Part II May/June 2015

Q1

A total of sixty three students chose to answer this question and, in the most part, the question was answered well.
Parts (a) ad (b) were trivial for most. Either Wade's Rules or a valence bond approach were taken to explain the bonding in $B_3H_8^-$. Most spotted that in B_2H_6 there is no formal B-B overlap which leads to a longer B-B distance than in $[B_6H_6]^{2-}$.
Part (c) required the students to use Wade's Rules to predict the structures of compounds that they had not seen previously. Since three of the four compounds are metalloboranes this also required the students to use the $v + x - 12$ rule taught in lectures. Again most students knew how to tackle this but mistakes were made in many cases either simply through miscounting or misinterpreting how the transition metal would contribute to the cluster. There were a couple of different ways that the sulphur atom could be considered – either as a vertex or as in interstitial atom. Provided the electron count was appropriate for the assumption made about the sulphur's role full marks were awarded in either case.
Part (d) again required students to use Wade's Rules to predict the structures of some new compounds. Since the products of the reactions needed to be derived before the structure prediction could take place students appeared to find this more tricky than part (c). Those that struggled here did not think carefully enough about the reactants in terms of the isolobal analogy and so ended up with the wrong number of electrons contributing to the clusters in the products **A**-**D**.

Q2d
The candidates were mostly able to get to an explanation of why and how F3UCH has covalent bonding, identifying plausible bonding interactions between (H)AOs. It was not always possible for them to give the correct bond order, often due to trivial errors like not correctly keeping count of numbers of orbitals and electrons. Discussion of F3NdCH tended to be too superficial: Nd properties mentioned were usually correct but explanation of why Nd has those properties was often missing.

Qu 5 (32 answers)
Despite being on an unfamiliar topic (asymmetric tops), the question was relatively easy, as those who answered it found
a) Straightforward. The only thing that most people missed was to specify the range of J in their final expression. There was a lot of talk about P and R branches, which is confusing rotational fine structure with pure rotation spectra.
b) Just about everyone spotted that there 4 transitions; as few failed to spot the (000) – (101) transition.
c) Generally well done, but a few people failed to draw the explicit comparison with the prediction of (a)
d) Generally well done, apart from the usual numerical errors or failing to use the requested units. There were some poor sketches of the spectra. Lines were as 72,848 150,371 141,019 and 145,628 MHz.

e) Hardly anyone spotted that the key point here is that unless you can *assign* the lines you cannot start to use the line frequencies to find *A*, *B* and *C*. The responses were most brain dumps of matters that were not relevant.

f) Well done. The angle is 126.5°

Qu 6 (49 answers)

This question was too easy.

a) Many people scored full marks on this section. Those who did not mainly fell down on identifying the point groups (which were C_s, C_{2v}, C_s, D_{3h}, C_{2v}, C_s)

b) This part provide to be more discriminating

    i. Generally people knew how to come up with the ground state of O_2, but there was quite a lot of fudging of the details.

    ii. Those who did (i) properly had little trouble with the excited state, but those whose understanding was not so secure struggled to get all of the terms and identify the ground state ($^3\Delta_u$) and the state to which the transition took place ($^3\Sigma_u^-$). Despite being clearly told to the contrary in the question, many people insisted that Σ^- had to be triplets and Σ^+ has to be singlets.

    iii. This was a trivial part, which is easily solved with a diagram (the states do not dissociate to the same atomic states).

    iv. This turned out to be surprisingly difficult for people. It's just the familiar calculation of D_e from the Morse parameters, but expressed in an unfamiliar way which floored people.

q7

This question about Huckel theory proved most popular gathering 80% of the answers. Indeed it is standard Huckel theory of pi electrons switching been ring and linear polymers with a bit of first order perturbation theory as taught in the lectures and practised in the examples. The catch was that the equations for orbital energies and coefficients were not given but had to be remembered (derivation was not required). The question was answered very well. The main error was starting the count of the molecular orbitals of the linear polymer not at 1 but at 0. The question required a substantial amount of work, but this turned out not be a problem. There were remarkably few calculation errors showing again that the student are well trained in Huckel theory. Running out of time was the other major cause of a low mark. But this was probably because doing the A4 questions is usually put off till the very last.

