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# Advanced Physical Chemistry Problems (II), Hydrogen Atom and Hydrogen Molecular Ion

Carl W. David

*University of Connecticut*, [Carl.David@uconn.edu](mailto:Carl.David@uconn.edu)

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# Problems for the Advanced Physical Chemistry Student

## Part 2, The Hydrogen Atom and the Hydrogen Molecular Ion

C. W. David\*  
*Department of Chemistry*  
*University of Connecticut*  
*Storrs, Connecticut 06269-3060*  
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### I. SYNOPSIS

This is a set of problems that were used near the turn of the century and which will be lost when the web site they were on disappears with my demise. Because these problems are being taken from the web and are being edited, their statements and the hints/answers offered are subject to the typical editorial errors that ensue when such work is undertaken in the vacuum of a non-teaching situation. Therefore, I claim any errors for myself, and hate to note that there most likely is no point in contacting me about them for obvious reasons.

### II. THE H ATOM

- For the H atom's electron (in the infinite nuclear mass approximation), the Schrödinger equation has the form

$$-\frac{\hbar^2}{2m_{electron}}\nabla^2\psi - \frac{Ze^2}{r}\psi = E\psi$$

A possible wave function is

$$xe^{-\alpha r}$$

Obtain a value for  $\alpha$  which makes this true if it can be made to be true.

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Answer and/or Hint

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Defining

$$\psi(x, y, z) = xe^{-\alpha\sqrt{x^2+y^2+z^2}}$$

one forms

$$\left(\frac{\partial\psi}{\partial x}\right)_{y,z} = -x\alpha\frac{x}{r}e^{-\alpha\sqrt{x^2+y^2+z^2}} + e^{-\alpha\sqrt{x^2+y^2+z^2}}$$

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\*Electronic address: Carl.David@uconn.edu

so that

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\frac{\partial\psi}{\partial x}$$

which, mechanically, leads to a large number of terms. Repeating the process two more times, once for  $y$  and once for  $z$ , results in still more terms which, when combined, results in enormous simplification as  $r^2$  terms cancel.

At the end, one obtains an equation involving  $E$ ,  $h$ ,  $\pi$ ,  $m$  (electron mass), and some terms which include 'r'. But this resultant equation can not depend on 'r', so the coefficient of 'r' must be zero! From that observation  $\alpha$  emerges. It turns out that we've been dealing with a  $2p_x$  orbital.

- Obtain the value of the wave function:  $ze^{-r/2}$  at the point  $P(3, 3, -3)$ .

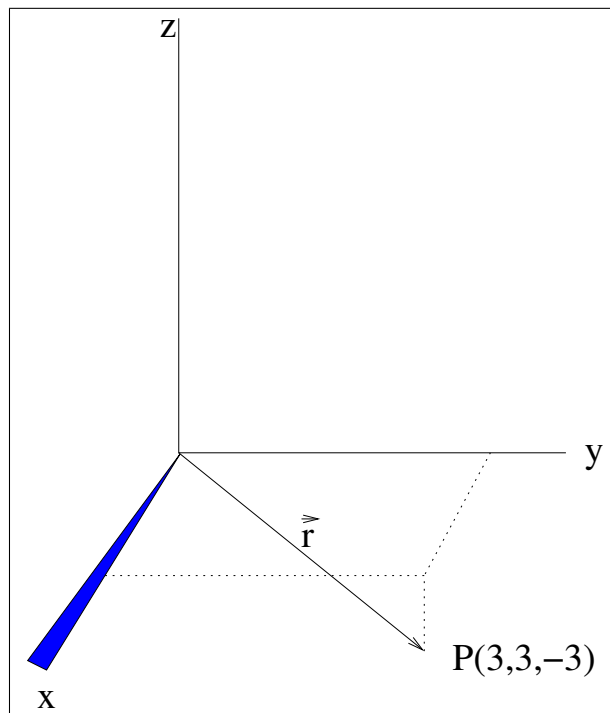


FIG. 1: The Cartesian coordinate frame with a vector of the form  $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$ .

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Answer and/or Hint

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Since  $r = \sqrt{3^2 + 3^2 + (-3)^2}$ , we have

$$\psi(3, 3, -1) = -3e^{-\sqrt{27}/2}$$

3. Two possible wave functions for H,  $\psi_A$  and  $\psi_B$  are

$$\psi_A = (2 - r)e^{-r/2}$$

and

$$\psi_B = (6 - r)e^{-r/3}$$

By explicit integration, demonstrate whether or not these two functions are orthogonal to each other.

