^2 | \psi \rangle = \frac{1}{2} [\langle a | r_2^2 | a \rangle + \langle b | r_2^2 | b \rangle]. \quad (6)$$

Multiplying out the third term in Equation 4 gives

$$\begin{aligned} 2 \langle \psi | \mathbf{r}_1 \cdot \mathbf{r}_2 | \psi \rangle &= - \langle a | \mathbf{r}_1 | a \rangle \langle b | \mathbf{r}_2 | b \rangle + \langle a | \mathbf{r}_1 | b \rangle \langle b | \mathbf{r}_2 | a \rangle \\ &\quad + \langle a | \mathbf{r}_1 | a \rangle \langle a | \mathbf{r}_2 | b \rangle - \langle b | \mathbf{r}_1 | b \rangle \langle a | \mathbf{r}_2 | a \rangle \quad (7) \end{aligned}$$

Note that \mathbf{r}_1 and \mathbf{r}_2 are the same operator acting on different electrons. So $\langle u_a(1)|r_1^2|u_a(1)\rangle = \langle u_a(2)|r_2^2|u_a(2)\rangle \equiv \langle a|r^2|a\rangle$ and so on. Finally, combining Equations 5, 6, and 7, we get

$$\langle R^2 \rangle = \langle a|r^2|a\rangle + \langle b|r^2|b\rangle - 2\langle a|\mathbf{r}|a\rangle \langle b|\mathbf{r}|b\rangle + 2\langle a|\mathbf{r}|b\rangle \langle b|\mathbf{r}|a\rangle. \quad (8)$$

With the given definitions, this becomes

$$\boxed{\langle R^2 \rangle = (\mathbf{r}^2)_a + (\mathbf{r}^2)_b - 2|\mathbf{r}_a||\mathbf{r}_b| + 2|\mathbf{r}_{ab}|^2}. \quad (9)$$

- (b) If we reflect all coordinates, note that $\mathbf{r} \rightarrow -\mathbf{r}$, while $u_a^*u_a$ and $u_b^*u_b$ are unchanged. So

$$\int u_a^* \mathbf{r} u_a d^3r = - \int u_a^* \mathbf{r} u_a d^3r = 0$$

and similarly for u_b . Thus $\mathbf{r}_a = \mathbf{r}_b = 0$, and

$$\boxed{\langle R^2 \rangle = (\mathbf{r}^2)_a + (\mathbf{r}^2)_b + 2|\mathbf{r}_{ab}|^2}.$$

- (c) Separating the space and spin coordinates gives

$$u_a(\mathbf{r}_1, s_1) = u_a(\mathbf{r}_1) |s_1\rangle. \quad (10)$$

Since \mathbf{r}_1 does not operate on $|s\rangle$, this gives

$$\mathbf{r}_{ab} = \int u_a^* \mathbf{r} u_b d^3\mathbf{r} \langle s_a | s_b \rangle. \quad (11)$$

Different spin states are orthogonal, so electrons of different spins have $\langle s_a | s_b \rangle = 0$, and thus $\mathbf{r}_{ab} = 0$.

- (d) From parts (b) and (c), we have

$$\langle R^2 \rangle = \begin{cases} (\mathbf{r}^2)_a + (\mathbf{r}^2)_b + 2|\mathbf{r}_{ab}|^2 & \text{(same spins)} \\ (\mathbf{r}^2)_a + (\mathbf{r}^2)_b & \text{(different spins)} \end{cases}$$

Since $|\mathbf{r}_{ab}|^2$ is positive, this means that $\langle R^2 \rangle$ is larger for same-spin electrons by a factor of 2 $|\mathbf{r}_{ab}|^2$.

2 Saha Equation

- (a) The Saha equation is,

$$\frac{n_e n_{i+1}}{n_i} = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \frac{U_{i+1}}{U_i} \exp\left(-\frac{\chi_i}{kT}\right), \quad (12)$$

where U is the partition function and χ_i is the ionization potential. For hydrogen, this is,

$$\frac{n_e n_{\text{HII}}}{n_{\text{HI}}} = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \frac{U_{\text{HII}}}{U_{\text{HI}}} \exp\left(-\frac{13.6 \text{ eV}}{kT}\right). \quad (13)$$

Since an ionized hydrogen atom is just a proton, $U_{\text{HII}} = 1$. By recalling that $U = \sum_i g_i e^{-E_i/kT}$, and assuming that almost all the neutral hydrogen atoms are in ground state, we get $U_{\text{HI}} \approx g_0 = 2$ (2 spin states of e^-).