q8

This was this years Hartree-Fock question. This subject was added two years ago and this year was only the second year it appeared in the exam. The question was probably attempted by a minority of better and more motivated students. It involved computation of the total energy of the triplet ground state and first(S1) and second (s2) singlet state of

the CH2 radical. The equation for the total energy of a Slater determinant was given. The students had little difficulty with using this equation which I found encouraging. There were only a couple of answers which got the sign of the exchange energy in the Triplet state wrong. The tricky part was question ci asking to write down the energy of S2. With one exception nobody realized that this is a two determinant state and is the singlet counterpart of the triplet state. This was extensively treated in an example of the He atom and was also the subject of last years exam question, so I was rather disappointed. Fortunately missing ci did not lead to confusion in answering cii and d, which afterall were done rather well (including d).

Q9
This question was attempted by 3 candidates. Two candidates answered part d acceptably, with problems in apprehending that the energies of the box should remain unchanged on a change of origin, which introduced difficulties in starting part d. Parts a, b and c were generally well done.

Q10
The question was attempted by 7 candidates, with many scoring highly. Part (c) had a minot typo, but Candidates who attempted part (c) constructively, or who used consistent algebra, were rewarded accordingly. The mean score was 18, reflecting the high proportion of near-complete high-quality answers.

Q12

Part (a)-Many candidates included good points in their answers to this part of the question, but it would have been beneficial if a very small amount of time had been spent thinking about the structure of the answer before starting to write.

Part (b)-With the exception of a few candidates who invented a new reaction between CO and an alkene, this part of the question was answered quite well. Many candidates couldn't see how product E is formed, but I think this is the hardest part of the question. In particular, there were some very nice discussions of the relative donor/acceptor properties of phosphines versus phosphites and the consequence for the reactivity of coordinated CO.

Part (c)-This presented a good test of candidates' understanding of reactivity. Some candidates misunderstood the question and included H2 as a reactant.

Question 13 (41 scripts)
The question was splits into essentially four parts, with the balance of marks rewarding those giving sensible and credible answers to (a), (b) and (c)ii with on average 11-13 awarded out of the overall 25 marks for the question. Part (c)i for 40% of the 25 marks provided the breadth that discriminated between thoughtful and informative answers from those that provided some basic concepts but failed to address the data in the question. The scripts were read once to gauge the level of information presented across the cohort, and then read a second time to allocate the appropriate marking scheme that reflected the appropriate breadth of questions. Many students presented good answers(high II.2 to

First class standard), but those who did poorly/very poorly tended to either write very little (perhaps lack of time) or give brief answers that had no bearing on questions – in both cases marks were awarded generously for anything related to the course (mean 16.05/25).

Question 14

There were 63 answers to this question.
Mean mark = 14.8
Min. mark = 0
Max. mark = 23.5

This was a popular question and there was a very wide spread of marks. Some answers were excellent. There were several very low scores that skewed the average mark considerably and despite extensive re-marking (taking several hours) and a generous mark scheme it proved impossible to increase the average because there were so many very low scores.

(a) Most recognized that DMF could solvate the Na cation, leaving the oxyanion centre relatively unsolvated. However, very few provided a reason for *why* O-alkylation would be favoured over C-alkylation. Fewer candidates spotted that CF_3OH can solvate the oxyanion centre through the formation of strong hydrogen bonds. Many answers incorrectly stated that C-alkylation was favoured in this case because the CF_3OH cannot solvate the Na cation. No candidates commented upon 'selective solvation' of the more electronegative oxyanion centre. Generous marking scheme adopted – correct approach automatically got 4 marks, ranging to 5 marks for additional comments. (5/25)

(b) Generally answered very well. The majority of candidates provided the expected mechanism based on the intramolecular trapping of a benzyne intermediate. [6 marks]

(c) This part of the question proved to be very challenging and enabled effective discrimination between the candidates. Only a minority of students identified the correct reaction sequence. Most did not add the borane across the alkene (even though hydroboration was covered by all at Part IA). Very generous marking scheme adopted – correct approach automatically got 4 marks, ranging to 5 marks for additional comments (e.g. orbital alignment). [5 marks]

(d) This part of the question was generally answered well. Most of the students spotted the correct reaction sequence. Woodward-Hoffmann rules were generally applied correctly. [9 marks]

Q 15 (paper 2) 63 answers. This question was reasonably well done with the exception of part (d). In part (a), the majority of the candidates were able to correctly assigning

the protons correctly, indicating their ability to systematically process chemical shift and coupling constant data. For parts (b) and (c), most of the candidates correctly assigned the stereochemistry in the separate rings but many struggled with the anomeric spiroacetal carbon and could not draw suitably clear conformational diagrams. A large proportion of the candidates could not translate 3D stereochemistry into a 2D representation of configuration as required in part (d) which therefore proved to be a challenge for everyone.

