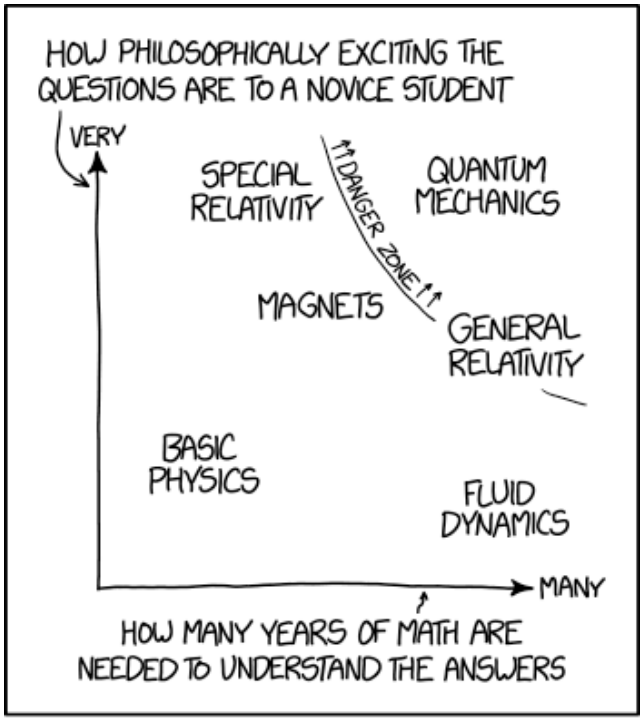
CH2203 Physical Chemistry

Problems: Solutions and Hints



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. Key point is that the square of the wavefunction is a probability distribution. Such that $P(x) \propto |\Psi(x)|^2$.

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? Wavefunction squared is the important thing, so 0.144 at r_1 and 0.212 at r_2. Hence, answer is r_2.

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 $i^2 = -1$.

   Remember here that for any operator $\hat{O}$ that we will encounter, the corresponding observable o is given by $\hat{O}\Psi = o\Psi$ where Ψ is the wavefunction.

   i Derive an expression for the momentum, p_x of the particle.
   $-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}(\mathrm{e}^{-ikx}) = (-i\hbar)(-ik)\mathrm{e}^{-ikx} = -\hbar k\Psi$. Momentum is therefore $-\hbar k$.

   ii Derive an expression for the energy, E, of the particle.
   $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}(\mathrm{e}^{-ikx}) = \frac{k^2\hbar^2}{2m}(\mathrm{e}^{-ikx}) = \frac{k^2\hbar^2}{2m}\Psi$. Energy is therefore $\frac{k^2\hbar^2}{2m}$.

   iii Show that the answers to (i) and (ii) are consistent with the classical expression for kinetic energy:

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

   From (i) $p = -\hbar k$ then clearly by the classical expression $\frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$, which is the expression derived in (ii).

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

   Normalisation of a wavefunction is done to ensure that the chance of finding the particle the wavefunction describes is one when we look over all space ('particle has to be somewhere'). Mathematically, it amounts to choosing a constant N such that:

$$N^2\int_{\infty}\Psi^2(x)\mathrm{d}x = 1$$

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:

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

Set up problem and use identity to get:

$$\int_0^L \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)\mathrm{d}x = \frac{1}{L}\int_0^L 1 - \cos\left(\frac{2\pi x}{L}\right)\mathrm{d}x$$

Evaluate the integral on the RHS term by term:

$$\frac{1}{L}\left[(L-0) - (\sin(2\pi) - \sin(0))\right] = \frac{1}{L}(L) = 1$$

Therefore, integral is normalised.

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. From L to R: the kinetic energy of the nucleus, kinetic energy of the electron, and Coulomb attraction between the electron and nucleus.

   ii What additional terms would need to be included in the Hamiltonian for the helium ion, He^+? No additional terms, but need to modify the mass of the nucleus in the first term.

   iii What additional terms would need to be included in the Hamiltonian for the helium *neutral*, He? Extra electron now, so need an extra electron KE, an extra Coulomb attraction between the new electron and the nucleus, and an extra Coulomb *repulsion* between the two electrons.

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*. The electron-electron repulsion is the source of all our woes. The problem is that the electron positions are correlated, which means that the position of electron affects all the others. The problem with this for us is that:

   - You need to know the Coulomb repulsion to write down the Hamiltonian for this system.
   - To work out the Coulomb repulsion you need the distance between the electrons.
   - You need to know the positions of both electrons to know the distance between them.
   - You can't know these without having solved the SE already.
   - So the SE depends on its own solutions, and our problem isn't analytically solvable.