---

Answer and/or Hint

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We need to form

$$\int_0^\infty r^2 dr \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi \left( (2 - r)e^{-r/2} \right) \times \left( (6 - r)e^{-r/3} \right)$$

and see what happens. The rest is left to the reader. Note that had we used  $p_x$ , for example, against  $s$ , we would have found orthogonality easily in the angular integrations, but since these are both  $s$  type orbitals, such simplification eludes us.

4. The un-normalized 2s wave function for H is:

$$\psi_{2s} = (2 - r)e^{-r/2}$$

What fraction of the electron is contained in a sphere of radius 0.5?

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Answer and/or Hint

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This is a non-standard but lovely problem which requires us to evaluate the integral

$$\text{numerator} = \int_0^{0.5} r^2 dr \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi \left( (2 - r)e^{-r/2} \right)^2$$

and divide it by the integral

$$\text{denominator} = \int_0^\infty r^2 dr \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi \left( (2 - r)e^{-r/2} \right)^2$$

So, the answer appears to be

$$\frac{\int_0^{0.5} r^2 dr \left( (2 - r)e^{-r/2} \right)^2 \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi}{\int_0^\infty r^2 dr \left( (2 - r)e^{-r/2} \right)^2 \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi}$$

The resultant pair of integrals are elementary.

5. The un-normalized 2s wave function for H is:

$$\psi_{2s} = (2 - r)e^{-r/2}$$

What fraction of the electron is contained in the solid angle which constitutes the first octant?

---

Answer and/or Hint

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Another good one. Here we need to evaluate

$$\text{numerator} = \int_0^\infty r^2 dr \left( (2 - r)e^{-r/2} \right)^2 \int_0^{\pi/2} \sin \vartheta \int_0^{\pi/2} d\vartheta d\varphi$$

and divide it by the integral

$$\text{denominator} = \int_0^\infty r^2 dr \left( (2 - r)e^{-r/2} \right)^2 \int_0^\pi \sin \vartheta \int_0^{2\pi} d\vartheta d\varphi$$

We should get a value of (drum roll please) 1/8.

The important point is the limits of integration!

Notice that the  $r$  integration cancels from numerator and denominator.

6. Obtain a formula for the current equivalent of a single electron traversing a Bohr orbit in the  $n=1$  state.

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Answer and/or Hint

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This constitutes a discussion of magnetic moments, with the answer to the query embedded somewhere in the middle, where it has some use.

For a magnetic field (vector)  $\vec{B}$  acting on an arm of a current loop, a square current loop and a Bohr orbit are similar. The force on each single charge ( $q$ ) travelling in the arm comes from the Lorentz force:

$$\vec{F} = q\vec{v} \times \vec{B}$$

Since  $\vec{v}$  is perpendicular to  $\vec{B}$  (in our case), the cross product simplifies. The current is given by:

$$i = n \frac{\text{charge}}{\text{cm}^3} \times q \frac{\text{stat coul}}{\text{charge}} \times v \frac{\text{cm}}{\text{sec}} \times \sigma \text{ cm}^2 = \frac{\text{stat coul}}{\text{sec}}$$

where  $\sigma$  is the cross sectional area of the wire-loop, and the force on each charge is:

$$q|\vec{v}||\vec{B}| = q \times v \times B \times \sin \frac{\pi}{2} = qvB$$

Since the number of charges is  $n \times a \times \sigma$ , the force on one arm of the loop (of length 'a') is

$$F = (n \times a \times \sigma) \times q \times v \times B = iaB$$

which is reversed on the other (opposite arm) leg of the loop.

The loop is  $a \times b$  in area (and  $2a + 2b$  in circumference), the moment arm about the pivot point is  $\frac{b}{2} \sin \alpha$  if  $\alpha$  is the angle between the loop and the field.