Report on Q16 Part II Biological catalysis

The question was only attempted by 8 students. One answer was very poor and pulled average down.
   (a) Explain k_{cat} etc. Generally well done but still lack of clarity about K_m v K_d
   (b) Transaldolase mechanism. Ping pong aspect not well explained. Most recognized Shiff base. Some did not draw out a mechanism.
   (c) Stereochemistry of b-eliminations. Described in lectures and well done
   (d) The dehydroquinase inhibition mechanism went beyond the scope of the lectures, and it showed. Most recognized the Shiff base, some recognized loss of fluoride in first part. Second part very poorly done. Surprising how little use appeared to be made of mass spec data given.

Q17

Set and Marked by DRS
Answers = 26
Average mark = 16.42
SD = 4.51
Min mark = 8
Max mark = 25

The question was well answered by most candidates. Part (a) asked for the PLP mediated mechanism of taurine-pyruvate aminotransferase. This was similar to transformations that they had seen before, and so almost every answer started on the right lines. The problems that the students often had were not forming PMP and therefore having to use unusual chemistry. Part (b) asked for the TPP mediated mechanism of sulfoacetaldehyde transferase. Pleasingly the use of TPP was generally well understood. Part (c) asked for the mechanism of the reaction catalysed by phosphate acetyltransferase. This gave a wide range of answers and students quickly displayed their depth of knowledge of the course.

Question 18

Question 18 focused on core material covered in lectures. Namely the major odd oxygen destroying cycles in the stratosphere. The question contained a mixture of numerical calculations

mixed with questions asking for background information on the catalytic cycles. A key question was to explain the altitude dependence, which very few students did. There were 26 attempts of the exam question. Other than two candidates, all candidates attained > II.2 mark, with most students (20/26) attaining a II.1 or higher. The average mark for the paper was 65%.

Q19

(a)(i) This part of the question was answered best. Almost all students could calculate the effect of NOx on the peroxy radical concentration.

(a)(ii) Average marks were achieved for this part with some students having difficulties to quantify the effect of the heterogeneous reaction.

(b) This part of the question was answered the least well. Many students failed to identify the PAN precursor in the reaction scheme as well as the involved reactions, although this was discussed in the lecture and in supervision material.

(c) This question was answered reasonably well with a couple of students who seem to have run out of time as they did not attempted to answer this question at all.

Question 22 (Statistical mechanics) [12 answers: mean 18.2, min 8.5, max 22.5]

This question on Schottky defects was similar to those set in previous years and was answered by a number of candidates. The standard of responses was for the most part high, although a handful of candidates would probably have been better off choosing a different question. The question was about a real physical problem and, in particular, how the 'standard' derivation in the microcanonical ensemble neglects the fate of the disappearing atoms, and how this can be corrected by considering the problem in the grand ensemble instead. Some specific points about the candidates' answers follow:

 – Too many candidates thought that $1 = \ln x / = \ln 1 = x /$ (where in this case, x was $.N − n/=n$); some candidates rather skilfully managed to make this mistake several times to obtain the correct answer in the end.
 – Rather too many candidates thought that at high temperature, there are only vacancies in the system – but there is no driving force for that: 50 % occupation is the entropic limit.
 – Few candidates commented on the soundness of the approximation that vacancies don't interact, or how 'crys- talline' a crystal with 50 % vacancies really is, or whether the assumption that $" \gg k_B T$ holds, as $1 = T ! 0$, even though they were asked to comment on the physical reasons for the behaviour of C_V in the two regimes.
 – A number of candidates appeared to swap the labels M and N defined by the question in part (d), many without
noticing that they had done so, leading to some confusion when it came to comparing the result to that of part (b). Some candidates clearly spent a considerable amount of time deriving a (wrong) result for the chemical potential because of this mistake. One candidate expressed their distaste at the notation used for the number of lattice sites (N); of course this labelling was used for consistency with part (a), where this notation is standard.
 – Many candidates failed to notice the negative sign for the interaction energy – but of course the energy of forming a vacancy in part (a) must be the negative of binding to the surface in part (d), so it seems many candidates did not really think about the problem but rather just worked through the maths.
 – Some candidates thought that the mean occupancy number is the same as the mean number of vacancies, when clearly the occupancy number is the opposite of the number of vacancies: i.e. the two added together must equal the number of lattice sites.
 – The answer for the imposed chemical potential ($\mu D 0$) should be physically obvious, so it is difficult to understand why so many candidates got it wrong.

Question 23 (Statistical mechanics) [2 answers: mean 19.25, min 15.25, max 23.25]

This question was rather unpopular, with only two candidates attempting it. The question itself was not particularly challenging, but some candidates may have been scared away by the relatively large amount of text. It is also true that the question was fairly synoptic, linking different parts of the course (diffusion on a lattice, thermal averages, conditions for equilibrium and macroscopic flux laws), which may well have contributed to the candidates' reluctance to attempt it. However, of the two scripts that were marked, one candidate made a reasonable attempt and the other an excellent one.

Report on Question 24 (B7 Symmetry)

There were 5 attempts at this question, somewhat lower than in previous years
Part (a) regarding the relation between symmetry transformations and coordinate transformations was surprisingly poorly answered given that it was standard material carefully covered in the lectures. Only one or two candidates pointed that one can evaluate the transformed function at r by evaluating the untransformed function at the point obtained by operating the inverse of R on r! !

Part (b) was reasonably well answered except for the last part on rapid detection of non-irreducibility of a representation. !

Part (c)(i) was well answered (standard material)!

Part (c)(ii) was well answered in both parts, indicating that the students had grasped the idea of using the character of spherical harmonics under rotations to figure out the irreps of d and f functions in finite point groups. !

Part (c)(iii) was partly well answered in terms of the MO diagram, but no-one commented on the final part of this question (on the existence of f-only irreps). !

Question 25 (Perturbation theory) [4 answers: mean 17, min 4, max 24]

This question covered an application of time-independent perturbation theory to calculating special relativistic corrections to the energy levels of a hydrogen atom. It was a fairly straightforward question, but the words 'special relativity' may have (needlessly) frightened off some candidates, and only 4 candidates attempted the question. The question was very well answered by most of those who attempted it, with three first class answers.

The remaining candidate must have chosen to attempt this question as a last resort and only gained 16 % of the marks. What was particularly disappointing about this is that they failed to gain most of the 'easy' marks: for example, the only thing part (a) asked for was for the candidate to expand an expression that was given in a Maclaurin series that was also given. Any candidate should have been able to attain near full marks here, whether they attended the perturbation theory course or not.

The remaining candidates fared very well in most of the mathematical aspects of the question, although one candidate could not quite remember what a commutator was. Very pleasingly, even those parts of the question asking for comments were well answered. The only slightly disappointing aspect was that no one commented on the use of the first-order perturbation expression applied to the (degenerate) hydrogen atom. While credit was given for comments about second-order energy corrections, this is not really what the question was about: degeneracy affects first-order perturbation corrections, too. However, on the whole, the standard of all the scripts bar one was excellent.

Q29

Candidates were generally able to give good explanations of their chosen
relaxation mechanisms. Symmetry of the selenium compounds was not always
discussed in the explanations for the numbers of lines in the spectra, and a
listing of assumptions was often absent from the calculation of exchange
rate. Those candidates who didn't get to a correct assignment of the 2-D
spectrum were given appropriate credit for what turned out to be mostly
clear, logical, and chemically sensible arguments.

