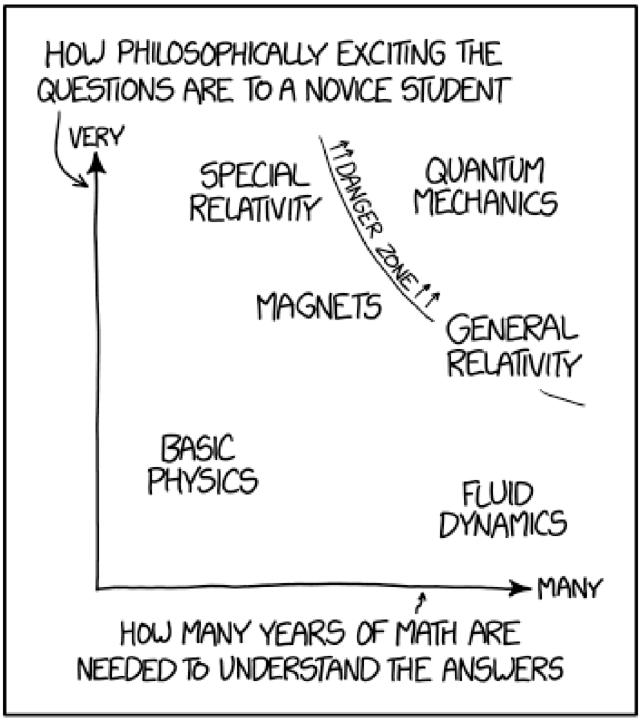
CH2203 Physical Chemistry

Problems



WHY SO MANY PEOPLE HAVE WEIRD IDEAS ABOUT QUANTUM MECHANICS

Problem Sheet 1

1. Outline what is meant by the **Born Interpretation** of the wavefunction.

2. The wavefunction for an electron in a hydrogenic atom has a value of 0.38 at position r_1 and -0.46 at position r_2.

   At which position is the electron most likely to be found?

3. The operators for position, $\hat{p}_x$ and energy, $\hat{H}$ for a particle moving in one dimension along x are given by:

$$\hat{p}_x = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

   The wavefunction for the particle, Ψ, is given by:

$$\Psi = \mathrm{e}^{-ikx}$$

   Where k is a constant and i is defined such that $i^2 = -1$.

   i Derive an expression for the momentum, p_x of the particle.
   ii Derive an expression for the energy, E, of the particle.
   iii Show that the answers to (i) and (ii) are consistent with the classical expression for kinetic energy:

$$E = \frac{p^2}{2m}$$

4. What is meant by the term **normalisation** as applied to wavefunctions? Why is it important that wavefunctions are normalised?

5. The wavefunction for the first energy level of a particle in a 1D box is given by:

$$\Psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$$

   Where L is the length of the box. Demonstrate that this wavefunction is normalised over the length of the box, i.e. that:

$$\int_0^L \Psi(x)^2 \mathrm{d}x = 1$$

   You may find it helpful to use the trigonometric identity below when evaluating the integral:

$$2\sin^2(a) = 1 - \cos(2a)$$

Extended Problems 1

1. The wavefunctions for a particle in a 1D box are given by:

$$\Psi_n(x) = N\sin\left(\frac{n\pi x}{L}\right) \text{ between 0 and L}$$

Where L is the length of the box, N is a normalisation constant, and $n = 1, 2, 3\ldots$.

i Sketch the first three wavefunctions between 0 and L. How does the number of nodes change with n?

ii Annotate on your sketches the places where the chance to find the particle is highest. Is the particle most likely to be found in the middle of the box, or at the edges, in the $n = 1$ state?

iii Classically, if we threw a tennis ball (or any other kind of ball) into a box, we would expect that it would be equally likely to end up in any part of the box.

