

Problem Set 8
SOLUTION KEY

P10.3) Is $\psi(1,2) = 1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)$ an eigenfunction of the operator \hat{S}_z ? If so, what is its eigenvalue M_S ?

$$\begin{aligned} \hat{S}_z [1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)] \\ = (\hat{S}_{z1} + \hat{S}_{z2}) [1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)] \\ = \frac{\hbar}{2} [1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)] \\ + \frac{\hbar}{2} [-1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)] \\ = \frac{\hbar}{2} (0) \end{aligned}$$

The function is an eigenfunction of \hat{S}_z with the eigenvalue $M_S = 0$.

P10.6) Write the Slater determinant for the ground-state configuration of Be.

$$\psi_{Be} = \frac{1}{\sqrt{4!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\beta(4) \end{vmatrix}$$

P10.9) In this problem, you will use the variational method to find the optimal $1s$ wave function for the hydrogen atom starting from the trial function $\Phi(r) = e^{-\alpha r}$ with α as the variational parameter. You will minimize

$$E(\alpha) = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}$$

with respect to α .

a) Show that

$$\hat{H}\Phi = -\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Phi(r)}{\partial r} \right) - \frac{e^2}{4\pi\epsilon_0 r} \Phi(r) = \frac{\alpha\hbar^2}{2m_e r^2} (2r - \alpha r^2) e^{-\alpha r} - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r}$$

We start with $\frac{\partial e^{-\alpha r}}{\partial r} = -\alpha e^{-\alpha r}$ and $\frac{\partial (r^2 e^{-\alpha r})}{\partial r} = 2r e^{-\alpha r} - \alpha r^2 e^{-\alpha r}$. Using these results,

$$\hat{H}\Phi = -\frac{\hbar^2}{2m_e r^2} (2r e^{-\alpha r} - \alpha r^2 e^{-\alpha r}) - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r} = \frac{\alpha\hbar^2}{2m_e r^2} (2r - \alpha r^2) e^{-\alpha r} - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r}$$

b) Obtain the result $\int \Phi^* \hat{H} \Phi d\tau = 4\pi \int_0^\infty r^2 \Phi^* \hat{H} \Phi dr = \frac{\pi\hbar^2}{2m_e \alpha} - \frac{e^2}{4\epsilon_0 \alpha^2}$ using the standard integrals in the Math Supplement.

$$\begin{aligned} \int \Phi^* \hat{H} \Phi d\tau &= \frac{\alpha \hbar^2}{2m_e} \left(2 \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r e^{-2\alpha r} dr - \alpha \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 e^{-2\alpha r} dr \right) \\ &\quad - \frac{e^2}{4\pi\epsilon_0} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r e^{-2\alpha r} dr \\ &= \frac{4\pi\alpha\hbar^2}{2m_e} \left(2 \int_0^\infty r e^{-2\alpha r} dr - \alpha \int_0^\infty r^2 e^{-2\alpha r} dr \right) - \frac{e^2}{\epsilon_0} \int_0^\infty r e^{-2\alpha r} dr \\ &= \frac{2\pi\alpha\hbar^2}{m_e} \left(2 \frac{1!}{2^2\alpha^2} - \alpha \frac{2!}{2^3\alpha^3} \right) - \frac{e^2}{\epsilon_0} \frac{1!}{2^2\alpha^2} = \frac{\pi\hbar^2}{2m_e\alpha} - \frac{e^2}{4\epsilon_0\alpha^2} \end{aligned}$$

c) Show that $\int \Phi^* \Phi d\tau = 4\pi \int_0^\infty r^2 \Phi^* \Phi dr = \frac{\pi}{\alpha^3}$ using the standard integrals in the Math

Supplement.

$$\begin{aligned} \int \Phi^* \Phi d\tau &= \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 e^{-2\alpha r} dr \\ &= 4\pi \int_0^\infty r^2 e^{-2\alpha r} dr = 4\pi \frac{2!}{2^3\alpha^3} = \frac{\pi}{\alpha^3} \end{aligned}$$

d) You now have the result $E(\alpha) = \frac{\hbar^2\alpha^2}{2m_e} - \frac{e^2\alpha}{4\pi\epsilon_0}$. Minimize this function with respect to

α and obtain the optimal value of α .

$$\frac{d}{d\alpha} \left(\frac{\hbar^2\alpha^2}{2m_e} - \frac{e^2\alpha}{4\pi\epsilon_0} \right) = -\frac{e^2}{4\pi\epsilon_0} + \frac{\hbar^2\alpha}{m_e} = 0$$

$$\alpha_{\text{optimal}} = \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}$$

e) Is $E(\alpha_{\text{optimal}})$ equal to or greater than the true energy? Why?

$$E(\alpha) = \frac{\hbar^2\alpha^2}{2m_e} - \frac{e^2\alpha}{4\pi\epsilon_0} = \frac{\hbar^2}{2m_e} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right)^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right) = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$$

$E(\alpha_{\text{optimal}})$ is equal to the true energy because our trial wave function has the same form as the true wave function.