Q32

a) Schmidt-type reaction, as in lectures; more substituted centre migrates after initial addition.
A Friedel-Crafts process is less plausible and would not explain the products.
b) trans double bond must first become cis - this is what the hv does. TsOH is an acid.
c) Addition-elimination reactions; Baylis-Hillman-like introduction of bromine; Na2S2O4
reduction (mechanism given in the lectures); final step has tricky regioselectivity. Answers had
too many benzynes in the first step

Q33

Set and Marked by DRS
Answers = 65
Average mark = 16.25
SD = 5.37
Min mark = 5
Max mark = 25

The question was challenging to the class, with a significant number not answering every part.
Part (a) was familiar and all correctly predicted cyclopropanation from the top face with
chelation control. There were a few odd intermediates suggested however. From: J. Med. Chem.
2014, 57, 2107-20. Part (b) required a chelation controlled addition of the Gignard reagent to
the ketone. This aspect was well answered. Some mistakes were due to prediction using the
wrong model and simple errors in translating the correct model to the correct product. Part (c)
proved to be a more problematic part. The majority spotted a Claisen rearrangement step, but
most did not spot the Johnson-Claisen rearrangement first, and proposed an unlikely
transformation to get to the second rearrangement step. Many gave a good chair-like TS
representation to explain the double bond geometry, which was good to see. From: JACS 2014,
136, 6598-6601. Part (d) was the most problematic part of the question. Several did not even
attempt it, even though it constituted 35% of the marks. Common errors included
misunderstanding of the Boc protecting group and its facile deprotection in TFA (not step ii),
lack of enamine formation, lack of iminium reduction directed by the hydroxyl, and a general
lack of any attempt to explain the stereochemical outcome. From: ACIE 2014, 53, 13826-9.

Part II Q35
This question was attempted by 21 candidates and was generally well answered.
The general description of the phase problem was well attempted by all except one candidate. The role of centrosymmetric structures and the phases of reflections were also well done by most candidates. The direct methods approach was also good, although some were less clear on unitary structure factors. Unfortunately several candidates could not correctly calculate the lattice spacing, nor even recall Braggs law, but all but one could convert intensities to the amplitude of the reflection. A good number of candidates successfully determined the phase of the (003) reflection using the electron density and a reasonable number could then identify the dominant role of the (003) reflection in the overall phase determination.

Q36

This question sets up the FCI matrix for H2 in 2 basis functions. Most people did not use symmetry (as stated in the question) to see that the 4x4 matrix turned in to simpler 2x2 matrices or to reduce the number of matrix elements to work out. Also not many people used the hint to work out the general matrix element. This meant that a few people found the hint to diagonalise just the symmetric 2x2 very useful to get the correct answer. Overall, I thought the question was done well.

Q37

The question was on the Kohn-Sham equations and scaling relations in DFT. Along with the development of functionals. The part on scaling relations was relatively straightforward and although one part was in 2D which hasnt been covered the maths of it was similar to the previous part of the question. The part on rearranging the KS equation given a KS orbital was harder with more mistakes. Also the discussions reflected the knowledge of the material covered in the course.

Question 38
Exam report by Professor Balasubramanian
30 answers
Average score 16.4
This question generated a wide distribution of marks ranging from 10.5 to 21. The range of marks was equally wide for part (a) as it was for part (b) and thus all sections of the question appeared to clearly separate strong responses from weaker responses. Very few answers included the stereogenic center at P in part (b). The discussion on molecule **3** proved to be the most challenging aspect of part (a).

II Q40
23 candidates attempted this question.
There was a spread of answers to this question. The first part on Wilhelmy Plate was generally answered well although some candidates were not sure of which were the relevant lengths. The derivation of the Gibbs equation was also generally good with some full derivations of the relative surface excess. Almost everyone correctly submitted an appropriate graph and estimated the cmc. Rather fewer correctly determined the surface excess and area per molecule, but there were a decent number of good answers and comments. The extension to solution behaviour was also well done with a fair number of appropriate areas per molecule and some sensible comments in comparison to the earlier air liquid interface value.