3. Outline what is meant by the **orbital approximation**.
   The issue outlined above is essentially that the total wavefunction Ψ is a function of many electron coordinates, $\Psi(r_1, r_2, ...)$. All these coordinates are correlated and thus depend on each other. The **orbital approximation** assumes that the total wavefunction can be written as a **product of one-electron wavefunctions**:

$$\Psi_{total}(r_1, r_2, ...r_n) = \prod_i^n \phi_i(r_i)$$

   where $\phi_i(r_i)$ are one electron wavefunctions. This is an approximation because we are assuming that the correlated electron coordinates are not really correlated and can be separated out and treated independently - which is fine, provided that we ignore the electron-electron repulsion! (or at least find a way to treat it implicitly..).

   How can wavefunctions derived under the orbital approximation be made as 'exact' as possible? Iterative methods can be used to refine the approximate wavefunctions so that they become closer and closer to the exact wavefunctions. Self-consistent field theory was met in the lectures - examples of this kind of approach are Hartree-Fock Theory and Density Functional Theory (DFT). These methods are the bedrock of modern computational chemistry. We wouldn't know any chemistry today without them.

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. Radial nodes are when $R(r) = 0$. Solving this equation leads to two solutions, $r = \infty$ (boring af, not a node because the wavefunction just goes *to* zero, it doesn't change sign), or $(2-r) = 0 \rightarrow r = 2$, where the wavefunction does change sign. So the radial node is at $r = 2$ in atomic units (in Bohr radii).

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. Plug in the wavefunction given to the formula for the RDF to find:

$$F(r) = 16\pi r^2 e^{-2r}$$

ii Explain the meaning of the radial distribution function. What does a radial distribution function tell you? **Not in the lecture notes explicitly, so you'll need to read widely!** The RDF $F(r)$ tells you the probability of finding an electron at a radius r away from the nucleus in an atom. It is better at this than just the wavefunction squared, because even though the wavefunction maybe non-zero at the nucleus, the electron can't actually be found *at* the nucleus - the RDF accounts for this through the factor of $4\pi r^2$ (for an s-orbital).

iii Show that the electron is most likely to be found at a position where $r = 1$. To find the place where the chance of finding an electron is at a *maximum*, we need to find the maximum in the RDF. Thus via the product rule:

$$\frac{\mathrm{d}F(r)}{\mathrm{d}r} = 16\pi\left[-2r^2\mathrm{e}^{-2r} + 2r\mathrm{e}^{-2r}\right] = 0$$

Dividing through by constants and the exponential term gives:

$$r - r^2 = r(1-r) = 0$$

Which has two solutions, either $r = 0$ or $r = 1$. You can either check the second derivative to work out that $r = 1$ is the maximum (and thus most likely position), or use *chemical intuition* :).

Problem Sheet 3

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

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

   i Explain the origin of each term in this Hamiltonian. Why is every term negative except for the term involving R_{12}? From left to right: KE of nucleus 1, KE of nucleus 2, KE of electron, attraction between electron and nucleus 1, attraction between electron and nucleus 2, repulsion between the two nuclei. The repulsion term is positive because it's a destabilising (raising the energy of the system) interaction. The attractions are negative for the opposite reason. Admittedly the KE terms are harder to explain, one hand-wavy answer is that the minus sign in front gives you a positive energy eigenvalue for the wavefunction.

   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, $\hat{H}_{elec}$. Separating nuclear and electronic motion removes the KE of the nuclei essentially::

$$\hat{H}_{elec} = \hat{H} - \hat{T}_{nuc} = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R_{12}}$$

   The Hamiltonian still depends on the nuclear separation, but this is now fixed.

   iii How does the Born-Oppenheimer Approximation help us in our quest to understand molecular structure at a quantum mechanical level? The SE for a molecule before the BOA is applied is even more impossible to solve than normal, because the wavefunction that solves it would depend on the (coupled) nuclear and electronic coordinates. The BOA separates these out so we can consider the problem of nuclear motion separately to electron motion, which is a simpler problem to solve.

2. Outline situations in which the Born-Oppenheimer Approximation breaks down. Main one here is when nuclear and electronic motion have similar timescales (i.e. when the nuclei move fast). This happens most often when bonds are dissociating, so the BOA breaks down when molecules are close to dissociation. It also breaks down when two different electronic states have similar energies, but this isn't discussed in depth in this course.