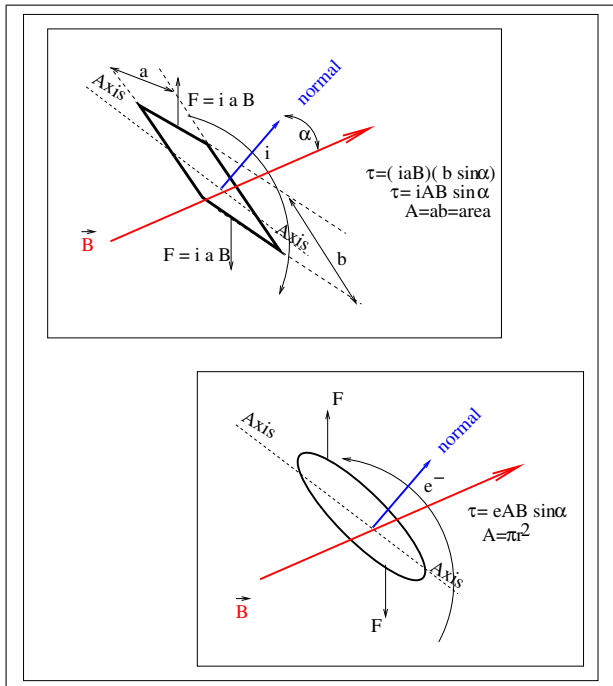


FIG. 2: A current loop in a magnetic field

In Figure 2, the length of the horizontal arms are 'a' while the moment arm's length 'b/2', i.e., from the axis to a horizontal arm is b/2 (cm). The torque ( $\vec{\tau}$ ) is

$$\vec{\tau}(orque) = 2 \left( \frac{b}{2} \sin \alpha \right) iaB$$

but, since  $ab$  is the area ( $A$ ) of the loop, we have

$$\tau = iAB \sin \alpha$$

Commonly, this torque is related to a magnetic moment equivalent, i.e.,

$$\vec{\tau}(orque) = \vec{\mu} \times \vec{B}$$

in analogy with an electric dipole in an electric field. A current loop is equivalent to a magnetic moment, a tiny bar magnet.

We assume that the above would hold for a Bohr orbit.

From Bohr Theory we had (for the radius):

$$r_n = \frac{n^2 \hbar^2}{Z m_e e^2}$$

and the angular momentum is

$$m r^2 \dot{\vartheta} = n \hbar = p_{\vartheta}$$

so, solving for  $\dot{\vartheta}$  we obtain

$$\dot{\vartheta} = \frac{n \hbar}{m r^2}$$

and then the current (= stat-coul/sec) = charge/transit-time, ( $= \frac{e}{\tau}$ ), where (we use  $\tau$  twice here, once for the torque, and once for the period-both usages are common) is the period.

$$\frac{\Delta \vartheta}{\Delta t} = \dot{\vartheta} = \frac{n \hbar}{m r^2} = \frac{2\pi}{\tau}$$

so

$$\frac{charge}{period} = \frac{e}{\tau} = i = -\frac{en\hbar}{2\pi m r^2}$$

but, since the area of the loop is  $\pi r^2$ , we have (THE ANSWER)

$$iA = -\frac{en\hbar}{2\pi m r^2} \pi r^2 = -\frac{en\hbar}{2m}$$

(and some more just to clean up why we're doing this) which defines the Bohr magnetic moment

$$\mu_B = -\frac{e\hbar}{2m}$$

(known as the Bohr magnetron). We then have

$$\tau(orque) = iAB \sin \alpha = -\frac{en\hbar}{2m} B \sin \alpha$$

which is finally

$$\tau(orque) = n\mu_B B \sin \alpha$$

The energy associated with rotating the current loop (Bohr orbit) about the axis perpendicular to the field ( orienting the loop relative to the field) is

$$E = \int_{ref\ pos}^{\alpha, final\ ang\ pos} \tau(\alpha) d\alpha$$

i.e.,

$$E = \int_{90}^{\alpha} \tau(x) dx$$

which gives

$$E = -n\mu_B B \cos \alpha$$

or

$$E = -n\vec{\mu}_B \cdot \vec{B}$$

7. The hybrid orbital:

$$s = P_x + p_y + p_z$$

in polar coordinates, neglecting the radial part, is:

$$1 + \sin \vartheta \cos \varphi + \sin \vartheta \sin \varphi + \cos \varphi$$

Since this orbital is purported to be part of the set, it should point at the corner of a tetrahedron. To see if this is true, take the partial derivative of this function with respect to  $\varphi$ , set this equal to zero, and find out the optimal value of  $\varphi = \varphi_{corner}$ . Next, take the partial derivative with respect to  $\vartheta$  and search for its optimal value. When done, you should have a reasonable result.

