Answers: Problem set III

1. **(a)** Using the relation, $\langle\psi|\,\hat{H}_1\,|\psi\rangle \sim \int r^2 dr \psi^* \hat{\mathbf{p}}^4 \psi \sim \int r^2 dr |\nabla^2\psi|^2$, consider the change of variables $\mathbf{u} = Z\mathbf{r}/a_0$. Since $\partial_x = \frac{Z}{a_0}\partial_{u_x}$, $\nabla^2 = (\frac{Z}{a_0})^2\nabla_u^2$ and

$$\langle\psi|\,\hat{H}_1\,|\psi\rangle \sim Z^3 \int \frac{u^2 du}{Z^3}\left(\frac{Z}{a_0}\right)^4 \left|\nabla_u^2 G(u) e^{-u/n}\right|^2 \sim Z^4 \,.$$

(b) For the Coulomb interaction, $V = -\frac{Ze^2}{4\pi\epsilon_0 r}$, so $\partial_r V = \frac{Ze^2}{4\pi\epsilon_0 r^2}$ and

$$\langle\psi|\,\hat{H}_2\,|\psi\rangle \sim \int r^2 dr |\psi|^2 \frac{Z}{r^3} \sim Z^4 \int \frac{dr}{r} G_{n\ell}\left(\frac{Zr}{a_0}\right) e^{-2Zr/na_0} \,.$$

The integral is independent of Z, as can easily be seen by making a change of variables $u = Zr/a_0$, and hence $\langle\psi|\,\hat{H}_2\,|\psi\rangle \propto Z^4$.

(c) Making the usual substitution $\mathbf{u} = Z\mathbf{r}/a_0$, we have $\delta^3(\mathbf{r}) = (\frac{Z}{a_0})^3\delta^3(\mathbf{u})$ and thus the expectation value of this term in the Hamiltonian is

$$\langle\psi|\,\hat{H}_3\,|\psi\rangle \sim \int r^2\, dr\, Z\delta^{(3)}(\mathbf{r})|\psi|^2 \sim \int \frac{u^2 du}{Z^3} Z \left(\frac{Z}{a_0}\right)^3 \delta^3(\mathbf{u}) \left(\frac{Z}{a_0}\right)^3 G^2(u) e^{-2u/n} \,,$$

which is proportional to Z^4 again.

2. $(2s)(3p)$ The allowed values of L and S are $S = 0, 1$, $L = 1$. Since the electrons are inequivalent, all combinations of L and S are allowed, i.e. ${}^1\mathrm{P}_1$, ${}^3\mathrm{P}_{0,1,2}$.

$(2p)^2$ Since the electrons are equivalent, we may take $S = 0$ (antisymmetric) with symmetric spatial wavefunction $L = 0, 2$, or alternatively $S = 1$ (symmetric) with antisymmetric spatial wavefunction $L = 1$, i.e. ${}^1\mathrm{S}_0$, ${}^1\mathrm{D}_2$, ${}^3\mathrm{P}_{0,1,2}$.

$(3d)^2$ Since the electrons are equivalent, we may take $S = 0$ (antisymmetric) with symmetric spatial wavefunction $L = 0, 2, 4$, or alternatively $S = 1$ (symmetric) with antisymmetric spatial wavefunction $L = 1, 3$, i.e. ${}^1\mathrm{S}_0$, ${}^1\mathrm{D}_2$, ${}^1\mathrm{G}_4$, ${}^3\mathrm{P}_{0,1,2}$, ${}^3\mathrm{F}_{2,3,4}$.

$(3d)^{10}$ This is a completely filled shell, so $L = S = J = 0$, i.e. ${}^1\mathrm{S}_0$.

$(3d)^9$ The shell has just one unoccupied state, so the values of L, S and J are just those for a single electron in the shell, i.e. $L = 2$, $S = 1/2$ and the terms are ${}^2\mathrm{D}_{3/2,5/2}$.