By considering your answers to (i) and (ii), predict the location where the chance to find the particle is highest as $n \to \infty$. Can you rationalise this with the expected classical result?

iv Show that the value of the normalisation constant, N of the wavefunction is given by:

$$N = \sqrt{\frac{2}{L}}$$

You may find the trigonometric identity given in problem sheet 1, question 5, useful.

v An important property of acceptable wavefunctions is that *wavefunctions of states with different quantum numbers are orthogonal*. Orthogonality means that:

$$\int_0^L \Psi_n\Psi_m \mathrm{d}x = 0 \text{ if } m \text{ and } n \text{ are different}$$

Show that the wavefunctions corresponding to the $n = 1$ and $n = 2$ states of the particle in a box are orthogonal.

You may find it helpful to note that:

$$2\sin(a)\sin(b) = \cos(a + b) + \cos(a - b)$$

2. This question is about nodal planes in p- and d-orbitals.

i Sketch a 2p$_z$ orbital and a 3d$_{z^2}$ orbital on separate graphs, identifying the nodal planes in each case.

ii The mathematical form of the angular parts of these orbitals is given by:

$$Y_{2p_z}(\theta) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$

$$Y_{3d_{z^2}}(\theta) = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$

Calculate the angles θ of the nodal planes in the 2p$_z$ and 3d$_{z^2}$ orbital (hint: there are three nodal planes in total).

Problem Sheet 2

1. The Hamiltonian for the hydrogen atom, in atomic units, is:

$$\hat{H} = -\frac{1}{2m}\nabla_n^2 - \frac{1}{2}\nabla_e^2 - \frac{1}{r}$$

   - i State the physical meaning of each term in the above Hamiltonian.
   - ii What additional terms would need to be included in the Hamiltonian for the helium ion, He^+?
   - iii What additional terms would need to be included in the Hamiltonian for the helium *neutral*, He?

2. Outline why it is impossible to solve the SE for the neutral helium atom, including a description of what is meant by *electron correlation*.

3. Outline what is meant by the **orbital approximation**.

   How can wavefunctions derived under the orbital approximation be made as 'exact' as possible?

4. The radial wavefunction, $R(r)$, for an electron in a 2s orbital on a hydrogen atom in atomic units is given by:

$$R(r) = \frac{1}{2\sqrt{2}}(2 - r)\mathrm{e}^{-\frac{r}{2}}$$

   Determine the positions of any radial nodes in this wavefunction.

5. The radial distribution function, $F(r)$, for an electron in an s-orbital is given by:

$$F(r) = 4\pi r^2 R(r)^2$$

   The radial wavefunction for an electron in a 1s orbital on a hydrogen atom in atomic units is given by:

$$R(r) = 2\mathrm{e}^{-r}$$

   - i Write down the radial distribution function for a 1s electron in a hydrogen atom.
   - ii Explain the meaning of the radial distribution function. What does a radial distribution function tell you?
   - iii Show that the electron is most likely to be found at a position where $r = 1$.

Problem Sheet 3

1. The Hamiltonian for the H_2^+ molecular ion is given by:

$$\hat{H} = -\frac{1}{2m}\nabla^2_{n1} - \frac{1}{2m}\nabla^2_{n2} - \frac{1}{2}\nabla^2_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R_{12}}$$

   i Explain the origin of each term in this Hamiltonian. Why is every term negative except for the term involving R_{12}?

   ii The Born-Oppenheimer Approximation states that nuclear and electronic motion are separable, and that nuclei are essentially stationary on the timescale of electron motion.

   Apply the Born-Oppenheimer Approximation to the Hamiltonian above, and obtain the electronic Hamiltonian, $\hat{H}_{elec}$.

   iii How does the Born-Oppenheimer Approximation help us in our quest to understand molecular structure at a quantum mechanical level?

2. Outline situations in which the Born-Oppenheimer Approximation breaks down.

3. LCAO theory can be used to explain the bonding in simple diatomics such as H_2. Starting with atomic orbitals on each hydrogen atom, ϕ_1 and ϕ_2, we can define the overall molecular orbital Ψ as:

$$\Psi = c_1\phi_1 + c_2\phi_2$$

   i Identify the meaning of the coefficients c in the above equation.

   ii Using a symmetry argument, show that for a homonuclear diatomic like H_2, this equation produces two MOs from our two AOs, which are given by:

$$\Psi^+ = c(\phi_1 + \phi_2)$$
$$\Psi^- = c(\phi_1 - \phi_2)$$

   iii Which of these MOs corresponds to the bonding and anti-bonding molecular orbital?