Answer and/or Hint

We have

$$f = 1 + \sin \vartheta \cos \varphi + \sin \vartheta \sin \varphi + \cos \vartheta$$

and form

$$\left(\frac{\partial f}{\partial \varphi}\right)_{\vartheta}$$

obtaining

$$f'_{\varphi} = -\sin \vartheta \sin \varphi + \sin \vartheta \cos \varphi \rightarrow 0$$

and

$$f'_{\vartheta} = \cos \vartheta \cos \varphi + \cos \vartheta \sin \varphi - \sin \vartheta \rightarrow 0$$

The solution of these two simultaneous equations yields a value of  $45^\circ$  for  $\varphi_{extremum}$  ( $\varphi_{corner}$ ) and  $54.7^\circ$  for  $\vartheta_{extremum}$ . This latter angle is one-half of the tetrahedral H-C-H angle  $109.471^\circ$  which, by the way, also happens to be  $\cos^{-1}(-\frac{1}{3})!$  Wow!

Why one-half? Where are the other extrema? Is there one above and one below some plane, each at  $54.7^\circ$  so that the interorbital angle is the desired tetrahedral one?

8. Given two hybrid orbitals

$$\psi_1 = \frac{1}{\sqrt{2}}\psi_{2s} + \frac{1}{\sqrt{2}}\psi_{2p_y}$$

and

$$\psi_2 = \frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{3}}\psi_{2p_y}$$

where the contributing atomic orbitals are pre-normalized, calculate the numerical value of the overlap between them.

Answer and/or Hint

We are asked to evaluate the integral

$$\int_0^\infty r^2 dr \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi \left(\frac{1}{\sqrt{2}}\psi_{2s} + \frac{1}{\sqrt{2}}\psi_{2p_y}\right) \times \left(\frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{3}}\psi_{2p_y}\right)$$

but we know that each contributing atomic orbital (AO) is normalized, i.e., the integral of the three domains to the “square” of any one of them is one (1). Further, we know that the AO’s are orthogonal to each other, so the integral of any two different ones over the domain will vanish.

The rest is mechanics. We write

$$\langle 2s || 2p_x \rangle = \int_0^\infty r^2 dr \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi \psi_{2s}^* \psi_{2p_x}$$

as a notational device, so the orthogonality integral becomes

$$\frac{1}{\sqrt{2}} \frac{1}{\sqrt{3}} \langle 2s || 2s \rangle + \frac{1}{\sqrt{2}} \frac{1}{\sqrt{3}} \langle 2s || 2p_x \rangle + \frac{1}{\sqrt{2}} \frac{1}{\sqrt{3}} \langle 2s || 2p_y \rangle + \frac{1}{\sqrt{2}} \frac{1}{\sqrt{3}} \langle 2p_y || 2s \rangle + \frac{1}{\sqrt{2}} \frac{1}{\sqrt{3}} \langle 2p_y || 2p_x \rangle + \frac{1}{\sqrt{2}} \frac{1}{\sqrt{3}} \langle 2p_y || 2p_y \rangle$$

Most of these integrals are zero, since  $s$  is orthogonal to any  $p$ , and each  $p$  is orthogonal to any other  $p$  orbital.

When finished, we end up with a non-zero value, indicating that these orbitals are not orthogonal.

9. For the hybrid orbital

$$\psi_{hybrid} = \frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2p_x} - \frac{1}{\sqrt{6}}\psi_{2p_y}$$

obtain the values of  $\vartheta$  and  $\varphi$  which makes the orbital maximally positive.

Answer and/or Hint

First, notice that the  $2s$  orbital is irrelevant, since its spherically symmetric.

Now, a  $2p_x$  orbital has the form

$$\psi_{2p_x} \sim x e^{-r/2}$$

and

$$\psi_{2p_y} \sim y e^{-r/2}$$

so, converting to spherical polar coordinates, we have

$$\psi_{2p_x} \sim r \sin \vartheta \cos \varphi e^{-r/2}$$

and

$$\psi_{2p_y} \sim r \sin \vartheta \sin \varphi e^{-r/2}$$

which allows us to take the partial derivatives of  $\psi_{hybrid}$  with respect to  $\vartheta$  and  $\varphi$  separately, set them equal to zero, solve the set of equations simultaneously, and achieve the answer desired!

10. To compute the tetrahedral angle in hybridization, assume there exists a cube surrounding the origin [1], with corners (1,1,1), (1,-1,1), (-1,-1,1), and (-1,1,1) above the x-y plane and (1,1,-1), (1,-1,-1), (-1,-1,-1), and (-1,1,-1) below the x-y plane. Choosing the points (1,1,1) and (-1,-1,1), which might be places where H atoms could reside in methane ( $\text{CH}_4$ ), say, form the dot product of the vectors joining the origin to these two points. Thus

$$\vec{r}_1 = \hat{i} + \hat{j} + \hat{k}$$

$$\vec{r}_2 = -\hat{i} - \hat{j} + \hat{k}$$

Then

$$\vec{r}_1 \cdot \vec{r}_2 = |\vec{r}_1| |\vec{r}_2| \cos \vartheta_{tetra}$$

so, obtain an equation for  $\cos \vartheta_{tetra}$ . You will have to figure out the magnitudes of  $\vec{r}_1$  and  $\vec{r}_2$ . Then solve for the  $\cos \vartheta_{tetra}$  and compute  $\vartheta_{tetra}$  via the arccos.