$(4f)^6$ Applying Hund's first rule, the maximum $S = 3$. Being maximal, this spin state is symmetric with respect to interchange of electrons, so the spatial state must be totally antisymmetric. Hence the six electrons must occupy six different m_ℓ values out of the seven $(2\ell + 1)$ available. As a result, the M_L of the atom can take one of seven possible values, $M_L = \pm 3$, ± 2, ± 1, 0. As a result, we can deduce that $L = 3$ is the only possibility. The shell is less than half full, so Hund's third rule requires $J = |L - S| = 0$, i.e. ${}^7\mathrm{F}_0$.

3. The ${}^3P_0$ notation signifies the total angular momentum quantum numbers in the form ${}^{2S+1}\mathrm{L}_J$, hence $S = 1$, $L = 1$ and $J = 0$ in this case. The notation implies that the LS coupling approximation is appropriate, so that L and S are good quantum numbers, which will be valid if the residual Coulomb interaction is much greater than the spin-orbit interaction.

Considering the $(3p)^1(4s)^1$ configuration:

(i) In LS coupling, the allowed values of S and L are $S = 0, 1$ and $L = 1$. According to Hund's first rule, $S = 1$ lies lower in energy. The $S = 1$, $L = 1$ state can take three values of $J = 0, 1, 2$, which are split by the spin-orbit interaction, with $J = 0$ lying lowest in energy by Hund's rules. The energy levels therefore form a triplet ${}^3\mathrm{P}_{0,1,2}$ and a higher lying singlet ${}^1\mathrm{P}_1$.

(ii) In jj coupling, the spin-orbit interaction makes a larger contribution that the Coulomb term. In this scheme, we must first find the j values for the two electrons, i.e. $j = 1/2, 3/2$ for the $3p$ state and $j = 1/2$ for the $4s$. These j values will be separated by the spin-orbit interaction. The smaller Coulomb term will then differentiate between the different values of J which can be formed by combining the values of j, giving the following terms,

$$(j_1, j_2)_J = (1/2, 1/2)_{0,1}, \qquad (3/2, 1/2)_{2,1}\,.$$

The states thus form two doublets in this case.

The given energy levels clearly form two doublets (a,b) and (c,d), so the jj coupling scheme is the better approximation in this case. The electric dipole selection rules ($\Delta J = \pm 1, 0$; but $0 \to 0$ forbidden) tell us than only the $J = 1$ levels can decay to the ground state. We also expect the $(1/2, 1/2)$ level to lie lower, since $\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle \propto (J(J+1) - L(L+1) - S(S+1))$, so this suffices to identify the levels: (a) is $(1/2, 1/2)_0$; (b) is $(1/2, 1/2)_1$; (c) is $(3/2, 1/2)_2$; (d) is $(3/2, 1/2)_1$.

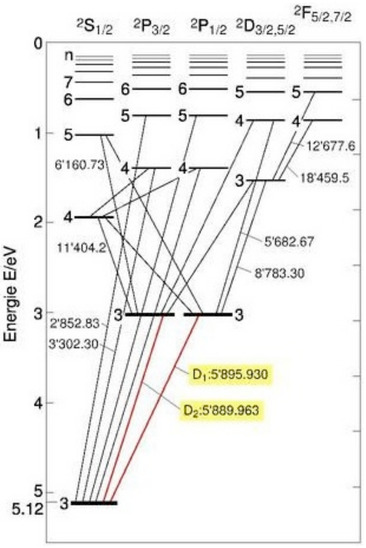
4. Firstly, in answer to the introductory questions:

(i) As an alkali atom, sodium has a single electron outside closed shells. The low energy excited states involve excitation of this electron. The appropriate quantum numbers are ℓ, s and j (the quantum numbers for the whole atom being the same as for the unpaired electron). The allowed states for the electron are $[3s(\text{ground state}), 3p, 3d]$, $[4s, 4p, 4d, 4f]$, $[5s, 5p, 5d, 5f, 5g]$, etc.