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. The coefficient c_i tells you how much of wavefunction ϕ_i there is in the overall LCAO sum to give the wavefunction Ψ. Like a recipe, ϕ_1 are the ingredients and c_i are the amounts you need. Electron density is proportional to the coefficient squared.

   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:

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

   Done in depth in the lecture notes, but main idea is to state that because of symmetry, the electron density $\rho = c_i^2$ has to be same on each atom. This leads to $c_1 = \pm c_2$, and given that $|c_1| = |c_2|$ we can drop the subscripts and write the answer as shown.

iii Which of these MOs corresponds to the bonding and anti-bonding molecular orbital? Ψ^+ is the bonding orbital and Ψ^- is the anti-bonding orbital. Can think about the signs of the coefficients (if they are the same then we have a bonding orbital, different and we have a node in the middle: anti-bonding). Or think of it as constructive vs destructive interference of the two atomic orbitals.

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? Advantages are that you get a more accurate result and can more accurately model complex systems. Disadvantage is that doing this makes the calculation take much much longer. Always a trade off between calculation speed and calculation accuracy.

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. MO diagram as shown in the lecture notes. Observations explained:

      i H_2^{2-} has both bonding and anti-bonding MOs filled, and because the anti-bonding MO is more anti-bonding than the bonding MO is bonding, the molecule has a higher energy than two individual ions, so it is unbound. H_2^{2+} has no electrons on it, so no way for any bonding to happen.

      ii H_2 has two electrons in a bonding MO (overall bond order $= 1$). He_2^+ has the same MO diagram but with three electrons, two in the bonding MO and one in the anti-bonding MO. The overall bond order is then 0.5, and the bond is weaker (due to the electron in the anti-bonding MO). The bond length and strength are going to decrease, which lowers the vibrational frequency (from CH2200), hence the observed behaviour).

      iii HeH^+ and H_2 are isoelectronic - both have two electrons in a bonding MO. Because the bond length and strength are dictated by the electronic structure rather than the mass of the nuclei, these properties are similar between the two species.

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.

   Sketches are all in the lecture notes. First pair differ in the inversion symmetry (u is odd wrt inversion, g is even wrt inversion). The second pair different in their cylindrical symmetry, the π orbital has a nodal plane on the internuclear axis where the σ doesn't - an end-on sketch (as in the notes) makes this obvious.

2. Describe three key rules that dictate how atomic orbitals overlap to form molecular orbitals. Rules are:

   a) Orbitals must have similar energies (the more different they are, the weaker the interaction: 1s won't overlap with 2p, for example.

   b) Orbitals must have the right symmetry (so the overlap integral is non-zero).

   c) Orbitals must be physically near each other (i.e. orbitals on atoms from different sides of the molecule don't interact).

   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.

   Answers:

   i No - overlap integral zero.

   ii No - too far apart.

   iii Yes - CO back-bonding (see inorganic courses).

   iv Yes - but likely a bit weak.

   v Yes - see MO diagram in notes.

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).

   MO diagram is in the notes. Explanations:

   i Bond order increases as you remove an electron from an anti-bonding orbital to make the cation.

   ii Unpaired electrons in the ground state make it paramagnetic.

iii Anion is made by adding an electron to the anti-bonding orbital, lengthens the bond and so lowers the vibrational frequency (a la CH2200).

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. Key is the mixing between 2s and 2p orbitals changes. As we go across the period the energy gap between 2s and 2p increases, so there is less mixing of these orbitals. Going from heavy to light, once we get to N_2 the mixing is strong enough that it pushes the $3\sigma_g$ orbital above the $1\pi_u$ in energy (among other things) which accounts for the different energy ordering in the MO diagram.

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.

   Hints:

   i Think about how the bond order must change in each case.

   ii Are you adding electrons to a bonding or anti-bonding MO to make the anion?

   iii Think about the bond order.

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:

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

   a) Outline the physical meaning of each term in the Hamiltonian, with reference to an appropriate sketch. Sketch is in the lecture notes, but simply: first two terms are nuclear KE, second two are electron KE, next four are attractive PE between the electrons and nucleus, penultimate term is nuclear-nuclear repulsion, and final term is electron-electron repulsion.

   b) Outline what is meant by the *Born-Oppenheimer Approximation* (BOA). The BOA states that because electrons move much faster than nuclei for the same applied force (due to their lower mass), the motion of electrons and nuclei are separable. Thus the total SE for a molecule (which, if exact, would depend on coupled nuclear and electronic coordinates) can be separated into two separate equations – one for the electronic energy and one for the nuclear energy e.g:

$$\Psi_{total}(r, R) = \Psi_{elec}(r) \times \Psi_{nuc}(R)$$

   Essentially decoupling the nuclear and electronic motions.