We would have  $\vec{r}_1 \cdot \vec{r}_2 = -1 - 1 + 1 = -1$  and  $|\vec{r}_1| |\vec{r}_2| = \sqrt{3}\sqrt{3}$  which allows us to solve for the angle in question,  $\vartheta_{tetra}$ .

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Answer and/or Hint

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11. Starting with the assumption that

$$\psi_{trial} = (1 + \alpha r)e^{-\beta r}$$

substitute this trial 2s candidate wave function into the Schrödinger Equation for the H-atom's electron and see if a choice of  $\alpha$  and  $\beta$  can be found which makes the candidate wave function a true eigenfunction.

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Answer and/or Hint

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The Schrödinger Equation for the s-states of Hydrogen is

$$-\frac{\hbar^2}{2m_e} \left( \frac{1}{r^2} \frac{\partial r^2 (\frac{\partial \psi_{trial}}{\partial r})}{\partial r} \right) - \frac{Ze^2}{r} \psi_{trial} \stackrel{?}{=} E \psi_{trial}$$

or

$$-\frac{\hbar^2}{2m_e} \left( \frac{1}{r^2} \frac{\partial r^2 (r^2 \frac{\partial (1 + \alpha r)e^{-\beta r}}{\partial r})}{\partial r} \right) - \frac{Ze^2}{r} (1 + \alpha r)e^{-\beta r} \stackrel{?}{=} E(1 + \alpha r)e^{-\beta r}$$

which is

$$-\frac{\hbar^2}{2m_e} \left( \frac{2(\alpha - \beta(1 + \alpha r))}{r} - \beta\alpha - \beta(\alpha - \beta(1 + \alpha r)) \right) e^{-\beta r} - \frac{Ze^2}{r} (1 + \alpha r)e^{-\alpha r} \psi_{trial} \stackrel{?}{=} E(1 + \alpha r)e^{-\alpha r} \psi_{trial}$$

Your job, if you should choose to take it, is to gather then  $\frac{1}{r}$  terms together, force them to zero choosing  $\beta(\alpha)$  and then use the remaining, non  $r$  terms, to ascertain what the correct value of  $\alpha$  must be. Good luck.

12. If one could turn off the electron-electron repulsion in the Helium atom i.e.,

$$\frac{e^2}{r_{12}} \rightarrow 0$$

what would be the energy required to remove both electrons from the neutral Helium atom if it existed in the excited state:  $2s3p_{m_\ell=0}$ ? (The assumption here is that both electrons see the full nuclear charge.)

---

Answer and/or Hint

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Although a silly problem, we obtain

$$-\frac{2^2 Ry}{3^2} - \frac{2^2 Ry}{2^2}$$

if both electrons see the charge  $Z(=2)$ . Actually, one could argue that the outer electron would see a charge of about +1 rather than +2, especially as it gets further and further from the nucleus (and the other remaining electron). Oh well.