(ii) The spin-orbit interaction splits each level into a doublet according to $j = \ell \pm 1/2$, except for the s-states for which $j = 1/2$ is the only possibility.

(iii) The strength of the spin-orbit interaction decreases with n, since the electrons in higher energy levels experience a smaller magnetic field as the nucleus is better screened.

(iv) Finally, the dipole selection rules require $\Delta J = \pm 1, 0$, parity change, and $\Delta \ell = \pm 1$.



The Grotrian diagram for sodium showing (some) of the dipole allowed transitions. The two sodium D-lines are emphasized.

Since the ns states are singlets with term $2S_{1/2}$ while the np states are doublets with terms $2P_{3/2,1/2}$, we can deduce that all the doublets must involve $s \leftrightarrow p$ type transitions. Since those in group II involve the same doublet spacing, they must all involve the same p state. They are therefore likely to involve $4s \to 3p$, $5s \to 3p$, $6s \to 3p$ and $7s \to 3p$ transitions respectively.

By contrast, those in group I are likely to involve p states decaying to the same s state. Noting that the first one has the same splitting as group II, we can deduce that the they are likely to involve $3p \to 3s$, $4p \to 3s$, $5p \to 3s$ and $6p \to 3s$ transitions respectively, with the spin-orbit splitting decreasing with n as expected.

The nd states have terms $2D_{5/2,3/2}$. However, since the selection rules prohibit transitions between $J = 5/2$ and $J = 1/2$, we can deduce that the transitions between $d \leftrightarrow p$ states must involve triplets, as observed in group III. Since the splittings are the same as in group II, we can deduce that $3p$ is involved again. They must be $3d \to 3p$, $4d \to 3p$, $5d \to 3p$ and $6d \to 3p$ transitions respectively. We can compare these predictions with the diagram (right) showing the spectra of sodium (known as a **Grotrian diagram**).

(a) The $5p_{5/2}$ and $5p_{3/2}$ states are involved in the transitions of frequency 1.05086 and 1.05079×10^{15} Hz, which differ by 7×10^{10} Hz. The energy splitting is thus $7 \times 10^{10} h = 4.6 \times 10^{-23}\,\text{J} = 0.29\,\text{meV}$.

(b) We expect the sodium energy levels to converge to the hydrogen levels for large n, and thus to scale like $1/n^2$. To test this, note that the ratio of the energy differences $(6s-5s)/(7s-6s) = 1.9$, compared with the expected ratio $(\frac{1}{25}-\frac{1}{36})/(\frac{1}{36}-\frac{1}{49}) = 1.65$, which is not too bad. The energy difference between the $7s$ state and the ionisation energy may be estimated as the energy difference between $7s$ and $6s$ (Planck's constant h times 0.049×10^{15} Hz) times $(\frac{1}{49}-\frac{1}{\infty})/(\frac{1}{36}-\frac{1}{49})$, which yields $h\times0.135\times10^{15}$ Hz. We add this to the energy difference between $7s$ and $3s$, inferred from the sum of the 0.63142×10^{15} Hz ($7s\to3p$) and 0.50899×10^{15} Hz ($3p\to3s$) transitions to obtain $h\times1.27\times10^{15}$ Hz, i.e. 5.2 eV. You could use other states instead in a similar way.

(c) The spin-orbit energy in the p-states can be estimated from the splittings of the corresponding doublets in group I. The Coulomb effect is given by the difference between the p- and s-levels for a given n. The ratios in the $n=3$ and $n=6$ cases are:

$$\begin{array}{ll} n=3: & \dfrac{\mathrm{spin-orbit}}{\mathrm{coulomb}} = \dfrac{0.00052}{0.51} = 1.02\ 10^{-3} \\ n=6: & \dfrac{\mathrm{spin-orbit}}{\mathrm{coulomb}} = \dfrac{0.00003}{0.028} = 1.07\ 10^{-3} \end{array}$$

i.e. both effects decrease with n at about equal rates.