P10.11) In this problem you will show that the charge density of the filled $n=2, l=1$ subshell is spherically symmetrical and that therefore $L=0$. The angular distribution of the electron charge is simply the sum of the squares of the magnitude of the angular part of the wave functions for $l=1$ and $m_l = -1, 0, \text{ and } 1$.

a) Given that the angular part of these wave functions is

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$$

$$Y_1^1(\theta, \phi) = \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{i\phi}$$

$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{-i\phi}$$

write an expression for $|Y_1^0(\theta, \phi)|^2 + |Y_1^1(\theta, \phi)|^2 + |Y_1^{-1}(\theta, \phi)|^2$.

$$|Y_l^0(\theta, \phi)|^2 + |Y_l^1(\theta, \phi)|^2 + |Y_l^{-1}(\theta, \phi)|^2 = \frac{3}{4\pi} \cos^2 \theta + \frac{3}{8\pi} \sin^2 \theta + \frac{3}{8\pi} \sin^2 \theta$$

b) Show that $|Y_l^0(\theta, \phi)|^2 + |Y_l^1(\theta, \phi)|^2 + |Y_l^{-1}(\theta, \phi)|^2$ does not depend on θ and ϕ .

$$\frac{3}{4\pi} \cos^2 \theta + \frac{3}{8\pi} \sin^2 \theta + \frac{3}{8\pi} \sin^2 \theta = \frac{3}{4\pi} (\cos^2 \theta + \sin^2 \theta) = \frac{3}{4\pi}. \text{ This is not a function of } \theta \text{ and } \phi.$$

c) Why does this result show that the charge density for the filled $n = 2, l = 1$ subshell is spherically symmetrical?

If a function is independent of θ and ϕ , then it has the same value for all θ and ϕ . This is what we mean by being spherically symmetrical.

P10.14) ~~Problem~~ Two angular momenta with quantum numbers $j_1 = 3/2$ and $j_2 = 5/2$ are added together. What are the possible values of J for the resultant angular momentum states?

$J = |J_1 + J_2|, |J_1 + J_2 - 1|, |J_1 + J_2 - 2|, \dots, |J_1 - J_2|$ giving possible J values of 4, 3, 2, and 1.

P10.18) ~~Problem~~ What atomic terms are possible for the following electron configurations?

Which of the possible terms has the lowest energy?

a) $ns^1 np^1$ b) $ns^1 nd^1$ c) $ns^2 np^1$ d) $ns^1 np^2$

a) $ns^1 np^1$ L can only have the value 1, and S can have the values 0 and 1. The possible terms are 1P and 3P . Hund's Rules predict that the 3P term will have the lower energy.

b) $ns^1 nd^1$ L can only have the value 2, and S can have the values 0 and 1. The possible terms are 1D and 3D . Hund's Rules predict that the 3D term will have the lower energy.

c) $ns^2 np^1$ L can only have the value 1, and S can only have the value 1/2. The only possible term is 2P .

d) $ns^1 np^2$ A table such as the table in the text for the p^2 configuration will have three columns, one for each of the electrons, for M_L and M_S . Each of the fifteen states for the p^2 configuration can be combined with $m_s = \pm \frac{1}{2}$ for the ns electron. This gives a total of 30 states. Working through the table gives $^2D, ^4P, ^2P,$ and 2S terms. Hund's Rules predict that the 4P term will have the lowest energy.