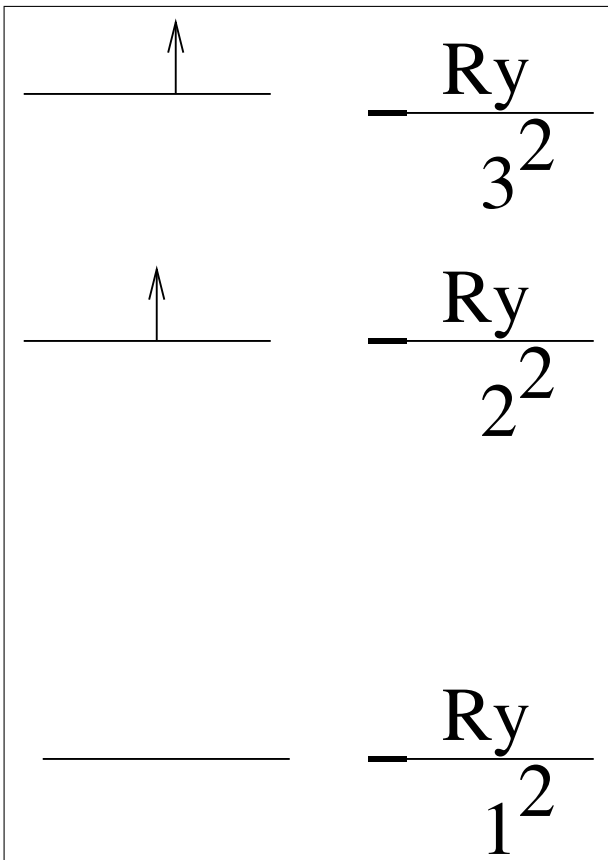


FIG. 3: Two electrons in an “excited” state of He

13. The simplest model of the Sodium atom, has its valence electron in an  $s$  state. The experimental ionization potential of Na is 5.138 eV. What is the value predicted by the simplest Bohr model for Na? Assume that the electron configuration is  $1s^2 2s^2 2p^6 3s$ , and that the inner electrons shield the protons of the nucleus. (Give your answer in e.V.)

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Answer and/or Hint

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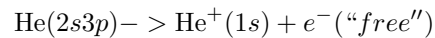
How about  $-\frac{Ry}{3^2}$ ?

14. An autoionizing state of a poly-electron atom (or molecule) is one in which at least two electrons are excited, such that when one electron drops down to a lower state, the other can become ionized. If one could turn off the electron-electron repulsion in the Helium atom i.e.,

$$\frac{e^2}{r_{12}} \rightarrow 0$$

and one created from ground state Helium an autoionizing state  $2s3p$ , what would be the kinetic

energy (positive definite) of the emerging electron? The reaction is:



(The assumption is that both electrons in neutral Helium see the full nuclear charge, i.e., no shielding.)

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Answer and/or Hint

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How about

$$-\frac{2^2 Ry}{3^2} - \frac{2^2 Ry}{2^2} + \frac{2^2 Ry}{1^2}$$

15. For a  $p_x$  orbital of the form

$$\psi_{2p_x} = x e^{-r/2}$$

what is the value of the function at its minimum?

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Answer and/or Hint

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The minimum will occur on the  $-x$  axis, at  $\varphi = 180^\circ$  and  $\vartheta = \pi/2$ . Then we just need to know how far away from the nucleus we need go to find the minimum in the function

$$r e^{-r/2}$$

which means taking its derivative with respect to  $r$

$$\frac{\partial r e^{-r/2}}{\partial r} = \left(1 - \frac{r}{2}\right) e^{-r/2}$$

and setting it equal to zero. Once we’ve found the values of  $\rho$ , call one of them  $\rho^*$ , one needs to back substitute these values into the original wave function to see which is bigger, more negative, or whatever; locating the minimum requires more than just mechanics!

16. For a  $3s$  orbital of the form

$$(6 - 6\rho + \rho^2) e^{-\rho/3}$$

what is its value at its minimum?

---

## Answer and/or Hint

Here, we need only take the derivative of this expression with respect to  $\rho$  and set it equal to zero, solving for the value of  $\rho$  which does the dirty deed.

17. In the accompanying figure, the non-Spin-Orbit coupling Zeeman effect is shown graphically for the Lyman  $\alpha$  line showing why this line is split into a triplet under a magnetic field. How many lines are expected for the  $2p \rightarrow 3d$  transition? The selection rules are  $\Delta m_\ell = \pm 1$  and 0.

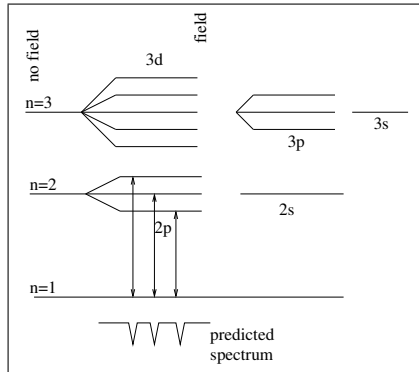


FIG. 4: A simplified explanation for the Zeeman effect in hydrogen.

## Answer and/or Hint

There will be 3 lines for each  $p$ -substate, thereby generating 9 lines.

18. The ground state of Beryllium

$$\left\| \begin{array}{cccc} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\beta(4) \end{array} \right\|$$

$$\left\| \begin{array}{cccc} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\alpha(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\alpha(4) \end{array} \right\|$$

$$\left\| \begin{array}{cccc} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2p(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2p(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2p(3)\alpha(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2p(4)\alpha(4) \end{array} \right\|$$

Which of the above is correct?