4. In deriving approximate solutions to the SE, what are the advantages and disadvantages of using a large basis set of orbitals in your calculations?

5. Draw an MO diagram for H_2, simply based on overlap of 1s atomic orbitals. Use this diagram to explain the following observations:

   i Both the H_2^{2-} and H_2^{2+} molecular ions are unbound and never observed under normal conditions.

   ii The vibrational frequency of H_2 is around 4400 cm^{-1}, whereas the vibrational frequency of the He_2^+ cation much lower, at around 1628 cm^{-1}.

   iii The helium hydride cation (HeH^+) has a similar bond length and strength to H_2.

Problem Sheet 4

1. Sketch the following pairs of molecular orbitals, explaining the how the symmetry of each orbital in the pair differs:
   - i A σ_g and σ_u orbital.
   - ii A π_g and a σ_g orbital.
2. Describe three key rules that dictate how atomic orbitals overlap to form molecular orbitals.

   Based on these rules, predict whether or not you would expect significant orbital overlap between the following pairs of orbitals:
   - i A 2s orbital and a side-on 2p_x orbital on adjacent atoms in an alkane.
   - ii A 1s orbital on the sulphur and a 1s orbital on a terminal hydrogen in $H_2SO_4{}^{2-}$.
   - iii The 3d orbital on Ni with orbitals of π symmetry on a CO ligand attached to the nickel.
   - iv The two 4d orbitals on each iodine in I_2.
   - v The 1s orbital on H with the 2s orbital on F in hydrofluoric acid.
3. Draw an MO diagram for molecular oxygen (O_2), labelling the orbitals with their symmetry labels, and populating the orbitals with electrons. Use this diagram to explain the following observations:
   - i The $O_2{}^+$ molecular cation has a shorter bond length than neutral O_2.
   - ii Liquid molecular oxygen is attracted to a magnetic field (i.e. is paramagnetic).
   - iii The $O_2{}^-$ molecular anion has a lower vibrational wavenumber than neutral O_2 (1556 cm^{-1} for the neutral and 1074 cm^{-1} for the anion).
4. Draw an MO diagram for diatomic carbon (C_2). Outline how, and why, this diagram is different to the diagram for O_2 from question 2.
5. Use your MO diagram for C_2 to answer the following questions:
   - i Rank the species C_2, $C_2{}^+$, and $C_2{}^{2+}$ in order of inceasing bond length.
   - ii Explain why $C_2{}^-$ has a slightly higher C-C vibrational wavenumber than C_2.
   - iii Predict what would happen to the bond length of C_2 if an electron was excited via electric discharge from the HOMO ($1\pi_u$) to the $3\sigma_u$ state.

Extended Problems 2

1. LCAO theory can also be applied to understand the structure and bonding in heteronuclear diatomics. In this case, the wavefunction for the molecular orbitals is given by:

   $$\Psi^{\pm} = c_1\phi_1 \pm c_2\phi_2$$

   However, in this case, $c_1 \neq c_2$. Furthermore, we can make a series of approximations and find that if $\alpha_2 - \alpha_1 = 2\beta$ the energy of each MO is given by:

   $$E^{\pm} = \frac{\alpha_1 + \alpha_2}{2} \pm \sqrt{2}\beta$$

   i If $c_1 > c_2 > 0$ on which atom (1 or 2) are the electrons most likely to be found? Why?

   ii Define the meaning of the terms α and β in the expression for the energy.

   iii Using the expression for the energy, sketch an idealised MO diagram for a heteronuclear diatomic. Take the AO energies as α_1 and α_2, where $\alpha_2 > \alpha_1$, and assume that β is a negative number.

   You do not need to populate the diagram with electrons.

   iv What happens to your diagram in the case that $\alpha_1 = \alpha_2$?