The ionizing fraction $y = n_{\text{HII}}/n$, where $n = n_{\text{HII}} + n_{\text{HI}}$ (total number density) and $n_e = n_{\text{HII}}$, so that Saha equation becomes,

$$\frac{ny^2}{1-y} = \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \exp\left(-\frac{13.6 \text{ eV}}{kT} \right). \quad (14)$$

Substituting the mass density $\rho = m_H n$, and plugging in $T = 1.5 \times 10^7 \text{ K}$ and $\rho = 150 \text{ g cm}^{-3}$, we find,

$$\boxed{y = 0.69}. \quad (15)$$

- (b) In reality, the core of the Sun is completely ionized. This is due to the pressure ionization – at such high densities, the separation between atoms is so small that Coulomb repulsion contributes to the electron ionization. Also, our assumption that all neutral atoms are in ground state is valid up to $\approx 10^4 \text{ K}$. It breaks down at high temperature.

3 Spectroscopic Terms

- (a) $2s^2$.

2 electrons with $n = 2$, $l = 0$.

The $2s$ shell is full with 2 electrons. Therefore, they must be in the opposite spin. Thus, $S = 0$, $L = 0$, and $J = L + S = 0$. Parity = $\sum_i l_i = 0 + 0 = \text{even}$. So the only possible term is $\boxed{{}^1S_0}$.

Degeneracies:

- Configuration ($2s^2$): Due to Pauli exclusion principle, there is only one possible state for spin degeneracies, so $N = 1 \times (2 \times l_1 + 1)(2 \times l_2 + 1) = 1$.
- $L-S$: $N = \sum (2 \times L + 1)(2 \times S + 1) = 1$.
- J : $N = \sum (2 \times J + 1) = 1$.

- (b) $2p3s$.

2 electrons with $n_1 = 2$, $n_2 = 3$, and $l_1 = 1$, $l_2 = 0$.

$\vec{L} = \vec{l}_1 + \vec{l}_2$, so $L = 1$. $\vec{S} = \vec{s}_1 + \vec{s}_2$, so $S = 0, 1$. $\vec{J} = \vec{L} + \vec{S}$. Parity = $1 + 0 = \text{odd}$. Therefore, we have the following table,

L	S	J	Term
1	0	1	${}^1P_1^o$
1	1	0,1,2	${}^3P_0^o, {}^3P_1^o, {}^3P_2^o$

Degeneracies:

- Configuration: Both of the electron can have 2 spin degeneracies. Therefore, $N = 2(2 \times 0 + 1) \times 2(2 \times 1 + 1) = 12$.
- $L-S$: $N = \sum (2 \times L + 1)(2 \times S + 1) = (2 \times 1 + 1)(2 \times 0 + 1) + (2 \times 1 + 1)(2 \times 1 + 1) = 12$.

- J : $N = \sum(2 \times J + 1) = (2 \times 1 + 1) + (2 \times 0 + 1) + (2 \times 1 + 1) + (2 \times 2 + 1) = 12$.

(c) $3p4p$. 2 electrons with $n_1 = 3$, $n_2 = 4$, and $l_1 = l_2 = 1$.

Parity = $1 + 1 = \text{even}$.

L	S	J	Term
0	0	0	1S_0
0	1	1	3S_1
1	0	1	1P_1
1	1	0, 1, 2	$^3P_0, ^3P_1, ^3P_2$
2	0	2	1D_2
2	1	1, 2, 3	$^3D_1, ^3D_2, ^3D_3$

Degeneracies:

- Configuration: $N = 2(2 \times 1 + 1) \times 2(2 \times 1 + 1) = 36$.
- $L-S$: $N = (2 \times 0 + 1)(2 \times 0 + 1) + (2 \times 0 + 1)(2 \times 1 + 1) + (2 \times 1 + 1)(2 \times 0 + 1) + (2 \times 1 + 1)(2 \times 1 + 1) + (2 \times 2 + 1)(2 \times 0 + 1) + (2 \times 2 + 1)(2 \times 1 + 1) = 36$.
- J : $N = (2 \times 0 + 1) + (2 \times 1 + 1) + (2 \times 1 + 1) + (2 \times 0 + 1) + (2 \times 1 + 1) + (2 \times 2 + 1) + (2 \times 2 + 1) + (2 \times 1 + 1) + (2 \times 2 + 1) + (2 \times 3 + 1) = 36$.