(1)

$$a) \text{ i) } \begin{vmatrix} 1s(1) \alpha(1) & 2s(1) \beta(1) \\ 1s(2) \alpha(2) & 2s(2) \beta(2) \end{vmatrix} = 1s(1) 2s(2) \alpha(1) \beta(2) - 1s(2) 2s(1) \alpha(2) \beta(1)$$

Given

The other 3 (spin) choices are:

$$\text{ii) } \begin{vmatrix} 1s(1) \alpha(1) & 2s(1) \alpha(1) \\ 1s(2) \alpha(2) & 2s(2) \alpha(2) \end{vmatrix} = [1s(1) 2s(2) - 1s(2) 2s(1)] \alpha(1) \alpha(2)$$

$$\text{iii) } \begin{vmatrix} 1s(1) \beta(1) & 2s(1) \alpha(1) \\ 1s(2) \beta(2) & 2s(2) \alpha(2) \end{vmatrix} = 1s(1) 2s(2) \beta(1) \alpha(2) - 1s(2) 2s(1) \beta(2) \alpha(1)$$

$$\text{iv) } \begin{vmatrix} 1s(1) \beta(1) & 2s(1) \beta(1) \\ 1s(2) \beta(2) & 2s(2) \beta(2) \end{vmatrix} = [1s(1) 2s(2) - 1s(2) 2s(1)] \beta(1) \beta(2)$$

b) clearly, $\text{ii} = \text{ii}$; $\text{iv} = \text{iii}$

then consider:

$$\begin{aligned} \text{i} + \text{iii} &= 1s(1) 2s(2) [\alpha(1) \beta(2) + \alpha(2) \beta(1)] - 1s(2) 2s(1) [\beta(1) \alpha(2) + \beta(2) \alpha(1)] \\ &= [1s(1) 2s(2) - 1s(2) 2s(1)] [\alpha(1) \beta(2) + \alpha(2) \beta(1)] = \text{iv} \end{aligned}$$

and, finally:

$$\begin{aligned} \text{i} - \text{iii} &= 1s(1) 2s(2) [\alpha(1) \beta(2) - \alpha(2) \beta(1)] + 1s(2) 2s(1) [-\beta(1) \alpha(2) + \beta(2) \alpha(1)] \\ &= [1s(1) 2s(2) + 1s(2) 2s(1)] [\alpha(1) \beta(2) - \alpha(2) \beta(1)] = \text{i} \end{aligned}$$

(2)

$$(a) \hat{H} = \underbrace{\left[\frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{3e^2}{4\pi\epsilon_0} \frac{1}{r_1} \right]}_{\hat{h}_1(z)} + \underbrace{\left[\frac{-\hbar^2}{2m_e} \nabla_2^2 - \frac{3e^2}{4\pi\epsilon_0} \frac{1}{r_2} \right]}_{\hat{h}_2(z)} + (3-2) \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (*)$$

NB: $3 = Z$

(b) Consider: $\langle \psi_T | \hat{h}_1(z) | \psi_T \rangle = \int d\tau_1 \int d\tau_2 \psi_{1s}(r_1; z) \psi_{1s}(r_2; z) \hat{h}_1(z) \psi_{1s}(r_1; z) \psi_{1s}(r_2; z)$

\nearrow
 Cf. "hint" $E_1(z) \psi_{1s}(r_1; z)$, or $E_1(z) =$ $n=1$ energy level for hydrogenic atom w/ nuclear charge Ze .

$$= -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0}$$

Equivalent contribution fr. $\langle \psi_T | \hat{h}_2(z) | \psi_T \rangle \Rightarrow \langle \psi_T | \hat{h}_1(z) + \hat{h}_2(z) | \psi_T \rangle = \frac{-3e^2}{4\pi\epsilon_0 a_0}$

(c) $\langle \psi_T | \hat{H} | \psi_T \rangle = \frac{-3e^2}{4\pi\epsilon_0 a_0} + (3-2) \frac{e^2}{4\pi\epsilon_0} \left(\frac{3}{a_0} + \frac{3}{a_0} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{5}{8a_0}$

\nearrow
see (*) above

$$= \frac{e^2}{8\pi\epsilon_0 a_0} \left\{ -2 \cdot 3^2 + 4 \cdot 3(3-2) + \frac{5}{4} \cdot 3 \right\} = E(z)$$

(d) $\frac{dE(z)}{dz} = 0$ to minimize $E \Rightarrow z = \frac{27}{16} < 2$

accounts (approximately) for shielding of nucleus by other electrons.] (e)

(f) $E(z) = \frac{-e^2}{4\pi\epsilon_0 a_0} \left(\frac{27}{16} \right)^2 = \boxed{77.46 \text{ eV}}$ \leftarrow about $\frac{1.5}{79} \approx 2\%$ error; but \leftarrow NB: Variational approximation is too high!

on absolute scale, $1.5 \text{ eV} \approx 35 \text{ kcal/mole}$ \leftarrow This is very significant on energy scale of chemical bonding. Hence more accurate variational calculations must be performed. [How?]