Question 41
In general, candidates coped well with this question, with a pleasing number of very good answers. Too many candidates gave heat of adsorption, q_{ads}, as a negative value, despite emphasis being placed in the lectures/notes on it being defined as a positive quantity. Some sloppiness over units (mostly omission) was also noted. In (a), some candidates incorrectly took a slight decrease in q_{ads} with coverage as significant; this actually arose from measurement error (the data was generated within the Langmuir model). More worryingly, a few candidates argued that such a decrease was consistent with the Langmuir model. In (b)(ii), several candidates gave a value of 10^{-13} s^{-1}, not 10^{13} s^{-1}, for the pre-exponential factor, indicating a lack of physical understanding of this quantity. Most candidates stated their assumptions; rather few justified them. In (c), the TPD and adsorption isotherm methods rely on adsorption being reversible. Not all candidates recognized the implication of oxygen dissolving into bulk Cu on heating: the adsorption is irreversible. Several candidates incorrectly suggested that dissolved O would behave like an adsorbed multilayer in TPD.
Stephen Driver, 5 June 2015.

Qu 52
The main problem people had with this is getting into a muddle with units, and hence producing completely silly answers. You would have thought that by the end of the third year people would have got units straight in their minds. Answer: 1.74×10^9 Hz.

Qu 53

Well done – it was really too easy in retrospect. Answers $B = 10.00$ cm^{-1}, $I_b = 2.8 \times 10^{-47}$ kg m^2,
$\theta = 107°$

Qu 54
I was persuaded by my fellow examiners to simplify this question, and the result was it was too easy. The original version did not have the levels pre-drawn on the diagram. Answers: IRs reading from left to right A_1, A_1, B_2, B_2, B_2; fundamental parallel $(0,0,0) \rightarrow (1,0,0)$, overtone perpendicular $(0,0,0) \rightarrow (0,0,3)$; combination perpendicular $(0,0,0) \rightarrow (1,0,1)$.

Qu 55
Done very well and clearly rather too easy.
Answers: $^1\Sigma_g^+$; $^3\Pi_g$ and $^1\Pi_g$; $^2\Sigma_g^+$; $^2\Pi_g$

q56
This question should be "routine" Huckel theory and went fairly well. The main mistake was getting the pi orbitals (and or number of electrons) wrong for the cyclopentadiene not realizing that the CH2 group interrupts the pi circuit.

q57
This question was a bit of a disaster. Evidently only a few students seem to be aware that the expectation value of an one-electron property with respect to a Slater determinant is the sum of the expectation values of this property for the one-electron orbitals. Clearly next years examples must include a similar problem. The question in its present form is however less suitable because the expectation value of the one-electron property in question, the dipole moment (referred to as mu) vanishes in the excited of state of He. This had slipped the attention of both the setter and checker. However, it doesn't seem to be the cause of the poor answers to the question and was noticed by only one or two students.

q58
One would have hoped that this question was a routine Huckel problem as well. Most students did know that the ionization energy in the Huckel approximation is simply the energy of the HOMO. However only a minority actually took the trouble of checking the orbital energy of the HOMO of the molecule mentioned in the question (the formate anion) to find out that it is non-bonding. This to me makes again the point why the A4 course is so important (and probably less popular). The focus is on calculation, and not on qualitative reasoning.

q59
Although I know that most students dislike normal modes, the answering of this question went fairly well. I was happy to see this. The main errors were getting the second derivative with respect the coordinate of the particle tied to the wall wrong and the mass

scaling.

Question 60 (61 scripts)
This was a simple question that offered the opportunity to draw on the material form the lectures to cover reaction mechanisms, isomerism, oxidation states, and the effect of ligands on transition states. All the scripts were read once to identify the breadth of material the students were able to incorporate into the answers in the available timeframe, and a second time to implement a marking scheme that suitably rewarded good answers and allocated some marks to those students who may have missed the key points. On average the answers very good, but those students who did poorly tended to produce very little that could attract any marks at all – in those cases some marks were given for anything that approached being relevant to the course or suggesting that the students were at least aware of what the problems was asking (mean 5.94/10).

Question 61

B2 Structure and reactivity

This questions was extremely popular (79 scripts) and marks ranged from 0 to 10.

The mean mark was 5.9. There were several very low marks (0.5 or below) that skewed the mean considerably. The majority of these low-scoring scripts did not recognise that a carbene (carbenoid) was being generated and there were a few truly odd mechanisms proposed. Removal of scores of 0.5 or below leads to a mean mark of 6.4. Most candidates recognised that a single carbene equivalent was being generated and could draw a concerted mechanism for insertion into the neighbouring alkene (though this was omitted by some). There was more variation in the subsequent ring-opening step(s), with credit given for anything sensible. The vast majority did not identify that oxygen-assisted ring opening was possible. Those that did tended to score more highly.