2. HF is a simple heteronuclear diatomic molecule. The wavefunction for the bonding σ MO in HF formed between the H 1s orbital and the F 2p orbital is given by:

   $$\Psi = 0.94\text{F} + 0.34\text{H}$$

   i Calculate the probability of finding the electrons on the fluorine.

   ii Calculate the probability of finding the electrons on the hydrogen.

   iii Does this result make sense based on what you know about electronegativity?

Exam Style Problems

These questions are the sorts of questions I will set in the exam. Each question would be worth roughly 25 marks (±5 marks). In the exam the questions will be slightly more guided than these are.

1. The Hamiltonian for the H_2 molecule is given by:

$$\hat{H} = -\frac{1}{2m}\nabla^2_{n1} - \frac{1}{2m}\nabla^2_{n2} - \frac{1}{2}\nabla^2_{e1} - \frac{1}{2}\nabla^2_{e2} - \frac{1}{r_{n1e1}} - \frac{1}{r_{n1e2}} - \frac{1}{r_{n2e1}} - \frac{1}{r_{n2e2}} + \frac{1}{r_{n1n2}} + \frac{1}{r_{e1e2}}$$

   a) Outline the physical meaning of each term in the Hamiltonian, with reference to an appropriate sketch.

   b) Outline what is meant by the *Born-Oppenheimer Approximation* (BOA).

   Show that applying the BOA to the Hamiltonian above leads to the following expression for the electronic Hamiltonian for H_2:

$$\hat{H}_{elec} = -\frac{1}{2}\nabla^2_{e1} - \frac{1}{2}\nabla^2_{e2} - \frac{1}{r_{n1e1}} - \frac{1}{r_{n1e2}} - \frac{1}{r_{n2e1}} - \frac{1}{r_{n2e2}} + \frac{1}{R_{n1n2}} + \frac{1}{r_{e1e2}}$$

   When does the BOA break down?

   c) The electronic Schrödinger equation is given by:

$$\hat{H}_{elec}\Psi_{elec}(R) = E_{elec}(R)\Psi_{elec}(R)$$

   Explain why, even after invoking the BOA, it is not possible to solve this equation for H_2 analytically.

   d) Outline why the electronic energy $E_{elec}(R)$ is a function of the bond length, R. Sketch potential energy curves for a bound and unbound electronic state, indicating on your sketch the equilibrium bond length R_0.

   e) A more mathematical statement of the BOA essentially boils down to the statement that:

$$\frac{\mathrm{d}^2\Psi_{elec}(R)}{\mathrm{d}R^2} \approx 0$$

   Whereas the statement of the BOA, in words, is:

   > *Electrons move much faster than nuclei for the same force, so their motions are separable.*

   Explain why these two statements are equivalent.

2. The radial wavefunction for a 1s electron in an atom with a nuclear charge of Z is:

$$\phi_{1s}(r) = 2Z^{\frac{3}{2}}\mathrm{e}^{-2Zr}$$

Within the orbital approximation, the radial wavefunction of the electrons in a helium atom is given by:

$$\Psi_{He}(r_1, r_2) = \phi_{1s}(r_1)\phi_{1s}(r_2)$$

a) Outline what is meant by *The Orbital Approximation*. Why is it an approximation?

b) Under what conditions does the orbital approximation become exact?

c) Write down the radial wavefunction $\Psi_{He}(r_1, r_2)$ for the electrons in a helium atom.

d) Calculate the value of this wavefunction in the following situations:

   - When $r_1 + r_2 = 0$
   - When $r_1 + r_2 = 0.5$
   - When $r_1 + r_2 = 1$
   - When $r_1 + r_2 \to \infty$

e) Hence sketch the graph of Ψ_{He} against $r_1 + r_2$. Explain the shape of this graph.

f) Explain what is meant by a *node* in a wavefunction. Does the wavefunction Ψ_{He} contain any nodes?

g) Outline why it is necessary to use iterative methods such *Self-Consistent Field* (SCF) approaches to solving the Schrödinger Equation, and briefly explain how such methods work. Include in your answer an example of a common SCF method.