5. The derivation of the Landé g-factor is standard bookwork. The ${}^3S_1$ level has $g=2$ and ${}^3P_1$ level has $g=3/2$. Bearing in mind the selection rules, $\Delta M_J = \pm1,\ 0$, the shifts in the energy levels are given by,

$$ {}^3\mathrm{S}_1 \left\{ \begin{array}{cc} M_J & \Delta E \\ 1 & 2\mu_B B \\ 0 & 0 \\ -1 & -2\mu_B B \end{array} \right. \qquad {}^3\mathrm{P}_1 \left\{ \begin{array}{cc} M_J & \Delta E \\ 1 & \frac{3}{2}\mu_B B \\ 0 & 0 \\ -1 & -\frac{3}{2}\mu_B B \end{array} \right. $$

and thus the shifts in the energies of the allowed transitions are as given right. The line therefore splits into seven components.

M_J	ΔE
$1\to1$	$+\frac{1}{2}\mu_B B$
$1\to0$	$+2\mu_B B$
$0\to1$	$-\frac{3}{2}\mu_B B$
$0\to0$	0
$0\to-1$	$+\frac{3}{2}\mu_B B$
$-1\to0$	$-2\mu_B B$
$-1\to-1$	$-\frac{1}{2}\mu_B B$

Viewing perpendicular to the magnetic field, all seven lines will be seen. The $\Delta M_J = 0$ lines corespond to dipoles parallel to the field, and thus the light will be plane polarised in the direction of the field; these will have energy shifts of $\pm\frac{1}{2}\mu_B B$ and zero. The $\Delta M_J = \pm1$ lines corespond to dipoles perpendicular to the field, and thus the light will be plane polarised perpendicular to the field; these will have energy shifts of $\pm\frac{3}{2}\mu_B B$ and $\pm2\mu_B B$.

6. (i) First two terms represent interaction between the magnetic moments of electron and proton respectively with the external field B; the final term represents the spin-spin (hyperfine) interaction between the electron and proton.

(ii) Neglecting the term in μ_p, and making use of the identity $\boldsymbol{\sigma}^{(\mathrm{e})}\cdot\boldsymbol{\sigma}^{(\mathrm{p})} = \sigma_z^{(\mathrm{e})}\sigma_z^{(\mathrm{p})} + \frac{1}{2}(\sigma_+^{(\mathrm{e})}\sigma_-^{(\mathrm{p})} + \sigma_+^{(\mathrm{e})}\sigma_-^{(\mathrm{p})})$, where

$$\sigma_z = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}, \quad \sigma_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}.$$

We therefore have

$$\begin{aligned} \boldsymbol{\sigma}^{(\mathrm{e})}\cdot\boldsymbol{\sigma}^{(\mathrm{p})}|\uparrow_\mathrm{e}\rangle\otimes|\uparrow_\mathrm{p}\rangle &= |\uparrow_\mathrm{e}\rangle\otimes|\uparrow_\mathrm{p}\rangle \\ \boldsymbol{\sigma}^{(\mathrm{e})}\cdot\boldsymbol{\sigma}^{(\mathrm{p})}|\uparrow_\mathrm{e}\rangle\otimes|\downarrow_\mathrm{p}\rangle &= -|\uparrow_\mathrm{e}\rangle\otimes|\downarrow_\mathrm{p}\rangle + 2|\downarrow_\mathrm{e}\rangle\otimes|\uparrow_\mathrm{p}\rangle\,, \end{aligned}$$

etc. From these results, we can deduce the matrix elements of the Hamiltonian and confirm the expression given in the problem.