Q62

Set and Marked by DRS
Answers = 28
Average mark = 6.79
SD = 0.79
Min mark = 4
Max mark = 8

It was pleasing to see that almost every candidate had understood TPP-mediated biological mechanisms and gave an excellent answer.

Question 65 (Statistical mechanics) [15 answers: mean 6.97, min 1, max 10]
This was a straightforward question on polymer statistics. The question was generally well answered. In part (a), many candidates thought that $(\cos{()iJ}) = \cos{(()iJ)}$, but this is only the case if the

angle *()iJ* is unsigned. In part (c), a large number of candidates thought that they were being asked about ideal polymers, even though the question specifically stated that we were considering *real* polymers within the approximation presented in part (b). Even many
of the candidates whose answer was correct inexplicably mentioned ideal polymers in their answer.

Question 66 (Perturbation theory) [13 answers: mean 6.65, min 0.5, max 10]
    This question on the Hellmann–Feynman theorem was purely a book-work exercise and asked the candidates to reproduce the proof of the theorem and then apply it to derive an expression for the ground state electric polarisability. Both of these were covered at length in the lectures. Most candidates who chose to answer this question did very well indeed. The only commonly occurring issue was that in part (b), many candidates failed to write down what the perturbing hamiltonian should be (i.e. the energy of a dipole moment in an electric field) and simply wrote a series expansion in p, without explicitly showing how the Hellmann–Feynman theorem applies, despite the question asking them to *derive* this relation. Worse, of those candidates who failed to write down an explicit expression for the perturbing hamiltonian, almost all subsequently got the sign wrong in the series expansion (and then did not notice that this would lead to a destabilising second order energy correction, which could have served as a useful check in the derivation). On the other hand, there were several candidates whose answers were truly exemplary.

Q70

Set and Marked by DRS
Answers = 58
Average mark = 6.53
SD = 2.49
Min mark = 1
Max mark = 10

This question proved to be a challenge to the class. Most could spot the acid catalysed deprotection of the ketal. The next steps included 7-endo-trig conjugate addition, tautomerisation, then enamine addition to the ketone. Many got this sequence. Often there was no attempt to rationalise the selectivity observed. Reference: JACS 2014, 136, 13442-13452.

Q72

Two integrals on the H atom and H2+. The result should have been that we find agreement between $E_x^{DFA} = -J$ for the H atom but it is much lower for H2+. This error is very large and reflects the problem that functionals have stretching bonds. There were a few mistakes on the integrals that meant the numbers did not always reflect the arguments that were hoped for but generally well done.

        Question 74
36 answers, mean mark 6.2, mark spread from 1 to 9.
This question involved a surface alloy, a type of structure not explicitly discussed in lectures, but fully described in the question. In part (a), not all candidates demonstrated convincingly that they understood the description, though a good number did, whilst a few clearly did not. The majority of candidates handled the geometry in part (b) correctly, although some confused atomic radius with diameter. Answers to part (c), however, were disappointing. No-one made the key point that the variability in the measured heights

cannot reasonably be accounted for by the geometric height difference. Many candidates described the sensitivity to electronic structure in terms of adsorbed Na atoms having a different work function. Bulk Na does have a different value to bulk Al, but work function isn't the right concept at single-atom level. Reference to local barrier height, or even to local work function changes, would have been preferable. Moreover, disappointingly few candidates gave charge transfer between adsorbate and substrate as the reason for the local changes in electronic structure. Quite generous marking, especially of parts (a) and (b), was needed to achieve a mean mark near the target. Stephen Driver, 8 June 2015.

Q75
Frequent failure to apprehend n=2 and n=3 were required. Average 3.3

Q76
Generally very well done, many complete answers. Average 4.3

Q77
Few people connected Pauli to the wavefunctions, or associated singlet with spin-antisymmetric functions. Average mark 3.4

Q78
Generally well done. Couple of failures to square Psi, only one candidate showing that r=1 was actually a maximum. Average 3.2

Qu 82

Generally well done, with a lot of candidates introducing the spurious requirement of normalised wave functions. Only one candidate failed to use any mathematics, receiving little credit. Average mark 3.8