## Answer and/or Hint

The second choice has the third and fourth columns identical, which makes the determinant zero which makes the choice invalid.

The third choice uses a  $2p$  orbital, i.e., not a ground state at all.

Hence, the first choice is the right choice.

III.  $H_2^+$ 

The coordinate system used for  $H_2^+$  is shown in Figure 5 for future reference.

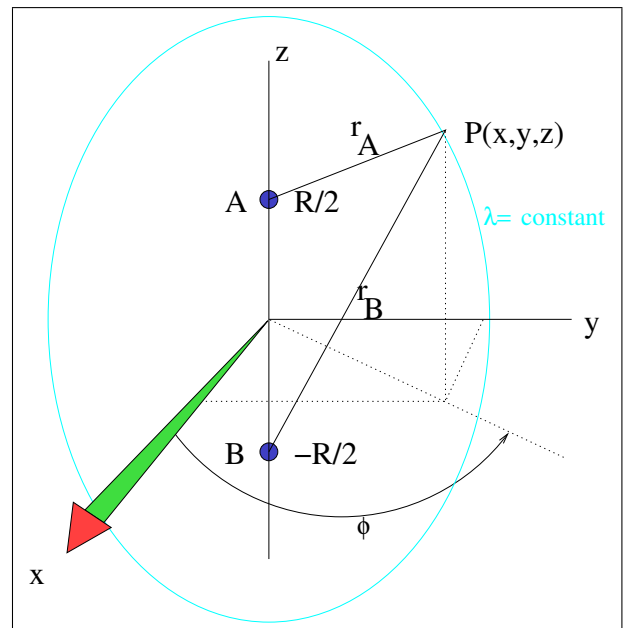


FIG. 5: Standard Coordinate Scheme for  $H_2^+$  Cation

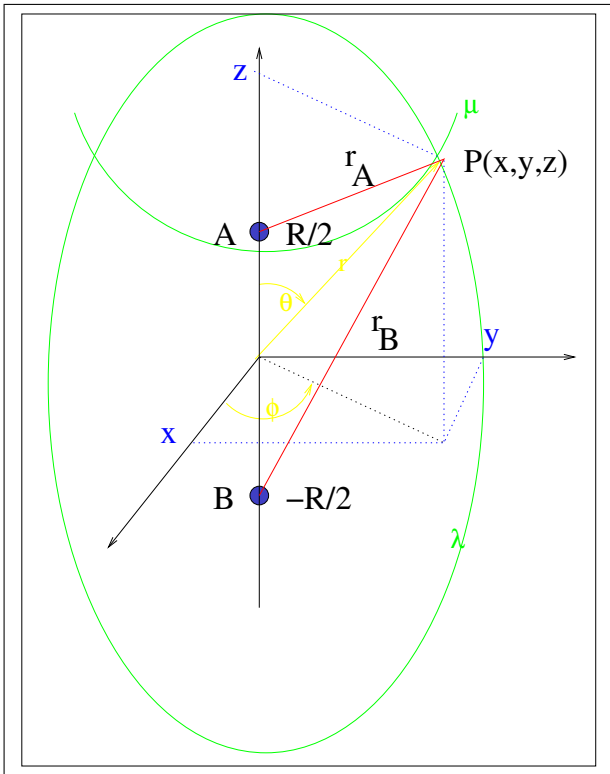
1. The standard coordinate system for diatomic molecules has the two nuclei on the  $z$  axis, one (say A) at  $+R/2$  and the other (say B) at  $-R/2$  (so that the internuclear distance is  $R$ ). Remember that

$$r_A = \sqrt{x^2 + y^2 + \left(z - \frac{R}{2}\right)^2}$$

and

$$r_B = \sqrt{x^2 + y^2 + \left(z + \frac{R}{2}\right)^2}$$



FIG. 6: Standard Coördinate Scheme for  $H_2^+$  Cation

so, for a trial LCAO-MO (an approximate wave function, not an eigenfunction of the system),

$$\psi_{app} = e^{-\alpha r_A} + e^{-\alpha r_B}$$

(which is intentionally left in un-normalized form) what is the value of this wave function at the point  $P(x,y,z) = P(R, -R/2, -R)$ ? Use an  $\alpha$  value of 1.