(iii) By inspection, the states $|\uparrow_e\rangle \otimes |\uparrow_p\rangle$ and $|\downarrow_e\rangle \otimes |\downarrow_p\rangle$ are energy eigenstates with energies $W + b$ and $W - b$ respectively. The other two energy eigenvalues are given by the solutions of

$$\begin{vmatrix} b - W - E & 2W \\ 2W & -b - W - E \end{vmatrix} = 0\,,$$

which leads to $E = -W \pm \sqrt{4W^2 + b^2}$. In the case where $b \ll W$, i.e. where the external magnetic field is very weak, these reduce to $W + b^2/2W$ and $-3W - b^2/2W$, so there is a triplet of $S = 1$ states with energy close to W, and the singlet $S = 0$ state with energy close to $-3W$. In the other limit where $b \gg W$, i.e. where the external magnetic field is very strong, this expression reduces to $\pm b$, so we have two states with energy close to $+b$ and two close to $-b$, corresponding to the two possible orientations of the electron spin.

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7. Taking the $1s$ hydrogen wavefunctions as our basis, the matrix elements of the Hamiltonian are defined in the question. Neglecting the overlap integrals, the upper bound E on the energy levels is given, according to the Rayleigh-Ritz variational method, by setting the determinant of the matrix $H_{ij} - E\delta_{ij}$ to zero. Multiplying out, and factorizing, this condition translates to the relation

$$(\alpha - E - \gamma\beta)\left[(\alpha - E)^2 + \gamma\beta(\alpha - E) - 2\beta^2\right] = 0\,.$$

This has three solutions:

$$E = \alpha - \gamma\beta, \qquad \alpha + \frac{1}{2}\beta\left(\gamma \pm \sqrt{\gamma^2 + 8}\right)\,.$$

As $\theta \to 60°$ we expect $\gamma \to 1$, as all the bond lengths become equal. The solutions in this limit are: $E = \alpha - \beta$, $\alpha - \beta$, and $\alpha + 2\beta$. As $\theta \to 180°$ we expect $\gamma \to 0$, as atoms 1 and 3 become separated. The solutions in this limit are: $E = \alpha$, and $\alpha \pm \sqrt{2}\beta$. Noting that $\beta < 0$, the lowest energy is $\alpha + 2\beta$ corresponding to $\theta = 60°$, so the stable configuration should be an equilateral triangle. Since this state is non-degenerate, it can only accommodate the two electrons of the H_3^+ ion if they are in an antisymmetric singlet ($S = 0$) spin state.

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8. Defining (with obvious notation) $|\mathrm{VB}\rangle = C[|a_1\rangle \otimes |b_2\rangle + |b_1\rangle \otimes |a_2\rangle]$, we have:

(i) the normalization $|\mathrm{VB}\rangle$: $\langle \mathrm{VB}|\mathrm{VB}\rangle = C^2\left[\langle a_1|a_1\rangle\langle b_2|b_2\rangle + 2\langle a_1|b_1\rangle\langle b_2|a_2\rangle + \langle b_1|b_1\rangle\langle a_2|a_2\rangle\right] = C^2(2 + 2SS^*)$, and hence $C^2 = \frac{1}{2}(1 + SS^*)$.

(ii) Defining the normalized bonding and antibonding orbitals, $|g\rangle = (|a\rangle + |b\rangle)/\sqrt{2(1+S)}$ and $|u\rangle = (|a\rangle - |b\rangle)/\sqrt{2(1-S)}$, we have

$$|a\rangle = \sqrt{\frac{1+S}{2}}|g\rangle + \sqrt{\frac{1-S}{2}}|u\rangle, \quad |b\rangle = \sqrt{\frac{1+S}{2}}|g\rangle - \sqrt{\frac{1-S}{2}}|u\rangle\,.$$

As a result, we find that $|\mathrm{VB}\rangle = C[(1+S)|g_1\rangle \otimes |g_2\rangle - (1-S)|u_1\rangle \otimes |u_2\rangle]$.