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

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

   When does the BOA break down? Applying the BOA to get the electronic Hamiltonian means:

   - Removing the nuclear KE terms.
   - Fixing the internuclear distance (here denoted by going from $r_{n1n2} \rightarrow R_{n1n2}$).

   Thus we get the electronic Hamiltonian, which leads to the electronic SE below. The BOA breaks down in any situation where nuclear and kinetic motions become strongly coupled (i.e. nuclei move fast), such as:

   - Close to dissociation, where nuclei move fast (discussed in lectures).
   - If two electronic states have the same energy (at curve crossings - not discussed in lectures. Heroes who have read Atkins MQM may know this).

   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. The BOA still doesn't get around the problem of electron-electron repulsions meaning that the electron positions are correlated. It decouples the nuclear positions from the problem (a big help), but we are still left with the correlated electron coordinates. Thus, need to do SCF iterative methods or invoke other approximations to make progress from here.

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. Sketches are in the lecture notes, but basically:

- Both curves go to infinity as $R \to 0$.
- Both curves go to zero as $R_{\to}\infty$.
- The bound state goes below zero into a well at $R = R_0$.
- The unbound state never goes below zero.

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. Challenging unseen question. Keys to the answer are:

- The second derivative is essentially telling you about the rate of change of the electronic wavefunction as the nuclear positions R change.
- If this second derivative is zero, then the electronic wavefunction is a slowly-varying function of the nuclear positions (rate of change of the wavefunction must be small as R changes).
- Ultimately this means that the electronic wavefunction doesn't have a strong dependence on R.
- Which is the same thing as saying the electronic motion (via $\Psi_{elec}(R)$) is not strongly coupled to the motion of the nuclei (via R), so their motions are separable.

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? The orbital approximation says that we can approximate the wavefunction of a many-electron system Ψ as a product of one-electron wavefunctions ϕ, i.e:

$$\Psi(r_1, r_2, ..., r_n) = \prod_i = 1^n \phi_i(r_i)$$

It is an approximation because in reality the electron positions are correlated and so can't be separated in this way, unless we ignore electron-electron interactions.

b) Under what conditions does the orbital approximation become exact? The OA becomes exact in the limit that we ignore electron-electron interactions (which is obviously not realistic for any real atom or molecule).

c) Write down the radial wavefunction $\Psi_{He}(r_1, r_2)$ for the electrons in a helium atom. Plug the first equation above into the second, with $Z = 2$ (helium):

$$\Psi_{He}(r_1, r_2) = (2 \times 2^{\frac{3}{2}}\mathrm{e}^{-4r_1})(2 \times 2^{\frac{3}{2}}\mathrm{e}^{-4r_2})$$

Rearrange to get:

$$\Psi_{He}(r_1, r_2) = 32\mathrm{e}^{-4(r_1+r_2)})$$

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 $r_1 + r_2 \to \infty$

Plug in numbers to the expression obtained above. For each case:

- $\Psi_{He} = 32$
- $\Psi_{He} = 4.33$
- $\Psi_{He} = 0.58$
- $\Psi_{He} = 0$

e) Hence sketch the graph of Ψ_{He} against $r_1 + r_2$. Explain the shape of this graph. Sketch axes and plot the four points above roughly. Clearly starts high and decays away to zero - exponential decay. Never crosses the x axis. Explanation:

- Wavefunction is non-zero at the nucleus (s-orbital, expected).
- Wavefunction goes to zero at large r (also expected, electrons aren't gonna be miles away from the nucleus).
- No radial nodes (also expected, 1s-orbital).

f) Explain what is meant by a *node* in a wavefunction. Does the wavefunction Ψ_{He} contain any nodes? Node is when the wavefunction *passes through zero*, or when the wavefunction changes sign. Not sufficient to just say 'wavefunction is zero', because that happens at $r \to \infty$ and that isn't a node.

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. Many answers possible here. Main idea is that we need iterative methods to enable us to deal with electron correlation. An SCF approach works by iteratively refining the wavefunctions under the orbital approximation so that they accurately model the electron-electron interactions. Specific examples are things like **Hartree-Fock Theory** or **Density Functional Theory**.