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Answer and/or Hint

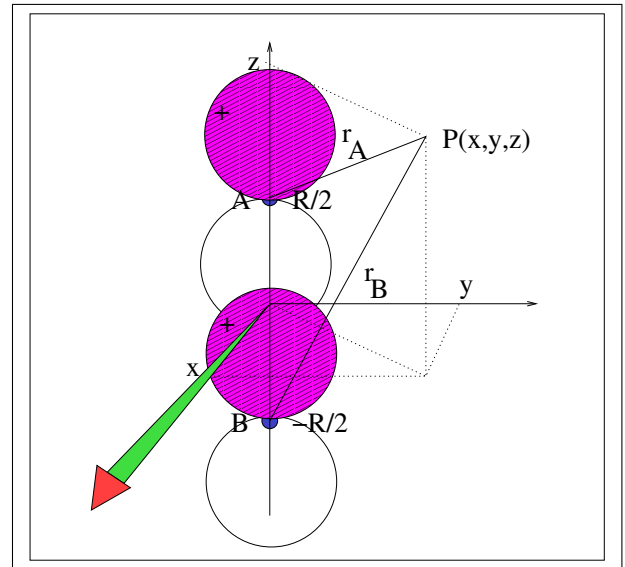
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$$r_A = \sqrt{R^2 + (-R/2)^2 + \left( (-R) - \frac{R}{2} \right)^2}$$

and

$$r_B = \sqrt{R^2 + (-R/2)^2 + \left( (-R) + \frac{R}{2} \right)^2}$$

which can be substituted into the wave function. So,  $r_A = \sqrt{\frac{7R^2}{2}}$ , and  $r_B = \sqrt{\frac{3R^2}{2}}$ . These values are easily back-substituted into  $\psi_{app}$  as requested.

FIG. 7: Standard Coördinate Scheme for  $H_2^+$  Cation

2. The standard coördinate system for diatomic molecules has the two nuclei on the  $z$  axis, one (say A) at  $+R/2$  and the other (say B) at  $-R/2$  (so that the internuclear distance is  $R$ ). Remember that

$$r_A = \sqrt{x^2 + y^2 + \left( z - \frac{R}{2} \right)^2}$$

and

$$r_B = \sqrt{x^2 + y^2 + \left( z + \frac{R}{2} \right)^2}$$

so, for a trial LCAO-MO (an approximate wave function, not an eigenfunction of the system)

$$\psi_{LCAO-p\sigma} = \left( z - \frac{R}{2} \right) e^{-\alpha r_A} - \left( z + \frac{R}{2} \right) e^{-\alpha r_B}$$

(which is intentionally left in un-normalized form) what is the value of the wave function at the point  $P(x,y,z) = P(R, -R/2, -R)$ ? Assume  $\alpha = 1$ .

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Answer and/or Hint

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$$\psi_{LCAO-p\sigma} = \left( -R - \frac{R}{2} \right) e^{-\alpha r_A} - \left( -R + \frac{R}{2} \right) e^{-\alpha r_B}$$

with

$$r_A = \sqrt{R^2 + \left( \frac{-R}{2} \right)^2 + \left( -R - \frac{R}{2} \right)^2}$$

and

$$r_B = \sqrt{R^2 + \left(\frac{-R}{2}\right)^2 + \left(-R + \frac{R}{2}\right)^2}$$

3. For an LCAO-MO

$$\psi_{LCAO-\pi_x^*} \sim xe^{-\alpha r_A} - xe^{-\alpha r_B}$$

(which is intentionally left in un-normalized form) is the function returned after operating on this LCAO-MO with the Hamiltonian:

$$-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Z_A e^2}{r_A} - \frac{Z_B e^2}{r_B}$$

with

$$H_{op}\psi \stackrel{?}{=} E\psi$$

an eigenfunction?

Answer and/or Hint

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NO! This answer is obtained by explicitly carrying out the required differentiation and finding that no factoring allows it to be phrased as the r.h.s. demands, i.e., as a constant times the original wave function (Ansatz).

#### IV. EPILOGUE

After editing this material for weeks, and continuously finding errors, some small, some huge, I have to wrap it up and send this off. If, in the years 2008-2010 or so, you come across an error, and you e-mail me, I will try to have it corrected.

But since this material is written in LaTeX there is some doubt whether or not I'll have access to a Linux machine, and access to the digitalcommons site. You can try; we'll see what happens, if anything. Thanks to all the students over the last 45 years who've taught me Physical Chemistry.

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[1] There are two literature references you might want to look at before doing this problem, C. J. Kawa, J. Chem. Ed., 65, 884 (1988), and G. H. Duffey, J. Chem. Ed., 67,35

(1990).