(iii) The state orthogonal to $|\mathrm{VB}\rangle$ is then given by $|\psi_\perp\rangle = C[(1-S)|g_1\rangle \otimes |g_2\rangle + (1+S)|u_1\rangle \otimes |u_2\rangle]$. Rewriting this in the $|a\rangle$ and $|b\rangle$ basis, after a little algebra we arrive at:

$$|\psi_\perp\rangle = \frac{C(1+S^2)}{(1-S^2)}\left\{|a_1\rangle \otimes |a_2\rangle + |b_1\rangle \otimes |b_2\rangle\right\} - \frac{2CS}{(1-S^2)}\left\{|a_1\rangle \otimes |b_2\rangle + |b_1\rangle \otimes |a_2\rangle\right\}\,,$$

of which the first term represents the ionic component and the second the covalent, i.e.

$$|\psi_\perp\rangle = \frac{(1+S^2)}{(1-S^2)}|\mathrm{IB}\rangle - \frac{2S}{(1-S^2)}|\mathrm{VB}\rangle\,.$$

(iv) Inserting the given value of ρ gives $S = 0.697$, and hence the ratio of IB/VB in the state $|\psi_\perp\rangle$: IB/VB $= [\frac{(1-S^2)}{2S}]^2 = 0.14$.

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9. For the rotation/vibration system, the energy levels have the form

$$E = E_0 + (n + 1/2)\hbar\omega + \frac{\hbar^2 J(J+1)}{2I},$$

and the selection rules are $\Delta n = \pm 1$ and $\Delta J = \pm 1$. Thus, neglecting any change in the moment of inertia, we have the following energy changes:

$$\begin{array}{llll} \text{R branch} & J \to J+1 & J = 0, 1, 2\cdots & \Delta E = \hbar\omega + \frac{\hbar^2}{I}(J+1) \\ \text{P branch} & J \to J-1 & J = 1, 2\cdots & \Delta E = \hbar\omega - \frac{\hbar^2}{I}J \end{array}$$

(i) The above formulae imply equally spaced lines above and below $\hbar\omega$, but the transition at $\hbar\omega$ ($\Delta J = 0$, the Q-branch) is not permitted by the parity change selection rule.

(ii) The double peaks are an isotope effect. Cl has two isotopes ^{35}Cl and ^{37}Cl with abundances in the ratio of roughly 3:1. The less abundant ^{37}Cl will have a larger reduced mass (by about 1 part in 1000) and thus a lower vibration frequency. Thus there are two separate spectra slightly displaced in frequency.

(iii) The uneven spacing results from the change in moment of inertia. If $\hbar^2/2I \equiv B$ initially and $B + \delta B$ finally (with $\delta B < 0$), the formulae for the energy changes become:

$$\begin{array}{lll} \text{R} - \text{branch} & J \to J+1 & \Delta E = \hbar\omega + 2B(J+1) + \delta B(J+1)(J+2) \\ \text{P} - \text{branch} & J \to J-1 & \Delta E = \hbar\omega - 2BJ + \delta BJ(J-1) \end{array}$$

So the spacing in the R-branch above $\hbar\omega$ decreases with increasing J while that in the P-branch increases with J.

(iv) The intensity of absorption depends on the population of the states, which is given by the product of the degeneracy of the rotational wavefunction and the Boltzmann factor, i.e. $(2J+1)\exp(-J(J+1)\hbar^2/2Ik_\mathrm{B}T)$, which exhibits first a rise and then a fall with increasing J, as observed.

From the central vibrational frequency ω we can infer the force constant of the bond k: $\omega = 2\pi\nu \simeq 5.4 \times 10^{14}$Hz. Then, $\omega = \sqrt{k/\mu}$, where μ is the reduced mass (approximately equal the mass of the Hydrogen atom in this case), so we deduce that $k = 490$ Nm^{-1}.

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